COD Reduction in Industrial Wastewater Using Activated Carbon Derived from *Wodyetia Bifurcata* Fruit

Noor Syuhadah Subki*¹, Najiehah Mohd Akhir¹, Nurul Syazana Abdul Halim¹ and Nik Raihan Nik Yusoff¹

¹Faculty of Earth Science, Universiti Malaysia Kelantan, Jeli, Kelantan, Malaysia

E-mail: syuhadah@umk.edu.my

Abstract. Industrial wastewater that being discharge without any prior treatment has become one of the major sources that contributes to pollution in water bodies. Textile industry specifically have great amount of chemicals input which eventually affect the value of acceptable conditions for discharge of industrial effluent especially the chemical oxygen demand (COD) value. Thus, this research was carried out to determine the efficiency of activated carbon prepared from *Wodyetia bifurcata* fruit or commonly known as foxtail palm fruit to reduce COD value in industrial wastewater. The morphology and functional group of the prepared activated carbon was done using SEM and FT-IR. The effect of contact time in COD reduction experiments was done at 60, 90, 120, 150 and 180 minutes. The results showed that the optimum reduction of COD value in textile industry wastewater is 65.31% at 90 minutes. There for it is proved that activated carbon prepared from *Wodyetia bifurcata* fruit have a potential to reduce COD value in industrial wastewater.

1. Introduction

Industrial wastewater has become one of the major sources that contributes to pollution in water bodies. The water discharge without any prior treatment from the industrial activities carries out contaminants and pollutant which can cause several impacts towards the human and environment. These contaminants will eventually affect the amount of organic and inorganic compounds in the water bodies [1]. As a consequence from this condition, the level of biochemical oxygen demand (BOD), chemical oxygen demand (COD) and other parameters of water quality assessment will be affected. Textile industry wastewater specifically have great amount of chemicals input which eventually affect the value of acceptable conditions for discharge of industrial effluent especially the value of chemical oxygen demand (COD) that will lead to water pollution.

Several treatment methods of physical, chemical and biological treatment had been proposed to remove or treat organic compounds from the wastewater. However, the effectiveness of these methods were compromised due to several factors. The high cost of preparation and a long period of experiments were some of the factors that limit the success of the treatments thereby giving the optional to practice adsorption method using activated carbon. Activated carbon is a microporous, homogenous structure with a high surface area which is widely used in the industrial process. The preparation cost of the activated carbon is very low making it to be a desirable material for treatment of wastewater [2]. Activated carbon prepared from biomaterials have been a great interest in order to
find inexpensive and effective alternatives to the existing commercial activated carbon [3]. In this study, wastewater collected from textile industry was treated with the activated carbon to identify its efficiency in reducing the COD value by determining the COD value in the textile wastewater and optimize the time used to reduce the COD value from textile wastewater using the activated carbon prepared from foxtail palm (*Wodyetia bifurcata*) fruit.

2. Methodology

This research involved the sampling process for industrial wastewater and activated carbon raw material. It continued with laboratory work for activated carbon preparation and characterization and finally the COD reduction experiments.

2.1 Sampling

In this study, *Wodyetia bifurcata* fruit or commonly known as foxtail palm fruit was used as the raw material for preparing activated carbon while wastewater from textile industry was collected as the sample water for the treatment using the activated carbon.

The *Wodyetia bifurcata* fruit was collected around Jeli and Kota Bharu district while the industrial wastewater was collected from one of the batik industri in Kota Bharu district.

2.2 Activated Carbon

In this study, *Wodyetia bifurcata* fruit or also known as foxtail palm fruit was activate using chemical activation process. The prepared activated carbon was then characterized using Scanning Electron Microscope (SEM) and Fourier Transform Infra-Red (FTIR).

2.2.1 Preparation

Foxtail palm fruit was collected and washed thoroughly with distilled water to remove the impurities and dirt on the fruits. The fruits were dried overnight in the oven at 100°C to remove the water molecules present in the fruits. The dried fruits were left outside to let it cool in room temperature [4]. The dried fruits were carbonized in the furnace at 300°C for two hours to enhance the pore development for adsorption. Next, the char produced from the carbonization processed was cooled in room temperature before being crushed into small pieces using mortar and pestle. Then, it was sieved through 250 µm [4] for a homogenised size. The char was stored in a tight polyethylene bag and kept dried in the desiccator before activation process.

For chemical activation process, about 40 g of foxtail palm fruit char was soaked and impregnated with 80 mL of concentrated nitric acid (HNO₃) in a beaker [5]. The mixture was mixed vigorously for 30 minutes with a constant stirring until it becomes a paste. Then, the paste was left impregnated overnight in the fume hood to ensure the chemical had fully reacted with the sample. After that, it was carbonized again at 500°C for two hours and 30 minutes in the furnace to complete the activation process [5]. Next, the activated carbon was washed using distilled water to adjust its pH to neutral. Then, the activated carbon was dried in the oven for 3 hours at 150°C before was stored in a tight polyethylene bag and kept in the desiccator for further use.

2.2.2 Characterization

The morphology structure and functional group of the prepared activated carbon was analysed before and after the activation process using Scanning Electron Microscope (SEM) and Fourier Transform Infrared (FT-IR).

The surface morphology structure was analysed by using JSM-IT 100 Scanning Electron Microscope (SEM). The prepared activated carbon was dried in oven for 24 hours to reduce water molecules hence decrease the chance for charging. After that, the sample was prepared by putting a very thin layer of dried powdered sample at the top of specimen stub and thus SEM was used to analyse it with specification of 7.0 kV and 1500x magnification as it is able to provide useful information about the composition at the specimen surface.
The functional groups were determined by using iZ10 Fourier Transformation Infrared (FT-IR) Spectrometer. About 0.1 mg of prepared activated carbon was taken and transferred to the analyzer to obtain a variety of wave lengths that represent different functional groups in the sample [2].

2.3 Chemical Oxygen Demand (COD)
COD analysis was conducted on the textile industry wastewater by following the Reactor Digestion Method (Hach Method 8000) intended for COD testing. About 2 mL of wastewater sample was added to a COD Digestion Reagent Test ‘N Tube vial and about 2 mL of deionised water was added to the second vial as blank. Both vials were placed in a preheated COD Reactor and heated for two hours at 150°C for digestion. Upon digestion, the vials were cooled to room temperature. The blank was set to zero and then the prepared samples were measured using HACH Spectrophotometer (DR5000, Range: 0.7 – 15,000 mg/mL).

COD analysis was conducted onto the textile industry wastewater before and after the treatment process. The percentage of COD reduction is defined as the difference in concentration before and after adsorption and the efficiency of the COD reduction was calculated using the equation below [6]:

\[
\text{Reduction (\%)} = \left( \frac{C_o - C_i}{C_o} \right) \times 100
\]

where, \( C_o \) is the initial reading of COD value (mg/L) and \( C_i \) is the final reading of COD value (mg/L).

The optimization of time for COD reduction was conducted for time interval 60, 90, 120, 150 and 180 minutes with a constant of 20 mL wastewater, 2 g of prepared activated carbon and 200 rpm retention time.

3. Result and Discussion
The characterization of the prepared activated carbon before and after the activation process and the time optimization for COD reduction in the industrial wastewater will be discussed.

3.1 Characterization of Activated Carbon

3.1.1 Morphology structure
The morphology structure of the foxtail palm fruit before and after the chemical activation processed are shown in Figure 1.

The morphology structure of raw material was determined by using SEM under specification of 5.0 kV and 1500x magnification.

Figure 1(a) showed the SEM image of raw material shown fiber structure, irregular texture, rough surface and only few small pores spotted on the surface. While Figure 3.1(b) showed the SEM image after the chemical activation processed.

It is clearly showed that the activation processed has increased the pore size and volume on the activated carbon surface structure. These well-developed pores result from evaporation of chemical reagent which was nitric acid during carbonization that leaving empty space on the surface. Thus, the pores that presented on surface of activated carbon may help to increase the COD reduction efficiency.
Figure 1. Morphology of surface area for foxtail palm fruit a) before the chemical activation (raw material) and b) after chemical activation process.

3.1.2 Functional Group

The functional group of the foxtail palm fruit before and after the chemical activation process are shown in Figure 2.

Figure 2. Functional group for foxtail palm fruit a) before chemical activation (raw material) and b) after chemical activation process.

The FT-IR spectra were obtained to characterize function group that found in raw material. Functional group of activated carbon plays an important role in determining the surface properties and quality of activated carbon which lead to affect the efficiency of the prepared activated carbon. Figure 3.2 shows that there were few peaks detected for the absorbance band of raw material at 3335, 1457, 1374, 1241, 1031 and 509 cm$^{-1}$ [7].

Figure 2 (a) showed a broad adsorption peak at 3335 cm$^{-1}$ which assigned to O-H stretching functional group. This indicated that the free hydroxyl group and adsorb water presented on the surface of foxtail palm fruit. Hence, the high intensity to absorb proven that foxtail palm fruit raw material has high potential as adsorbent which increases the removal efficiency of dye. Besides, adsorption peak of 3200 to 3650 cm$^{-1}$ also denoted that there were O-H group of alcohols and phenols and carboxylic acid on the surface.

Figure 2 (b) showed the functional group that presented after the chemical activation process. There were only few significant peaks observed which were at range between 1600 to 1450 cm$^{-1}$ and at
1116 cm\(^{-1}\). Peak range between 1600 to 1450 cm\(^{-1}\) indicated peak bond was attributed to C=C in aromatic ring whereas 1116 cm\(^{-1}\) denoted that the presence of C-O stretching bond in foxtail palm fruit activated carbon. Some functional group may disappeared due to the chemical reagent that used for impregnation and high temperature for carbonization. However, it proven that foxtail palm fruit was successfully converted into carbon [8].

3.2 COD Reduction in Industrial Wastewater
The initial concentration of COD in the industrial wastewater collected from the textile industri was 441 mg/L. This value is exceeded the standard value set by the Department of Environment (DOE) Malaysia. The acceptable value of COD for textile industry was 250 mg/L for effluent under Standard B as prescribed in the Environmental Quality (Industrial Effluent) Regulation 2009 [9].

After that, about 20 mL of textile wastewater was treated with 2 g of prepared activated carbon at 200 rpm retention time for 60, 90, 120, 150 and 180 minutes. The result for the effect of contact time on COD reduction efficiency was as shown in Figure 3.

![Figure 3](image)

**Figure 3.** Effect of contact time to COD reduction efficiency by activated carbon.

Figure 3 showed high percentage of COD reduction was obtained for the first 60 minutes. This is because, at the beginning of adsorption process, the pores or the surface area of the activated carbon has not been occupied yet, thus resulting a high percentage of COD reduction. An increase of percentage removal by 5.22\% between contact times of 60 minutes to 90 minutes was obtained with the reading of 60.09\% and 65.31\% respectively. The highest percentage of COD reduction was achieved at the 90th minute of contact time.

A slightly difference of percentage removal was obtained after the 90th minute with the reading of 65.08\% of COD removal for both reading at 120th minute and 150th minute. Previous study have prove that, as the contact time for the adsorption process increase, the percentage removal will decrease [10, 11]. The inclination of the result was due to saturation of the adsorbent pores that enabled for continuous adsorption process to take place.

4. Conclusion
The results indicate from this research proved that foxtail palm fruit activated carbon is capable to reduce the COD value in textile industri wastewater to the permissible limit by the Environmental Quality Act 1974, and subsidiary legislation act, regulation 6: Prohibition of discharge of effluent containing certain substance into inland water. Therefore, the prepared activated carbon by foxtail palm fruit have a good potential to be use in water treatment system at industry in order to reduce the pollution to the water body.

Acknowledgements
We offer our special appreciation to the Faculty of Earth Sciences, UMK Jeli Campus for providing the facilities used in this research. Our cordial appreciation also goes to all laboratory stafts from Faculty of Earth Science for their assistance through completion of this research. This research was supported by UMK Short Term Grant Scheme (R/SGJP/A08.00/A01412A/002/2018/000480).
References

[1] Al-Badaii F, Shuaimi-Othman M and Gasim M B 2013 *Journal of Chemistry* 2 1-10
[2] Pradhan P, Sripal S and Maheshkumar Y 2013 *Res J Chem Sci* 3(12) 12-15
[3] Thomas B N and George S C 2015 *iMedPub Journals* 1 1-7
[4] Zakir M 2013 Adsorption of lead ( II ) and copper ( II ) ions on rice husk activated carbon under sonication in International Symposium on Chemical and Bioprocess Engineering, Yogyakarta., 1-10.
[5] Chin S X 2014 Activated carbon’s adsorbent by agricultural wastes in textile waste water. Faculty of Earth Sciences.
[6] Kushwaha A K, Gupta N and Chattopadhyaya M C 2014 *Journal of Saudi Chemical Society* 18(3) 200-207
[7] Pavia D L, Lampman G M, Kriz G S and Vyvyan J A 2008 Introduction to spectroscopy: Cengage Learning.
[8] Bouchelta C, Medjram M S, Bertrand O and Bellat J P 2008 *Journal of Analytical and Applied Pyrolysis* 82(1) 70-77
[9] Environmental Quality Act., 1974.
[10] El-Dars F M S E, Ibrahim M A and Gabr A M E 2014 *Desalin. Water Treat* 52 (16-18) 2975-2986
[11] Abdel-Gawad S A and Abd El-Aziz H M 2019 *Air, Soil and Water Research* 12(1) 1-7