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Thermal Properties of Chitosan-Filled Empty Fruit Bunches Filter Media

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***Abstract*—**Non-woven fibrous filter media from empty fruit bunches were fabricated by using chitosan as a binder. Chitosan powder was dissolved in a 1 wt% aqueous acetic acid, and 1 wt% to 4 wt% of chitosan solutions was prepared. Chitosan-filled empty fruit bunches filter media have been prepared via wet-layup method. Thermogravimetric analysis (TGA) was performed to study various thermal properties of the fibrous filter media. It was found that the fibrous filter media have undergone several decomposition stages over a range of temperatures as revealed by TGA thermo-grams, where the temperature for 10% weight loss for chitosan-filled EFB filter media and binder-less filter media was at 150^{o}C and 300^{o}C, respectively.

***Keywords*—**Empty fruit bunches, chitosan, filter media, thermal property.

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I. Introduction

THE use of lignocellulosics biomass as filtration media is gaining more attention. At present the sorbents and filters market are dominated by synthetic materials. They are usually produced from polypropylene, polyethylene and polyester fibers. Natural fibers are used to a much lesser extent, but their potential in such applications is promising. This is due to its acceptable density range, high sorption capacity, feasibility, and environmental friendly characteristic. Several attempts have been made to use low cost, easily available materials as filter media for removal of metal [1], oil & grease [2] and dye [3] from domestic and industrial wastewater at different operating condition. These fibers include juniper [4], rice husks [5] , kapok [6], bagasse [7] and kenaf [8]. Other natural materials such as palm leaf [9], wood [4] and date palm [10] also have sorbent and filtration applications.

Natural fibers can be made into webs or mats, or packed into a column or chamber. Medium to high density mat of the natural fibers can be used as filtering aids to take particulates out of the waste in water and wastewater treatment. Webs or mats filter media increase the surface area of the filter and stabilize hydraulic pressure. Several attempts also shown that fibrous media in the form of non-woven filters have been used extensively in water treatment as pre-filters or to support the medium that does the separation. In some studies also shown that the fiber can be modified to selectively remove desired contaminants. 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 [11]. 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. The study showed that the iron species were deposited on the filter surface through chemical interaction and adsorption on active sites. The mat physically blocks the solid, so that the solid suspended on the mats. Thus, juniper fiber demonstrated relatively high heavy metal sorption capacity, implying that it can be a natural, inorganic, and hybrid adsorbent [12]. The potential of lignocellulosics fibers to act as filters is related to their sugar, extractives, and lignin contents and physical properties [13]. It is important to understand that lignocellulosics materials are not pure polymers. Their main constituents are cellulose, lignin, hemicelluloses, and extractives. Except for cellulose, the chemical structure of these components can differ widely. Consequently, removal of heavy metals can be governed by any of four basic mechanisms: absorption, adsorption, ion exchange, and chelation.

Recently, novel treatment using lignocellulosic filter media was investigated for reuse grey 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. The integration of the fiber filter media into first flush treatment unit allowed efficient treatment of rainwater. The approach successfully addressed the sustainable water management that employed lignocellulosics biomass, which shown great possibilities to lower the cost of water treatment and secure enough amount of alternative water resource.

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TGA have been widely used to study the thermal stability and characteristics of the thermal decomposition of polymer including chitosan. Thermo gravimetric analysis (TGA) is one of the oldest thermal analytical procedures used for the study of thermal stability of polymeric systems. The TGA is a technique of evaluating the thermal decomposition kinetics of materials by monitoring the weight loss of the sample in a chosen atmosphere as a function of temperature [15]. Changes of the mass usually occur during sublimation, evaporation, decomposition and chemical reaction, magnetic or electrical transformation of the material that is directly related to thermal stability. However, not all thermal events result in a change of the sample mass: melting, crystallization and glass transition do not exhibit a mass changes.

TGA is also the best known for its ability to provide information on the bulk composition of compounds. The usefulness of TGA for analyzing complex systems is greatly enhanced by the ability to record simultaneously the first derivative of the weight loss, that is, the derivative of the thermo gravimetric curve. The rate of change (a derivative) is often preferred since it clearly marks the point of maximum change in the degradation of the material. The temperature at which the rate of maximum degradation occurs may be taken as an indicator of the stability of the material in comparative studies. In this paper, the thermal properties of chitosan-filled empty fruit bunches filter media were evaluated using TGA measurements, and the results were analyzed and discussed with respect to chitosan content.

II. Experimental Procedures

A. Empty Fruit Bunches Preparation

The lignocellulosic used in the study is empty fruit bunches (EFB). They are obtained freshly from Sabutek (M) Sdn Bhd. EFB was obtained in the form of long strands of fibers. The fibers were dried in the oven at 60^oC to remove the moisture content. The fibers were oven dried until the weight of the fibers was constant. Then, the fibers have been ground into small particles using grinding machine. Endecott sieve have been used to separate the particles into different sizes.

B. Chitosan Preparation

In order to study the effect of chitosan addition to the non-woven EFB filter media, different concentration of chitosan solution were prepared. Chitosan powder was dissolved in a 1 wt% aqueous acetic acid, and 1wt% to 4wt% of chitosan solutions was prepared. The resulting solution was stirred at room temperature for about 6 hours. The molecular weight and degree of deacetylation were about 35000 and 80% - 90%, respectively. The viscosity of 1wt% dissolved in 1wt% acetic acid solution was 15mPa.S (20^oC).

C. Fabrication of Filter Media

Filter samples are formed from slurry of the fibers in water. The wet lay-up method was adopted for filter fabrication following TAPPI Test Method T205. The fibers are weighed and dispersed in a known quantity of water in a slurry tank using a stirrer set up. The slurry is continuously stirred for about 15min. Once the fibers are dispersed evenly, a known quantity of the chitosan is added to the slurry. The slurry was stirred for an additional 30 minutes prior to forming the filters to ensure sufficient mixing of the ingredients for obtain good media uniformity. The slurry was suspended in water in a deckle box so that the fibers would be distributed evenly across the box. The slurry is then filtered to form a medium. Randomly oriented mat fibers were prepared by using a forming box of 90mm x 90mm. A deckle box is a bottomless frame that is placed over a screen. A mat was formed on a fabric mesh as the water was flushed out at the bottom of the box. The mat was then dried in an oven at 105^oC for approximately 24hr before being pressed in a Carver Laboratory Press to obtain a more condense mat with varies thickness.

D. Termogravimetric Analysis (TGA)

Thermal Gravimetric Analysis (TGA) is an analytical technique that involves heating a sample and measuring the weight changes as a function of temperature as the sample begins to decompose and volatilize. TGA measurement was performed under nitrogen flow from room temperature to 800^oC at a rate of 20^oC/min with a TGA Perkin Elmer model Pyris 6 instrument. The weight of the sample used was approximately between 5 and 8mg.

III. Results and Discussion

In this study, the TGA measurement was done under N2 atmosphere. The thermal gravimetric analysis of the binder-less empty fruit bunches filter media sample is shown in Fig. 1. It can be clearly seen that the TG curve is a smooth curve with only one weight loss step. According to Julkapli et al. different regions can be associated with the loss of retained water at 100^0C, hemicelluloses degradation in the 200-260^0C regions, cellulose degradation at 240-350^0C and lignin degradation at 280-500^oC [16]. Between 100 and 250^0C, degradation turns the lignocellulosics fiber into a brownish color material, losing its strength though this is not quantified. At higher temperature, up to 500^0C, carbonization occurs with accentuated loss of material. Fig. 2 shows that there is only one peak on the DTG curve, indicating that the thermal degradation of filter in nitrogen is simple and there is one step reaction.

Fig. 3 is the TG curves of thermal degradation of fibrous filter media with chitosan binder. The changes in the mass could be divided into three distinct regions. In the first region, staring from room temperature up to 250^oC, the filter mass decreased about 10% wt losses due to water vaporization. The weight change was not significant and the filter was thermally stable. In the second rather narrow region, from 250 to 400^oC, the filter experienced a great loss because the thermal decomposition of the polymers, including the pyrolysis of the chitosan polymer and decomposition of fiber. At about 65% of the sample decomposed into volatiles. In the third region in the temperature range of 400 to 800^oC, the filter remained continued to decompose slowly with 10% weight loss. The maximum rate of the weight change is recorded as a peak in the DTG curve as shown in Fig. 4. The first peak, seen at about 50^{o}C, indicated the water loss from the sample due to vaporization. The second large peak at about 350^{o}C indicated the thermal decomposition of cellulosic species at increasing temperatures.

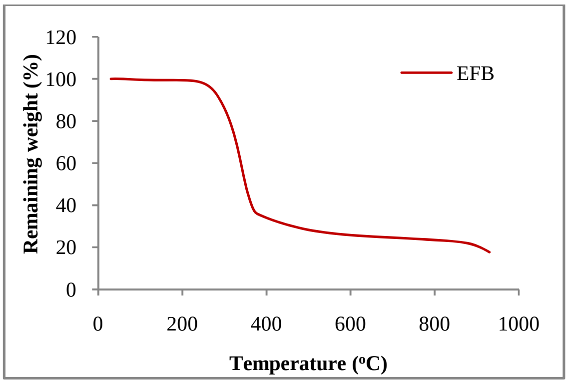

Fig. 1 Thermal gravimetric analysis of the empty fruit bunches filter media without chitosan binder

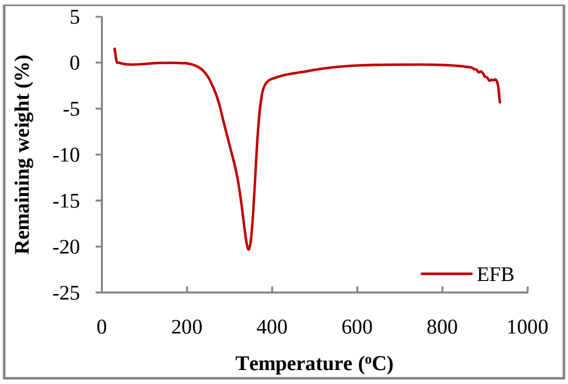

Fig. 2 TGA analyses on derivative weight of empty fruit bunches filter media without chitosan binder at certain heating temperature

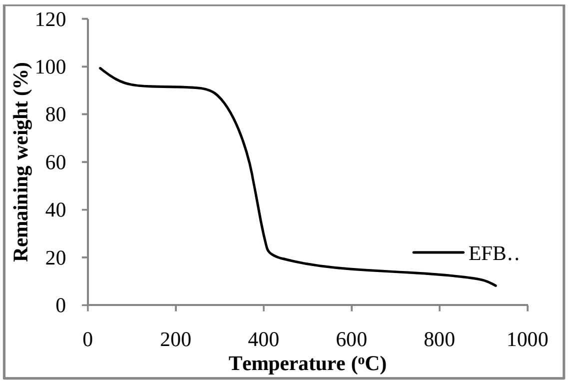

Fig. 3 Thermal gravimetric analysis of the empty fruit bunches filter media with chitosan binder

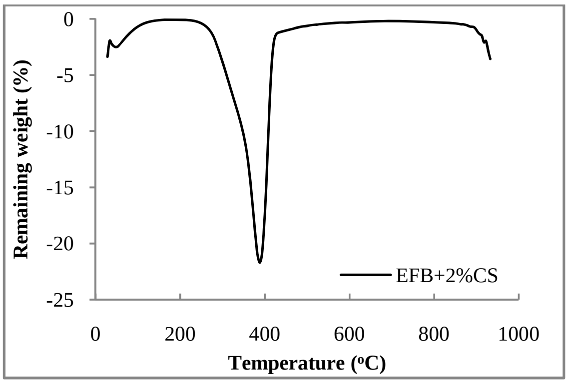

Fig. 4 TGA analyses on derivative weight of empty fruit bunches filter media with chitosan binder at certain heating temperature

The mass profile for filter media is usually the sum of the individual profiles of each component under the same experimental conditions. As shown in Fig. 5, the binder-less filter media had lower water content and a better thermal stability than the chitosan-filled EFB filter media. Compared to the weight loss of 10% chitosan-filled EFB filter media, the weight loss of binder-less filter media was insignificant at 200^{o}C. It was notices also that the chitosan-filled EFB filter media decomposed earlier than binder-less empty fruit bunch filter media, where the temperature for 10% weight loss for chitosan-filled EFB filter media and binder-less filter media was at 150^{o}C and 300^{o}C, respectively.

For non-woven filter media with different chitosan binder, degradation occurred in two stages as clearly seen in Fig. 5. With incorporation by certain amount of chitosan in fibrous media, the hydrophilic properties of fiber as lignocellulosics material expected to increase due to the hydrophilic properties of chitosan. This could also be explained by considering in the chitosan structure where the water molecules could possibly bound by two polar groups, OH and NH_2. By blending fiber and chitosan together, the concentration of OH group is anticipated to increase, since OH is the dominant polar group in cellulose structure of chitosan. It has been reported that the interactions of water molecule with the OH groups are stronger than the one with NH_2 groups. The change in the mass loss is therefore partly related to chitosan content. Hence, the addition of chitosan content manifests the increasing in loss of mass as compared to binder-less empty fruit bunch filter media.

In order to clearly visualize changes in weight as a function of temperature, derivative weight plot is presented in Fig. 6. The rate of the weight loss of chitosan-filled EFB filter media due to the thermal degradation in the second stage was lower than the binder-less filter media. The trends seen in the DTG curves at different concentration of binder are similar. The DTG curves shift toward high temperatures along with increasing the concentration of the chitosan binder. Small differences in peak size and position indicate that the samples contain different amount of chitosan content, which influences the water holding capacity of chitosan and its filter media.

Furthermore, some of NH_2 groups of chitosan polymer in chitosan filled EFB filter media are also reacted to form either

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intra- or intra-hydrogen bonding with a cellulosic portion of fiber. Consequently, a higher amount of chitosan imparts greater intermolecular interactions and lesser numbers of NH_2 groups present. As a result, more of the water molecules are bound to OH groups rather than to NH_2 groups. Therefore, the evaporation process of chitosan-filled EFB with higher chitosan concentration is expected to be more difficult, as compared to low chitosan concentration media.

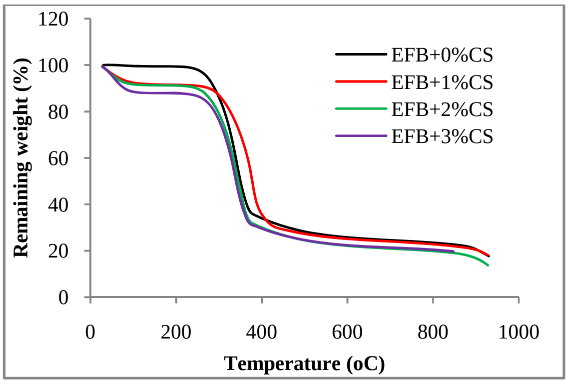

Fig. 5 Thermal gravimetric analysis of the empty fruit bunches filter media with different concentration of chitosan

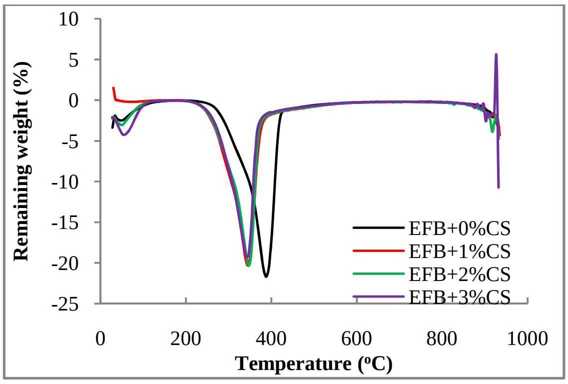

Fig. 6 TGA analyses on derivative weight of empty fruit bunches filter media with different concentration of chitosan binder at certain heating temperature

Compared to the a single peak of the binder-less empty fruit bunch filter media, the DTG curve of the chitosan-filled EFB exhibit a peak at a slightly lower temperature and have a peak hidden in the shoulder region. The single binder-less empty fruit bunch peak is more asymmetric as compared to the chitosan-filled EFB filter media which are likely to have a slightly shoulder in the end of the curve. The shoulder region was caused by the combination of thermal degradation of the polymers, including the decomposition of EFB fiber and the pyrolysis of the chitosan polymer. The complete thermal decomposition of the sample involving depolymerization is attained at temperature higher than 400°C.

IV. Conclusion

Eco-friendly filters media was obtained by the combination of biodegradable polymer as the binder and the biodegradable natural fibers as raw materials. Since both components are biodegradable, the filter media produced was expected to be biodegradable. Utilizing of renewable resources in commercial products may potential lead to reduction of environmental pollution due to their biodegradability. Although synthetic filter currently account for about 98% of the filter market, natural fiber-based filters should have good possibilities for increasing their share in the future. Research and development activities will be necessary to improve the marketability of the natural filter media in some aspects.

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