Utilization of Coconut Copra as Low Cost Biosorbents for Removal of Humic Substances from Peat Swamp Run-Off

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Abstract – *Nowadays, consumers are concerned about the quality of water supply that is being used. Consumers want to ensure that the supplied water is free from any harmful substances especially humic substances (HS). High concentration of HS in drinking water can cause diseases for human, such as stomach cancer. Thus, it is important to develop a new technology to improve the quality of drinking water. Therefore, the objective of this research is to investigate the potential of using coconut copra treated with citric acid as a low cost biosorbent in adsorbing HS contained in wastewater collected from the Asajaya Treatment Plant situated in the district of Samarahan, Sarawak. In this research, a batch stirred tank reactor was chosen, and the optimum condition of adsorption process was determined accurately. As such, two types of parameters were considered as the constant; temperature and pH of activated carbon, while solid-liquid ratio and residence time were varied. This research has shown that coconut copra possesses the capacity to adsorp 97.5% of HS contained in wastewater by using a batch stirred tank reactor.*

Keywords: Adsorption, Humic Substances, Batch Stirred Tank Reactor, Coconut Copra

1.0 INTRODUCTION

Environmental pollution has increased significantly in Malaysia, especially in water pollution. Water is one of the important needs of human on the earth. Consumers nowadays stress on the quality of water that is supplied to them in order to ensure the water is free from any harmful substances, for example humic substances (HS). HS are the most widely distributed products from biosynthesis that are contained in soil. Apart from soil, it can also be found in different level of concentrations in different sources like rivers, lakes, oceans, compost, sediments, peat bogs and soft coal. HS are formed by a process called humicification [1]. HS are divided into three main fractions, which are humic acid (HA), fulvic acid (FA), and humin. They can be classified based on their solubility in acid and alkali [2]. High concentration of HA in drinking water can cause some serious diseases on human health, such as stomach cancer, which is due to the disinfection caused by by-products namely trihalomethanes [3, 4, 5]. HA contains relatively high amount of basic amino; a combination of functional groups of amines and carboxylic acids, which becomes poisonous if the molecular weight of amines is relatively low [6, 7]. On the other hand, amine is not totally harmful but when it reacts with other compounds, it will form nitrosamines and nitramines that have an irreversible effect on environment, human and animals. Some of the amino compounds also are known or suspected as carcinogens due to the aromatic amine that can cause diseases like bladder infection [8]. Therefore, it is

important to remove HS, especially HA from drinking water. As mentioned by Hatam et al., a high amount of HA can become one of the etiological factors for Blackfoot disease [6]. Therefore, the objective of this research is to investigate the potential of using coconut copra as an activated carbon in adsorbing humic substances contained in wastewater collected from a local wastewater treatment plant namely the Asajaya Treatment Plant, is located in the district of Samarahan.

1.1 General overview of Humic Substances (HS)

HS are the end product of decaying organic matter that is formed by biodegradation of organic compound [9]. It is generally known as a complex compound possessing different molecular weights and sizes [10]. HS are considered as distributed products of biosynthesis that can be found in soil [11]. Apart from soils, it can be found as well at different level of concentrations in several places namely river, lake, ocean, compost, sediments, peat bogs and soft coal [12]. Even though HS can be found at every layer of soil and water, nobody has succeeded in the past 200 years to design their exact molecular structure [13]. According to Mayhew, HS are the compounds that are active in soils, which possess the cation and anion exchange capacities. In addition, the structure of HS depends on pH value and type of metal presence [12]. Moreover, as explained by Tombacz and Rice, the increase of pH value or the presence of multivalent ions such as Calcium (Ca^{2+}) can open up the HS long-chain polymers. However, if the pH value starts to decrease until it reaches the lowest limit, HS long-chain polymer will revert back to a closed-loop polymer. Furthermore, the changes in pH value, concentration or the presence of metal ions cause massive changes in physical structure of humic molecules [13]. Conventionally, HS is defined by their solubility in aqueous solution at any pH level and molecular weight [12]. There are three types of HS namely humic acid (HA), fulvic acid (FA) and humin, which are slightly different in terms of acidity level and chemical composition [14].
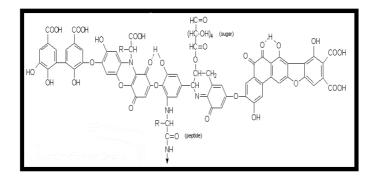

Figure 1: Model Structure of Humic Acid [22]

Firstly, HA is considered as the most dominant compound in HS that is generated from microbial degradation of biomolecules [15, 16]. Microbial degradation of HA is a vital process in forming humus with the aim of maintaining global carbon cycle. Other processes that are able to generate humus are humicification and followed by photosynthesis [17, 18]. Humicification is defined as the decay process that transforms biomolecules from dead organisms. Meanwhile, microbial activity is a process where HS are formed and non-HS are decomposed [19, 20]. Furthermore, HA consists of complex aromatic macromolecules namely amino acids, amino sugars, and peptides. Aliphatic compounds present in HA play the role in bridging all the aromatic groups as shown in Figure 1. In terms of the structure of HA, it

contains several functional groups namely phenolic OH groups, quinine structures, amine and oxygen as a bridge bonding and carboxylic (COOH) functional group that are situated at different positions at aromatic rings [21]. A combination of amine and carboxylic acid functional groups will form amino acid [7]. Meanwhile, amine is an organic molecule that consists of nitrogen and ammonia [8].

Moreover, HA is comprised of weak aliphatic (carbon chains) and aromatic (carbon rings) that are classified as an organic acid that is insoluble in water under acidic condition, but soluble in water under alkaline condition [23]. High concentration of HA in drinking water can cause some serious diseases like stomach cancer due to the presence of pathogens or other contaminants [6, 9]. Furthermore, low molecular weight of amines are poisonous to human, animal and environment. Besides, amines are not totally harmful, but when amines react with other compounds and form nitrosamines and nitramines, they possess an irreversible effect on the environment, human and animals. In addition, some amino compounds are classified under carcinogenic compound. Lastly, due to the presence of aromatic amine, it can cause diseases like bladder infection [8]. Therefore, the mineralization of drinking water and other water treatment process is very vital in order to ensure the drinking water supplied is free from HA [6, 9].

Secondly, the difference between HA and FA can be shown by analysing their molecular weight and also classification number of functional groups namely carboxylic, phenolic and amine [21]. FA is defined as the mixture of weak aliphatic and aromatic organic acid that is soluble in water at all conditions, either in acidic, neutral or alkaline medium. As reported by Mayhew, FA is considered biologically more active than HA due to its molecular size [12]. The size of FA is smaller than HA, and it possesses low molecular weight. Besides, FA also has the ability to improve the permeability of cell walls. In addition, FA comprises of higher quantity of functional groups of carboxyl, phenol, quinine and hydroxyl groups than HA as shown in Figure 2 [12, 23].
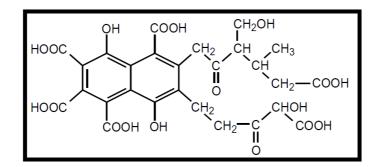

Figure 2: Model Structure of Fulvic Acid [22]

Furthermore, according to Mayhew, FA possesses higher total acidity than HA. However, in terms of chemical reactivity and chelating ability, FA possesses a similar capacity compared to HA. However, in certain cases, FA possesses low chemical reactivity and chelating ability compared to HA [12]. Nevertheless, Robert reported that FA is chemically more reactive than HA [23]. The quality and purity of extracted FA might be influenced by the method in which it is synthesized during a chemical process [12].

Lastly, humin is the third fraction of HS and presents at low quantity. As mentioned by Mayhew, humin is considered inert but somehow it might play a role as a sponge or soaking up nutrients [12]. Conversely, as reported by Hayes et al., humin is found to have the same quantity as HA and FA because humin, which is presents in HS, is associated with mineral oxides and hydroxides [24].

1.2 Overview of Adsorption of HS

Adsorption is one of the methods that have been applied to remove HS. In the past few years, several adsorbents have been employed to adsorb HS, namely activated carbon, clays, zeolite, chitosan, metal-modified silica, and mesoporous silica [25]. Previous research showed that activated carbon can be used to remove HS from water [6]. Furthermore, activated carbon has been widely used in water treatment systems to remove disinfection of by-products and compounds related to odour, taste, colour and other problems in drinking water [26, 27]. Additionally, it can be used as powdered activated carbon (PAC), which is added directly to untreated water or as granular activated carbon (GAC), which is used in fixed-bed reactor [28]. As a result, adsorption using activated carbon is proven to be the most efficient method because it can treat many types of pollutants. Additionally, in terms of kinetics, the research also proved that the adsorption phenomenon can occur at the highest rate of adsorption [29]. However, activated carbon is still considered as the most expensive material in the current market because the raw materials used are expensive and cannot be recycled, for example, the utilization of coal that can pollute the environment [25, 29, 30].

Therefore, recently, there are many researchers trying to use low-cost biosorbent as an activated carbon for the adsorption of HS. The material chosen is environmental friendly and cheap, and most of these materials are generated by industries and agricultural activities such as coconut copra, coconut shell, waste apricot, sugar beet bagasse, molasses and rubberwood sawdust, bamboo, rattan sawdust, oil palm fibre and coconut husk [25, 29]. Cost is the main factor in determining the best material as biosorbent. Generally, an adsorbent can be defined as a low-cost adsorbent if it requires only simple process, is abundant in nature or is a by-product or waste material generated from industries or agricultural activities [31].

1.3 Overview of Batch Stirred Tank Reactor Used for Adsorption of HS

Batch stirred tank reactor consists of several components, namely one cylinder tank equipped with one stirrer in the form of a propeller, and one heat exchanger equipped with a temperature control system. The main function of the temperature control system is to ensure that the adsorption process occurs at the desired temperature, which is the ambient temperature, throughout the adsorption process. In the case where the temperature starts to increase due to the heat transfer between biosorbent and the stirrer, proportional band (PB) will be activated with the purpose of maintaining the temperature at the ambient temperature (set point). The layout of this small scale reactor is shown in Figure 3.
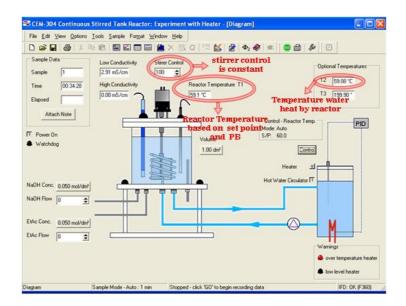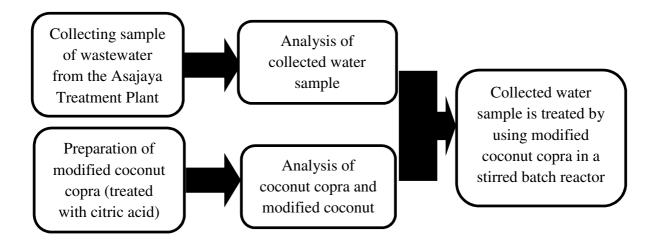
Figure 3: Layout of Batch Stirred Tank Reactor Used for Adsorption of HS

The main reason for choosing this reactor is because the contact time is consistently uniform compared to a continuous stirred tank reactor. Furthermore, feed material is treated as a whole for a fixed period in this type of reactor. Thus, almost all existing batch stirred tank reactor is well stirred, which indicates that the compositions are in uniform contact throughout the adsorption process. In addition, residence time is relatively consistent and constant in order to ensure the contact between solid, which is between biosorbent and liquid (i.e. wastewater), is sufficient. As a result, adsorption process can occur in the most efficient and optimum condition [32].

2.0 METHODOLOGY

The methodology of this research is summarized by using the following flow chart:
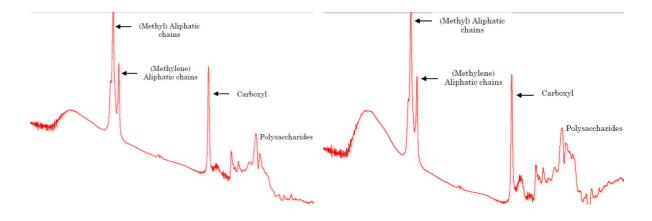
As this project is a collaboration project between the Department of Chemical Engineering and Energy Sustainability with the Department of Chemistry, thus, all the preparation of modified coconut copra was done by the Department of Chemistry. According to Siong Fong Sim et al. (2014), the biosorbent chosen, namely coconut copra residues, were obtained from the local market and undergone several processes, such as drying in an oven at 105°C, followed by refluxing in distilled water for 1 h at 100°C to remove fatty acid, as well as hydrolysis of hemicellulose and lignin. Then, the residues were subjected to washing and drying processes under agitation in citric acid for 1 h at room temperature. Lastly, the residues were washed again to achieve pH 3, and followed by drying process. It is proven that modified coconut copra possesses higher sorption capacity than untreated coconut copra with 96.58% and 45.16% removal of substance at laboratory scale respectively [33]. The role of citric acid in the preparation of modified biosorbent is to form an ester linkage via chemical modification to increase the performance of HS adsorption [34]. During the adsorption process, the temperature and pH of activated carbon remained constant throughout the experiments to maintain the sustainability of the design, as well as to increase the sorption capacity of HS. However, in order to find the optimum condition of this adsorption process, residence time and solid-liquid ratio were varied throughout the experiments. Finally, the treated water was analyzed using a spectrophotometer. Meanwhile, the modified activated carbon was analyzed using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM).

3.0 RESULTS AND DISCUSSION

This part is divided into two parts. First, the analysis of modified coconut copra prior to the adsorption process using FTIR and followed by SEM after the adsorption process and second, the analysis of treated water.

3.1 Analysis of modified coconut copra before adsorption process using FTIR

The results are shown in Figures 4 and 5.

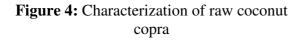**Figure 4:** Characterization of raw coconut copra

Figure 5: Characterization of modified coconut copra

The main functional groups for HS consisted of aliphatic, carboxylic, aromatic, and hydroxylic groups. The peak that shows the wavelength between $2850 - 2900 cm^{-1}$ indicated the C–H stretching of methyl and methylene groups of aliphatic chains. Next, the peak at wavelength between $1700 - 1710 cm^{-1}$ shows the C=O bond of carbonyl and carboxylic and C=C aromatic bonds. Finally, the band peak around $1100 - 1150 cm^{-1}$ shows the C–O stretch of polysaccharide. The modified coconut copra is mixed with citric acid, which makes the pH of coconut copra becomes more acidic. The presence of citric acid in the process may cause reaction between citric acid itself with cellulose, or known as acetylation reaction that forms ester linkage. By observing the wavenumber of modified coconut copra at $1150 cm^{-1}$, it shows the glycosidic linkage where the degradation of hemicelluloses occurs.

3.2 Analysis of modified coconut copra after adsorption process using SEM

After the adsorption process had been performed, two layers were observed in the reactor. These two layers can be easily differentiated due to their different colour and intensity. The top layer of coconut copra is more yellowish than the bottom layer. This is due to the non-homogeneity condition inside the reactor caused by to the mixing condition. In fact, the top layer adsorbs more HS compared to the bottom layer as the stirrer is fixed at the middle of the reactor. Therefore, the totality of the surface of the bottom layer does not get in contact with the wastewater throughout the adsorption process. The results of this analysis are shown in Figures 6 and 7.
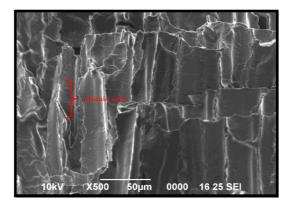

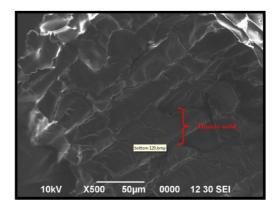**Figure 6:** Top layer of modified coconut copra

Figure 7: Bottom layer of modified coconut copra

The rough surface of coconut copra indicates the amount of HA that is being adsorbed. As the amount of coconut copra increased for solid-liquid ratio, the amount of adsorb HA also increased. This is due to the available surface area for the HA to be adsorbed.

3.3 Analysis of treated water using spectrophotometer

The reading taken from the spectrophotometer at the wavelength of 465cm^{-1} is the value for the concentration of wastewater after the adsorption process. The smallest reading value of the concentration was 0.1mg/L for sample C2. The smaller the reading, the higher the rate of the adsorption process. Table 1 shows the reading that are obtained for each sample.

Table 1: Concentrations obtained from spectrophotometer

Sample	Experimental Condition		Concentration, C (mg/L)			
	Solid-Liquid Ratio	Residence Time (min)	#1	#2	#3	Average
A1	80 g : 2,000 mL	60	1.7	1.8	1.7	1.7
A2	80 g : 2,000mL	120	1.3	1.2	1.2	1.2
B1	100 g : 1,500 mL	60	1.1	1.0	1.0	1.0
B2	100 g : 1,500 mL	120	0.6	0.6	0.6	0.6
C1	120 g : 1,000 mL	60	0.3	0.3	0.2	0.3
C2	120 g : 1,000 mL	120	0.1	0.1	0.1	0.1
Untreated Water	N/A	N/A	4.1	4.0	4.0	4.0

The following formula was used to calculate the removal percentage of HS:

$$\text{Percentage of Removal} = \frac{C_{\text{untreated water}} - C_{\text{water treated by modified coconut copra}}}{C_{\text{untreated water}}} \times 100 \qquad (1)$$

The results shown in table 2 demonstrated and proved that residence time and the quantity of modified coconut copra play an important role in increasing the efficiency of the adsorption of HS. As more modified coconut copra is added, more HS is adsorbed, and more wastewater comes into contact with modified coconut copra, hence, more HS is adsorbed. As a conclusion, there is a proportional relationship between residence time and quantity of modified coconut copra. Lastly, the optimum condition for this adsorption process is at residence time of 120 min and solid-liquid ratio of 120 g: 1,000 mL.

Table 2: Percentage of removal

Sample	% Removal	Sample	% Removal
A1	57.5	A2	70
B1	75	B2	85
C1	92.5	C2	97.5

4.0 CONCLUSION

As a conclusion, this research demonstrates and proves the potential of using coconut copra as a source of activated carbon in adsorbing HS contained in wastewater collected from the Asajaya Treatment Plant with the condition of solid-liquid ratio of 120 g: 1,000 mL, residence time of 120 min and by using a batch stirred tank reactor. For future work, this adsorption process will be scaled up to the real size of the Asajaya Treatment Plant with the intention of supplying clean drinking water to the Asajaya community.

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