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Feasibility of Agro Waste-Derived Adsorbent for Color Removal

Wijayarathne UPL*, Vidanage PW, Jayampath HKD and Kothalawala KWPM

University of Moratuwa,Department of Chemical and Process Engineering, Bandaranaika Mawatha, Katubedda, Moratuwa, Srilanka

Abstract

Feasibility of utilizing empty bunch (EB) fiber, a solid waste of palm oil extraction process, as an adsorbent is analyzed in this study. Empty bunch fiber is generated after the extraction of retained oil in the sterilized and threshed empty fruit bunches. Besides the numerous characteristics of EB fiber, which enable its utilization as a fuel, a bio-composite material, or mulch, EB fiber also shows exceptional characteristics of a good adsorbent. Fixed bed adsorption method is used to study the adsorptivity of EB fiber using a continuous adsorption column with Methyl-blue (1.13 ppm) as the feed. Adsorptivity is assumed to be solely dependent on the bed porosity keeping other parameters (feed flow rate, bed height, bed diameter, and operating temperature) constant. Bed porosity is changed by means of compact ratio and the variation of the feed concentration is analyzed using a photometric method. Break through curves are plotted at different porosity levels and optimum bed porosity is identified for a given feed stream. Feasibility of using the EB fiber as an inexpensive and an abundant adsorbent in wastewater treatment facilities, where the effluent color reduction is adamant, is also discussed.

Keywords: Adsorption; Methylene blue; Oil palm fiber

Introduction

Palm oil is the most consumed edible oil worldwide and a progressively developing industry with a high growth potential. Due to the favorable climatic and geographical conditions, palm oil industry thrives vastly near the equatorial region. Sri Lanka has a total palm cultivation of 8,000 Ha whilst plantation sizes of dominating palm oil producers like Indonesia and Malaysia, average in the 40,000 Ha range. Downstream value addition potential with beneficial waste and byproducts, further enhances the growth of the palm oil processing industry. Solid waste and byproducts generated during the palm oil extraction process are empty bunch (EB) fibers, mesocarp fibers, kernel shells, and kernel meal. In Sri Lanka, mesocarp fibers and kernel shells are used as a biomass fuel due to their high calorific value whilst kernel meal is utilized as an animal feed. Though EB fibers are currently used solely as mulch in plantation fields, EB fibers are worldwide used as a biomass fuel after reducing its moisture content and as a bio-composite material. Sri Lanka produces approximately around 17,500 MT per year of edible palm oil and this result a generation of 26,500 MT of oil palm fibers annually. Therefore the optimum utilization of EB fibers, an abundant natural resource, should be insisted on a more economically and ecologically convenient prospect.

Palm oil extraction is a physical separation process where mechanical forces (expeller press) are applied. First, fresh fruit bunches are sterilized injecting direct steam in an enclosed sterilizer. The sterilized bunches are then threshed to remove any oil palm fruits attached and are pressed to extract oil retained during the sterilization process, resulting in EB fibers. During sterilization, oil palm fibers are subjected to steam activation, which enlarges the pore structure and increase the surface area of dehydrated and devolatilized fibers. It is certainly presumable that, with this phenomenon together with the inherent properties of oil palm fiber, abundance, and low cost, EB fiber has exceptional characteristics of a good adsorbent.

In this study, the feasibility of utilizing EB fiber, a solid waste of the palm oil extraction process, as an adsorbent is analyzed. For the laboratory experiments, a continuous adsorption column is used and a 1.13 ppm solution of Methyl-blue is used as the feed. There are numerous parameters affecting the color removal during the adsorption process, such as feed flow rate, bed height, bed diameter, bed porosity and operating temperature. During this study, effect of bed porosity towards adsorption, thereby color removal in the feed stream, is analyzed while maintaining the other parameters constant.

Bed porosity is changed by means of compact ratio (mass of fiber to filled for a given bed height). This parameter has a direct impact on bed capacity since it changes the surface area available for mass transfer (adsorption) in a wide range in oil palm fibers, compared to other adsorbents like activated carbon. After a series of laboratory experiments, the break through curves are plotted under different bed porosity levels and the optimum bed porosity is identified. As a continuation of this research, other parameters such as bed height, bed diameter and the flow rate are also to be determined in future.

Several factors should be considered, when determining the feasibility of EB fiber as a commercial adsorbent. Abundance, pretreatment methods, unit cost, applicability, and efficiency are some of them. Since it is currently an existing and further expanding industry in Sri Lanka, there is a strong assurance for the continuity of the source of EB fiber. Applicability of this adsorbent is limited to several non-hygienic concern processes due to its less purity and inherent off-color. Inexpensive effluent color reduction in wastewater treatment facilities is one such definitive application, where EB fiber can be used as an adsorbent to reduce the effluent color. Most of the textile industries are concerned for an inexpensive method effluent color reduction.

Nomenclature

EB - Empty Bunch

X - Mass ration of adsorbate in solid phase

***Corresponding author:** Wijayarathne UPL, University of Moratuwa,Department of Chemical and Process Engineering, Bandaranaika Mawatha, Katubedda, Moratuwa, Srilanka, Tel: 94112708825; E-mail: udithaw@uom.lk

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Y - Mass ration of adsorbate in liquid phase

YIN - Concentration of adsorbate in feed solution

XT - Concentration of adsorbate in exhausted solid material (is in equilibrium with the feed solution having adsorbate concentrate of YIN)

XIN - Concentration of adsorbate in fresh adsorbent

Y^* - Concentration of adsorbate in the outlet stream (is in equilibrium with the fresh adsorbent having adsorbate concentrate of XIN)

Theory

Adsorption equilibria

Adsorption equilibrium is defined as the dynamic concept achieved when the rate of molecules adsorb on to a surface is equal to the rate of molecules desorb. The capacity of an adsorbent for a specified adsorbate rely on three properties namely, the concentration of the adsorbate in the fluid phase (Y), the concentration of the adsorbate in the solid phase (X) and the temperature (T) of the system. Common practice is to keep the temperature constant and to study the variation of (Y) against (X). The plot of (Y) against (X) is called an adsorption isotherm (Figure 1) [1].

There are five modes of Adsorption in practice as:

Single stage adsorption - batch or continuous

Cross flow adsorption

Counter current adsorption

Fixed bed adsorption

Fluidized bed system

This study is focusing on fixed bed adsorption and therefore only that section will be discussed in detailed.

For the understanding of adsorption process in a fixed bed, mass transfer is assumed to be take place in a thin layer of the bed with a thickness of dz. Since the feed solution is continuously passing through the bed, this bed volume gets saturated with time. Thereafter the adjacent layer with a thickness of dz is considered as the mass transferring zone [2]. In this manner, the hypothetical mass transferring zone is moving down along the fixed bed with time (Figure 2).With time, the hypothetical mass transfer region is moving along the packed bed. The adsorbate concentration of the liquid and solid phase is remains constant until the mass transfer region moves to the bottom of the packed bed (Figure 3). Thereafter, the outlet concentration (YOUT) is gradually increased up to the inlet concentration (YIN). Graphical representation of the outlet concentration is described in (Figure 4).

Bed capacity is defined as the amount of adsorbate that can be retained by the adsorbent in the packed bed. It can be graphically calculated by evaluating the area under the line Y=YIN and the S-curve.

Spectrophotometer

Shimadsu (UV 1800) is a double-beam spectrophotometer, where the light is alternately passed through the sample and the reference. The detector measures irradiance of the wave when it passes through the sample as well as through the reference and then compared to get absorbance (Figure 5) [3]. This method also provides automatic correction for changes of source intensity and detector response with time.

Methodology

Fiber preparation

The main raw material for the study was oil palm fiber collected from AEN Palm Oil Processing (Pvt) Ltd, Baduraliya - Sri Lanka. At the point of collection, material was hot and wet with moisture and remaining palm oil. After storing the fiber for a couple of days it was observed a growth of a fungal species. Therefore, the collected fiber was washed with water and dried in an oven to remove any moisture and remaining oil.

Then the measured amount of dry oil palm fiber was fed to the adsorption column and compressed until the bed height equal to 10 cm. Since the study required having fiber under hot-wet condition, adsorption column was washed with hot water at 60°C for a period of five minutes at the beginning of each adsorption cycle.

Determination of bed porosity

Bed porosity is an important parameter to be considered in Adsorption and still, it is difficult to measure and control such parameter for a packing material like oil palm fiber. Therefore, a separate test was carried out to identify the relationship between bulk density and the porosity of oil palm fiber.

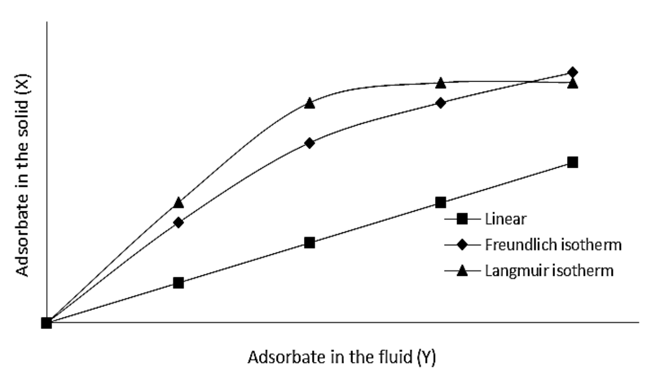

Figure 1: Adsorbate concentration in solid vs. liquid.

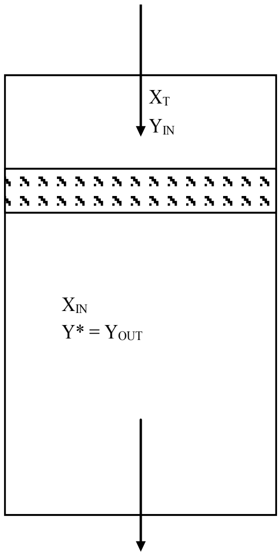

Figure 2: Hypothetical mass transfer zone.

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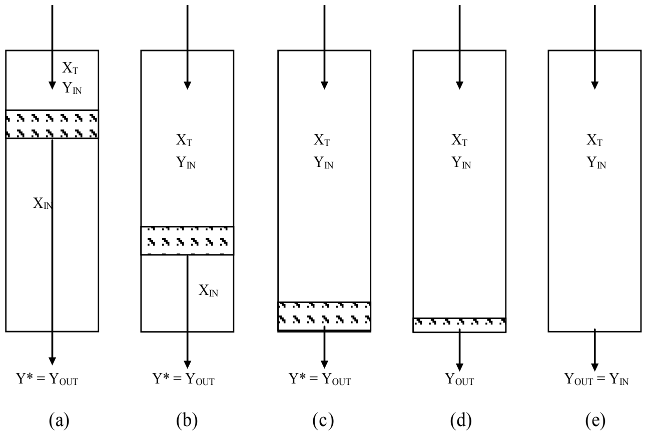

Figure 3: Movement of hypothetical mass transfer zone.

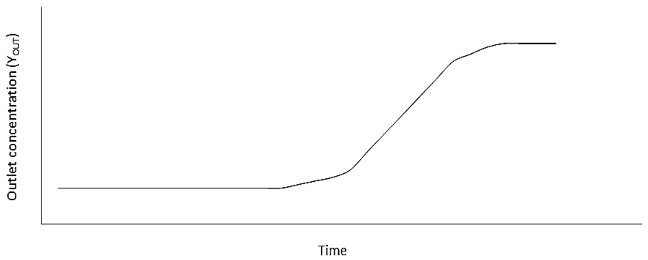

Figure 4: Variation of outlet concentration with time.

Five of 100 cm^3 measuring cylinders were filled with different weights of dry oil palm fiber and compressed to a total volume of 50 cm^3. Next, water was filled to the series of measuring cylinders through a burette up to the level of 50 cm^3. Burette readings were recorded in each sample and that amount of water is equal to the volume of voids available with the oil palm fiber under different bulk densities.

Experimental setup

Experimental setup for the study was comprised with three main units namely, storage for the feed solution, Peristaltic pump with variable flow rates and the cylindrical column and discharge valve at the bottom made out of glass (Figure 6). Feed solution for the preliminary laboratory experiments was Methylene blue with a concentration of 1.13 ppm. Known weight of dried and cleaned Oil Palm fiber was fed to the cylindrical column and compressed to a bed height of 10 cm. Diameter of the cylindrical column was 3 cm and the bed volume was calculated as 70.69 cm^3. Feed solution was introduced to the compressed fiber bed with a constant flow rate of 16 cm^3/minute using the peristaltic pump. Discharge valve at the bottom of the cylindrical column was adjusted such so that the feed rate to be equal to the discharge rate of the column. Samples were collected from the product stream with a frequency of 5 minutes.

Determining the methylene blue concentration in product

Photometric method was used to measure the concentration of Methylene blue in the feed solution as well as the product stream of the Adsorption column in different time intervals. Shimadsu (UV 1800) [4] spectrophotometer was used to measure the absorbance of light under a pre-determined wavelength for the samples collected from product stream. Specifying of the correct wave length was a critical factor to be considered when using the spectrophotometer. Samples with different concentration of Methylene blue were used to determine the wave length corresponding to the color of the solution (Figures 7 and 8). According to the spectrum in (Figure 9) corresponding wave length was determined as 664 nm. Next, the calibration curve was prepared with using a series of Methylene blue solution with different concentrations (Figure 10). This calibration curve was then used throughout the experiments to determine the Methylene blue concentration of product stream.

Results and Discussion

Relationship between bulk density and porosity

The amount of water required to fill the voids in the same volume of oil palm fiber under different bulk densities are summarized in (Table 1). According to the (Figure 11), it is possible to observe a linear trend in between the bulk density of the oil palm fiber and its porosity. Effect of compact ratio towards color removal and bed operating time

Bed porosity is a very important parameter to be considered in Adsorption. During this study, the effect of bed porosity is varied by changing the weight of the dry fiber used to prepare the adsorption bed while maintaining the bed height as a constant. (Table 2) summarizes the details of adsorption beds used in series of experiments to plot breakthrough curves. For the study, break through concentration is considered as 0.1 ppm.

During the experiment 1, bed porosity was 0.8234 and the corresponding breakthrough curve is in (Figure 12). According to the curve, breakthrough time is recorded as 25 minutes. For the 2nd and 3rd experiments, the bed porosities respectively of 0.8008 and 0.7926 has resulted breakthrough times of 100 minutes and 115 minutes respectively (Figures 13 and 14). The 4^{th} experiment was carried out under a bed porosity of 0.7555 and the corresponding breakthrough curve is in (Figure 15). According to the curve, breakthrough time is recorded as low as 15 minutes. During the 1st experiment, bed porosity was recorded as 0.8234. Furthermore, it was noticed channeling of Methylene blue solution through the bed. The main reason for this phenomenon is that the loosely packed EB fiber bed has made sufficient void space and flow paths to move bulk flow of feed solution without proper contact with fiber material. Therefore, considerable amount of Methylene blue solution was discharged through the bed without proper adsorption.

For the 4^{th} experiment, EB fiber has highly compressed to make the bed. In that experiment, it was noticed that the Methylene blue solution moved in-between the wall of the glass column and packed bed without proper adsorption.

Lower bed porosity has made a high resistance to flow through the bed and thereby Methylene blue solution tends to pass through the glass wall and EB fiber bed. This unexpected flow pattern again reduces the performance of adsorption column and thereby lower breakthrough time.

Effect of yellow color solute in dried fiber towards the study

Once the adsorption column was filled with dried oil palm fiber, it was washed with hot water at 60°C for a period of 5 minutes. At this stage, it was observed some yellow color in the wash water which was flowing through the EB fiber bed. There was a possibility of having an effect from this yellow color on the blue color of Methylene blue which was used as the feed solution (Figures 16 and 17). In order to avoid this unexpected color change, fiber was thoroughly washed with hot water before using it.

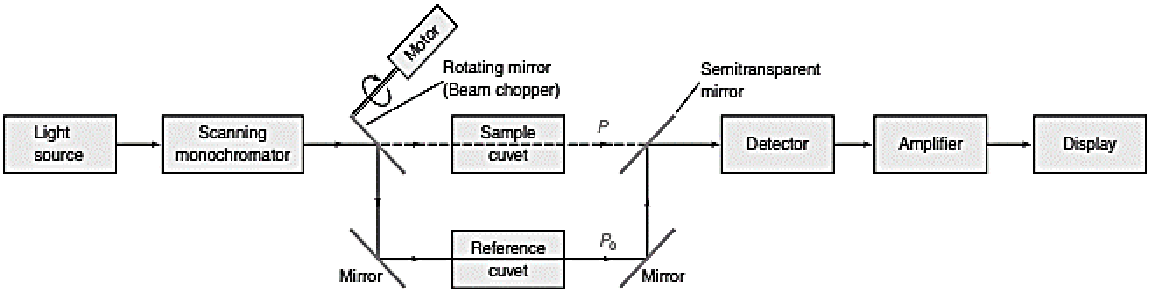

Figure 5: Schematic diagram of double-beam spectrophotometer.

Figure 6: Laboratory scale adsorption column.

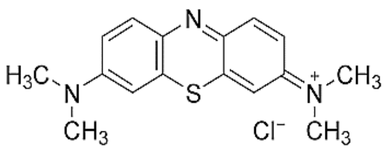

Figure 7: Chemical structure of the Methylene blue molecule.

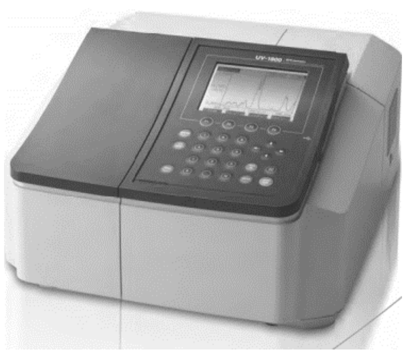

Figure 8: Shimadsu (UV 1800) spectrophotometer.

Simple test was carried out to quantify the amount of yellow colored solute available in EB fiber. Different amounts of oil palm fiber were added to constant volume of distilled water (40 ml) and completely immersed at room temperature (28°C). Then the color of the filtered solution was measured using the spectrophotometer after 1day (24 hours) and 6 days (144 hours) respectively (Table 3).

Conclusion and Further Works

EB fiber which generated by the palm oil extraction process was used for the study and the feasibility of using EB fiber as an adsorbent under the Fixed bed adsorption method was studied. Methylene-blue solution was used as the feed solution and the effect of bed porosity towards the breakthrough time was studies while maintaining other parameters constant.

During the experiment series, adsorption column was operated under different compact ratios. According to the results obtained and when the results are compared in (Figure 16), it is concluded that bed porosity of 0.8008 and 0.7926 has resulted higher breakthrough time compared to bed porosity of 0.8234 and 0.7555. Moreover, when considering (Figure 18) and (Figure 19), breakthrough curve under the bed porosity of 0.7926 has the highest breakthrough time [5].

EB fiber indicates characteristics of a viable adsorbent. An annual generation of 26,500 MT of EB fibers is supposedly adequate to be assumed as an abundant source of raw material. This study reveals several limitations of the usage of EB fiber as an adsorbent mainly due to its less purity and inherent off color. In the palm oil extraction process, a considerable amount of oil is absorbed to the empty bunch during sterilization and threshing. The oil retained is then extracted in the empty bunch press, yet the color pigments, which cause the reddish yellow in crude oil, might not be completely removed. Therefore it is advisable to pretreat EB fiber bed with hot water at 60°C for a period of 5 minutes, which would reduce the consequent yellow color in the liquid phase. As EB fiber is a cheap, waste material and the pretreatment is simple and inexpensive, unit cost of the adsorbent is certainly less.

Textile industry, one of the prevailed and established industry in Sri Lanka, is captive responsible for the discharge of large amount of discolored wastewater. With the tendency of using organic, fast responsive and stabilized dyes which are barely degraded in conventional treatment methods, textile industry is more susceptible in facing environmental and ecological problems in economical discharging. Many of the highly effective conventional treatment methods (coagulation, flocculation, bio sorption, and ultra-filtration) are expensive and sometimes inefficient in colour removal. And it is often presumed that only ecological parameters like BOD, COD, pH, and temperature are crucial in discharge requisites and neglect the long term plausible effect of eutrophication, organisms' exposure to acute and/or chronic effect, etc. However with the persistent environmental standards, necessity in colour removal is cogently emphasized. Adsorption is one frequently used economical and effective method wherein activated carbon is an effective adsorbate currently utilized in the industry. Conversely more cheaper and effective substitutions

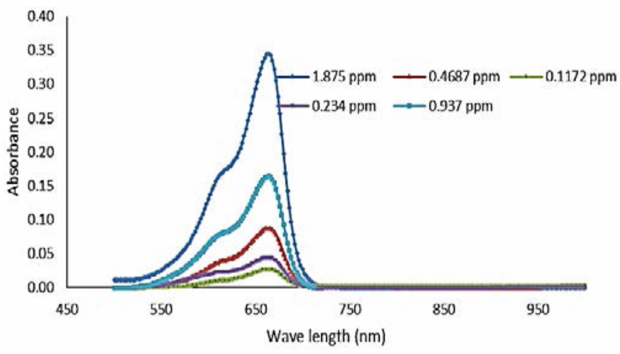

Figure 9: Absorbance vs. wave length.

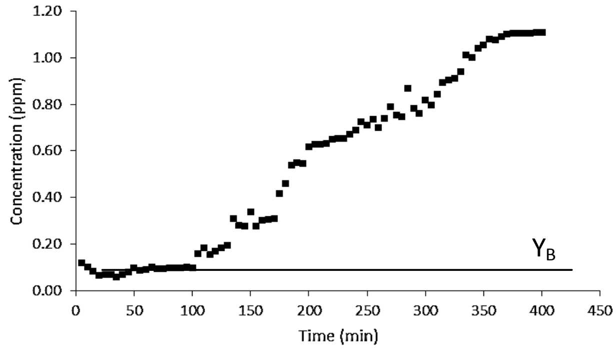

Figure 13: Outlet concentration vs. time – Bed Porosity 0.8008.

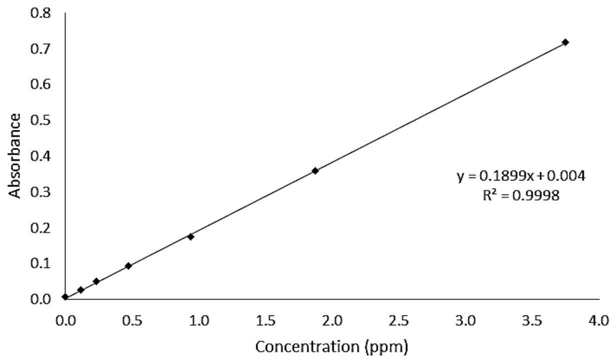

Figure 10: Absorbance vs. Methylene blue concentration.

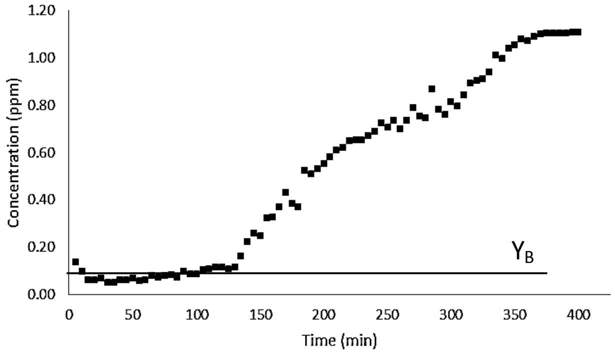

Figure 14: Outlet concentration vs. time – Bed Porosity 0.7926.

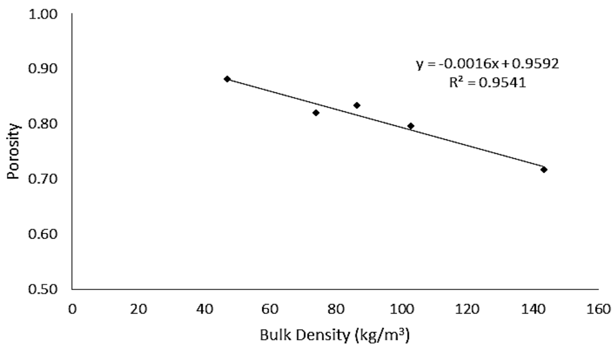

Figure 11: Bed porosity vs. bulk density.

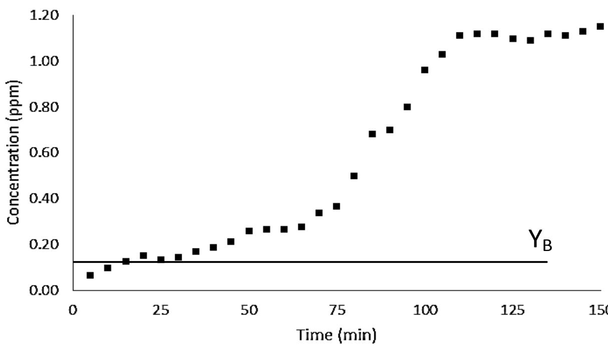

Figure 15: Outlet concentration vs. time – Bed Porosity 0.7555.

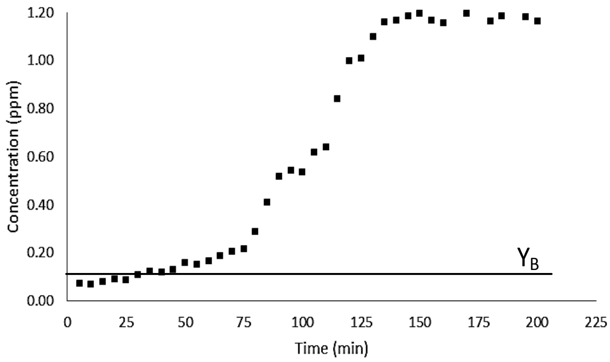

Figure 12: Outlet concentration vs. time – Bed Porosity 0.8234.

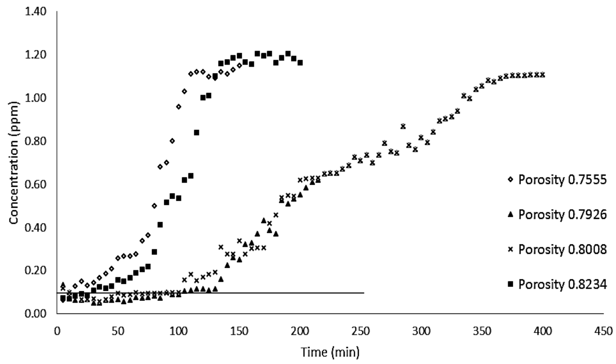

Figure 16: Comparison of breakthrough curves under different bed porosities.

Figure 17: Effect of yellow color in EB fiber on the color change at outlet stream.

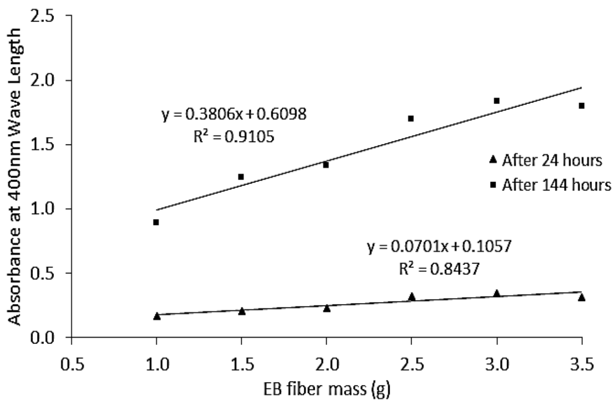

Figure 18: Absorbance at 400 nm after 24 hours and 144 hours.

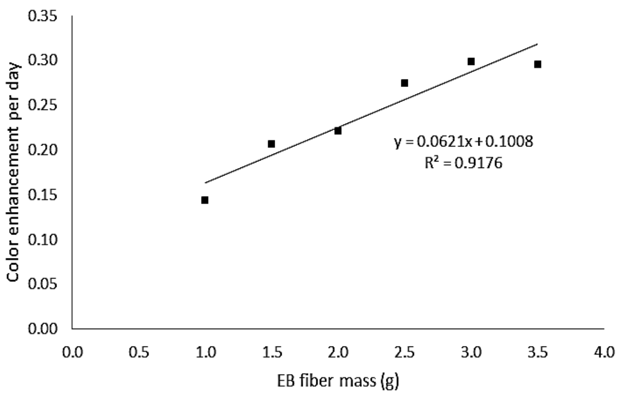

Figure 19: Color enhancement per day vs. EB fiber mass.

Sample Number	Dry Fiber (g)	Void volume (cm^3)	Bulk Density (kg/m^3)	Bed Porosity
1	2.36	44.1	47.2	0.882
2	3.70	41.0	74.0	0.820
3	4.33	41.7	86.6	0.834
4	5.15	39.8	103.0	0.796
5	7.18	35.9	143.6	0.718

Table 1: Variation of bed porosity with bulk density.

Experiment No	Weight of Fiber (g)	Bulk Density (kg/m^3)	Bed porosity
1	6.00	84.88	0.8234
2	7.00	99.03	0.8008
3	7.36	104.12	0.7926
4	9.00	127.32	0.7555

Table 2: Adsorption beds used in series of experiment.

EB fiber mass (g)	Absorbance at 400nm Wave Length		Color enhancement per day
	After 24 hours	After 144 hours	
1	0.167	0.889	0.144
1.5	0.207	1.243	0.207
2	0.23	1.339	0.221
2.5	0.322	1.696	0.274
3	0.34	1.836	0.299

Table 3: Absorbance at 400 nm after 24 hours and 144 hours.

are being researched (coal, fly ash, wood, silica gel, bentonite clay, bagasse, coconut shell, rice husk, zeolite, and bentonite), since usage of activated carbon is being limited due to its high cost. And most of these adsorbates require surface alteration and surface property modification in order to enhance their adsorptivity wherein EB fiber provides a cheap, effective, and an adsorbate with less unit cost. It provides an economical usage of a waste derived bulkily in palm oil industry and a cheap but an effective treatment method in wastewater treatment. Moreover there are several other processes, where a pertinent natural adsorbent like EB fiber would have advantage over synthetic and expensive alternatives. Further it reveals areas of future studies, such as the capability of enhancement on adsorption by studying the reaction kinetics of dyes and the catalytic improvement of fiber. Therefore it is concluded that the EB fiber is a potential, economical and an effective adsorbent that can be used in wastewater treatment facilities and in other primitive adsorption applications.

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