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ACTIVATED CARBON FROM MUKAH COAL FOR TEXTILE WASTEWATER BIOREMEDIATION TREATMENT

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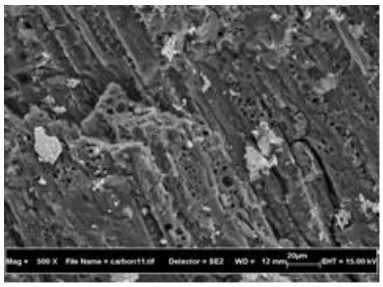
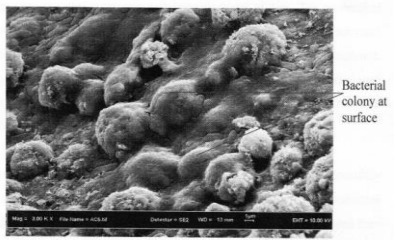
Graphical abstract





Abstract

Activated carbon is commonly used in water and wastewater treatment, removing organics that cause unpleasant odors, tastes and other detrimental effects. In this study, bioremediation treatment consists of biofilms of two types of microbes, i.e. *Bacillus* sp and *Escherichia* sp are grown and immobilized on the Mukah coal activated carbon from Sarawak. Prepared activated carbon was categorized by different physical geometries design such as SGAC I, SGAC II, SGAC III, HCGAC I, HCGAC II and HCGAC III. The target pollutants to be removed from the Ramatex textile wastewater were BOD_5, COD, TSS, color, phosphate, nitrate and sulfate. *Escherichia* sp with SGAC I was found to give the best results for the bioremediation process and the percentage of BOD_5, color, COD, TSS, nitrate, sulfate and phosphate removal were 71.4%, 91.1%, 96.4%, 98.8%, 80.3%, 90.3% and 60.3% respectively. The results indicated that combination between physical and biological treatment was the main factor for the best pollutants removal achievement.

Keywords: Activated carbon, wastewater, textile wastewater, biofilm, bioremediation system

1.0 INTRODUCTION

Activated carbon (AC) is a high-porosity material, which is useful in adsorption [1-8] of both gases and solutes from aques solution. Therefore it has been widely used for the treatment of raw water and wastewater from industrial effluents, the recovery of solvents, and the removal of organic pollutants from home or office drinking water. As environmental pollution is becoming more serious, utilization of activated carbon is growing steadily.

AC sources can be either biomass waste [1-2, 4, 8-10, 12-13] or coal [3, 5-7, 11, 14, 16] has been studied by many researchers. This project focused on the development of activated carbon from coal for textile wastewater bioremediation treatment.

A series of activated carbons was prepared from bituminous coal; by 1) chemical activation with potassium hydroxide and zinc chloride and 2) physical activation with carbon dioxide. The effect of process variables such as carbonization time, temperature, particle size, chemical agents, and method of mixing and impregnation ratio in the chemical activation process was studied in order to optimize those preparation parameters [14].

Treatment of complex Remazol dye effluent using sawdust and coal-based activated carbons was done by Vijayaraghavan *et al*. A detailed characterization revealed that the pore diameter of

the activated carbon played an important role in dye adsorption [5]. On the other hand, Hwang *et al*. [15] claimed that carbonization could remove a considerable amount of organic matter from waste. From their results, carbonization could be considered as a pre-treatment method for waste before landfilling, as well as for fuel recovery.

Physical and chemical activations sorption was done by Turkan and Atakan [16]. They have prepared coal activated carbon from Zonguldak region coals which are collected from two mines (Kilimli and Armutcuk). The BET surface area of the Kilimli coal samples which were initially have a value of 1.20 m^2/g were increased to 52.62 m^2/g after pyrolytic heat treatments at 800 °C and increased to a value of 830.5 m^2/g by treating the coals with KOH + NH_4Cl mixture at 750 °C followed by oxidation of the samples mixed with $ZnCl_2$.

In this project all the experiments will use Mukah Coal from Sarawak as the source of AC and activation process by CO_2 (physical treatment). Carbonization process will be held at 700 °C whereas activation process at 850 °C.

Refer to bioremediation side, many of researchers claimed successes to remove colour, BOD, COD and treating the non-biodegradable textile effluent. Reduction-biological treatment system for the decolourization of non-biodegradable textile dyeing is reported to be a successful technique to remove BOD, COD, and total suspended solid (TSS) [17]. Dyestuff wastewater having high salinity, colour and non-biodegradable organic concentration can be treats using Fenton's oxidation, physical adsorption and fixed bed biofilm process [18].

Anaerobic treatment of textile wastewater studied was possible to remove COD, BOD and colour with the supplementation of an external carbon source in the form of glucose [19]. An anaerobic technique has been applied to azo-reactive dye aqueous solution and cotton textile wastewater in order to eliminate the colour. The biodegradation ability of cotton textile wastewater was also examined without the addition of external substrate supply (acetic acid) resulting to poor decolourization results. However, anaerobic digestion of the same wastewater using the acetate-consuming bacteria and acetic acid as an external substrate supply lead to the complete decolourization [20].

Mukah coal AC will be formed into a different design shapes which are labelled as SGAC (Solid Granular Activated Carbon) and HCGAC (Hollow Cylinder Granular Activated Carbon). SGAC and HCGAC divided into three types and labelled as SGAC I, SGAC II, SGAC III, HCGAC I, HCGAC II and HCGAC III accordingly.

2.0 METHODOLOGY

2.1 Source of Granular Activated Carbon and Pre-treatment

Mukah coal was obtained from Global Minerals (S) Sdn Bhd, one of the main coal mining company in Sarawak. Mukah coal was dried at 90 °C for 24 hours before it sieved into 1.2 mm<size<4 mm. Sieved coal was dried again to remove balance moisture.

2.2 Carbonization and Activation Process

80 grams of raw material was prepared and then placed into a fixed bed reactor. N_2 gas with flow rate 1.5 L/min was used for carbonization. Then, the sample was activated using CO_2 (99.98% of purity) with the flow rate of 1.0 L/min.

Carbonization was done at 700 ° C for 1 hour with temperature rate 15 ° C/min and then cool down to room temperature. Produced charcoal was dried at 90 ° C for 24 hours before activation. Activation process was done at 850 ° C for ½ an hour (holding time) at 15 ° C/minute. After finished the samples was cooled down to the room temperature. All the processes have been repeated. Figure 1 shows the flow chart of carbonization and activation processes.

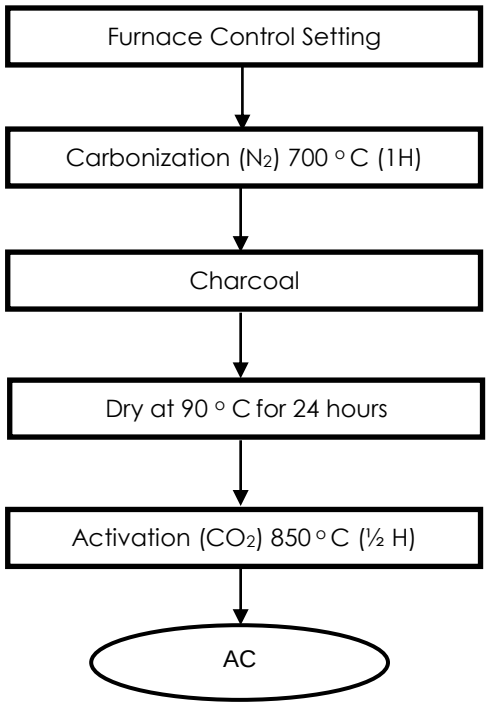


Figure 1 Carbonization and activation process

2.3 SGAC and HCGAC Design Shape

There are two different design shapes as shown in Figure 2 and Figure 3.

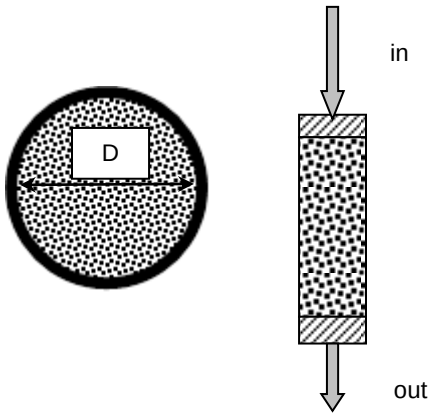


Figure 2 Design shape for SGAC

SGAC divided into three categories which are differentiate by diameter (D) of column:

1) SGAC I – D = 3.4 cm
2) SGAC II – D = 5.7 cm
3) SGAC III – D = 8.5 cm

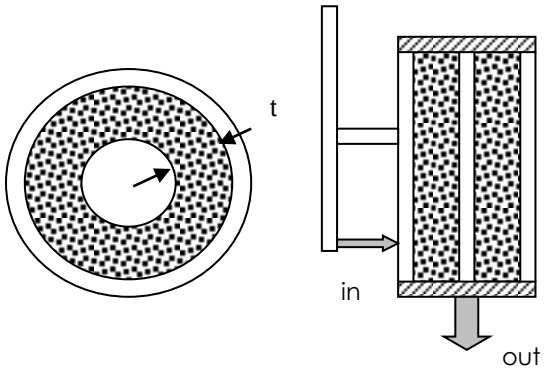


Figure 3 Design shape for HCGAC

HCGAC divided into three categories which are differentiate by thickness (t) of column:

1) HCGAC I – t = 2 cm
2) HCGAC II – t = 3 cm
3) HCGAC III – t = 4 cm

2.4 Bioremediation Process

Two types of microbes *Bacillus sp* and *Escherichia sp* were used to create a biofilm on the surface of AC. To have a good process treatment, holding time was implemented (4 Hours, 12 Hours and 24 Hours). This is to allow the microbes having enough time to react with the textile wastewater.

3.0 RESULTS AND DISCUSSION

3.1 BET Surface and Micropore Area Analysis

Characterization of Mukah coal AC has been carried out using a volumetric unit of Micromeritics ASAP2010 Inc. Norcross, GA, USA.

From the analysis BET surface area and micropore area was 397 m^2/g and 305 m^2/g respectively.

AC can be developed by using chemical or steam activation in order to increase the surface and micropore area.

3.2 Raw Textile Wastewater

Table 1 shows the results for raw wastewater characterization collected from Ramatex Textile Industries Sdn Bhd. Samples are collected daily for 5 times (Mon – Friday).

Table 1 Raw textile wastewater characterization

Parameters	Unit	Range Value
pH value	pH	8.10 – 9.92
BOD	mg/L	70.0 – 83.6
COD	mg/L	500.0 -610.0
TSS	mg/L	140.0 – 300.0
Nitrate	mg/L	7.5 – 14.0
Sulfate	mg/L	250.0 – 350.0
Phosphate	mg/L	15.0 – 13.1
Colour	ADMI	200.0 – 500.0

3.3 Scanning Electron Microscopy

The Scanning Electron Microscopy images were taken on a Philip XL at Faculty of Mechanical Engineering, UTM.

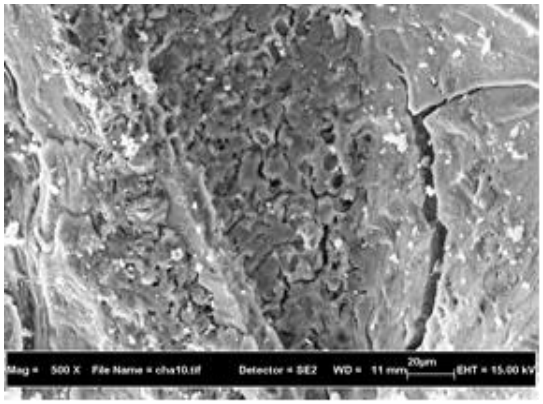


Figure 4 Mukah coal char morphology (Mag.500X)

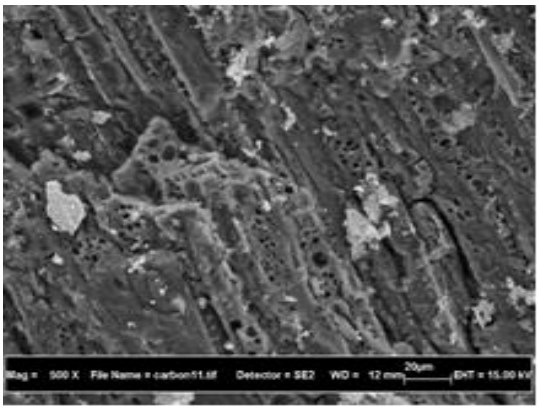


Figure 5 Mukah coal activated carbon morphology (Mag.500X)

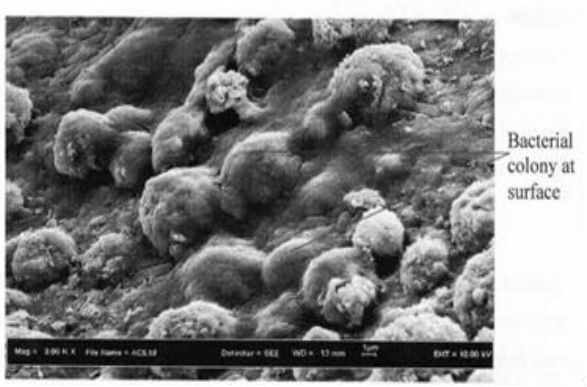


Figure 6 Bacteria immobilization on activated carbon morphology (Mag 3.0 KX)

Coal AC (Figure 5) shows more additional pore area compared to Figure 4 were developed on the sample surface.

From Figure 6 shows AC attached with bacteria colony. AC immersed into the solution of bacteria in a day to let the bacteria grows on the surface of activated carbon. It has shown more than one colony of bacteria grown on the activated carbon surface area.

3.4 Bioremediation with *Bacillus sp*

Bacillus sp is a genus of Gram-positive, rod-shaped (bacillus) bacteria. Bacillus species can be obligate aerobes (oxygen reliant), or facultative anaerobes (having the ability to be aerobic or anaerobic).

Amar *et al*., has been studied for biochemical characteristics of a textile dye degrading extracellular laccase from a Bacillus sp. ADR (Azo Dye Removal). The purified enzyme decolorized structurally different azo dyes with variable decolorization rates and efficiencies of 68–90%. This study is useful for understanding the precise use of Bacillus sp. ADR in the decolorization of textile dyes containing industrial wastewater [21]. Table 2-7 below show pollutants removal in percentage (%).

Table 2 SGAC I with *Bacillus sp* (% Removal)

Pollutants	4 H	12 H	24 H
BOD	1.9	24.2	30.4
COD	7.9	47.7	59.2
TSS	96.5	97.5	98.6
Colour	33.6	39.4	61.4
Phosphate	2.4	32.9	41.8
Nitrate	1.1	7.4	22
Sulphate	1.3	53.2	79.4

Basically, more holding times give the more retention times for some pollutants to be treated but in terms of total suspended solid (TSS) removal, no significant change can be seen for SGAC design.

Table 3 SGAC II with *Bacillus sp* (% Removal)

Pollutants	4 H	12 H	24 H
BOD	0.6	10.6	28
COD	25.8	37.3	80.8
TSS	95.8	96.5	98
Colour	1.6	49.4	59.4
Phosphate	1.3	5.7	57.4
Nitrate	22.9	27.7	71.4
Sulphate	14.6	51.7	83.2

Table 4 SGAC III with *Bacillus sp* (% Removal)

Pollutants	4 H	12 H	24 H
BOD	8.1	24.2	45.3
COD	26.9	45.1	76.5
TSS	95.2	96.2	96.8
Colour	2.3	18.6	54
Phosphate	0.5	4.7	31.4
Nitrate	0.3	40.9	70
Sulphate	28.3	64.5	85.2

Overall results accumulated for SGAC design shows 24 H is the best holding time with significant % removal observed.

Table 5 HCGAC I with *Bacillus sp* (% Removal)

Pollutants	4 H	12 H	24 H
BOD	10.2	53.4	34.9
COD	38.3	62.4	39.1
TSS	26.4	55.5	64.2
Colour	17.8	40.5	39.1
Phosphate	38.5	70.3	66.9
Nitrate	40.3	60.9	51.2
Sulphate	27.3	25.7	3.6

It was concluded that SGAC design was better than HCGAC design for TSS, COD, colour, nitrate and sulphate removal.

Table 6 HCGAC II with *Bacillus sp* (% Removal)

Pollutants	4 H	12 H	24 H
BOD	10	51.9	22.2
COD	5.9	27.6	20.7
TSS	48.8	56.4	62.9
Colour	26	53.9	44.4
Phosphate	20.1	68.2	78.8
Nitrate	20.5	52.1	43.7
Sulphate	17.1	10	34.8

Table 7 HCGAC III with *Bacillus sp* (% Removal)

Pollutants	4 H	12 H	24 H
BOD	11.1	52.6	30.3
COD	43.5	76.2	57.8
TSS	26.4	42.7	54.1
Colour	42.2	70.3	48.8
Phosphate	21	50.4	80
Nitrate	30.4	30.4	20
Sulphate	10.6	16.2	22.7

BOD % removal for SGAC's has no significant change compared to HCGAC but phosphate % removal with 80 % removal observed for HCGAC III. It was the higher value with 24 H holding time.

3.5 Bioremediation with *Escherichia sp*

Escherichia sp is a genus of Gram-negative, non-spore forming, facultatively anaerobic, rod-shaped bacteria from the family Enterobacteriaceae. In those species which are inhabitants of the gastrointestinal tracts of warm-blooded animals.

Mustafa *et al*., has done a study on the Effect of oxygen on decolorization of azo dyes by Escherichia coli and Pseudomonas sp. and fate of aromatic amines. The effects of two different microorganisms and aerobic/anaerobic conditions on decolorization were recorded with the monitoring of colour, pH, COD, dissolved oxygen, alkalinity, and volatile fatty acids concentrations. The aromatic amines (as benzidine) arising from the metabolites of anaerobic biodegradation of dyes and the recoveries of these aromatic amines were also monitored. The colour of the CR and DB 38 dyes were removed up to 98 and 72%, respectively, by E. coli at the end of anaerobic incubation, while no decolorization occurred throughout the aerobic incubation. Under microaerophilic conditions, the azo dyes CR and DB 38 were decolorized up to 39 and 75% by E. coli, respectively. In studies with Pseudomonas sp., the colour of the CR and DB 38 dyes were removed up to 100 and 83%, respectively, after 5 days of anaerobic incubation, while 76 and 74% colour removal efficiencies were observed under microaerophilic conditions [22].

Table 8 SGAC I with *Escherichia sp* (% Removal)

Pollutants	4 H	12 H	24 H
BOD	10.6	30.4	71.4
COD	83.7	94.7	96.3
TSS	97	97.6	98.8
Colour	62.7	80.8	91.1
Phosphate	9.9	15.1	60.3
Nitrate	72.6	76.6	80.3
Sulphate	18.2	85.3	90.3

TSS removal has no significant change for SGAC design but the result is better compared to HCGAC design. It was found that BOD removal was the highest value with 71.4 % removal if compared to others design as well as microbe type.

Table 9 SGAC II with *Escherichia sp* (% Removal)

Pollutants	4 H	12 H	24 H
BOD	14.3	34.2	64
COD	90.8	94.7	96.9
TSS	96	96.7	97.7
Colour	39.2	59.8	84.7
Phosphate	12.1	27.1	57
Nitrate	30.6	63.4	82.3
Sulphate	15	88.1	91.6

Table 10 SGAC III with *Escherichia sp* (% Removal)

Pollutants	4 H	12 H	24 H
BOD	9.3	34.2	56.5
COD	9	6.6	14.9
TSS	95.1	95.9	96.2
Colour	10.5	63.3	80.8
Phosphate	0.5	9.9	34.9
Nitrate	30.3	38.3	62.3
Sulphate	4	81.2	91.3

The results demonstrated that SGAC I dominated on the best performance of pollutants removal. That was happen because SGAC I allowed textile wastewater to be filtered effectively. Long pipe column was needed to fill 200 grams activated carbon, therefore more resistance or contact time needed to go through. The percentage of activated carbon take part is higher compare to other design condition. Pipe surface area and length was the major factor to obtained good result in the treatment process.

Table 11 HCGAC I with *Escherichia sp* (% Removal)

Pollutants	4 H	12 H	24 H
BOD	20.3	45.7	58.2
COD	5.8	36.2	42.6
TSS	30	44.5	53.9
Colour	39.4	44.4	52.8
Phosphate	16.8	62.4	69.1
Nitrate	10.2	32.4	50
Sulphate	57.3	63.8	22.1

Table 12 HCGAC II with *Escherichia sp* (% Removal)

Pollutants	4 H	12 H	24 H
BOD	18.3	30.6	61.8
COD	6.3	28.5	25
TSS	32.6	41.8	52.5
Colour	25.8	53.5	67.2
Phosphate	23.7	81.1	79.8
Nitrate	40.1	59.8	60
Sulphate	34	11.1	37.5

Table 13 HCGAC III with *Escherichia sp* (% Removal)

Pollutants	4 H	12 H	24 H
BOD	10.9	71.6	49.3
COD	5.5	60.7	50.1
TSS	34.7	40.3	50.9
Colour	42.8	66.2	79
Phosphate	35.3	60.7	72.5
Nitrate	10.5	42.7	29.5
Sulphate	28.5	19.7	41.2

HCGAC with *Escherichia sp* implemented shows uncertain test result. From the data HCGAC I removed TSS, color and sulfate more than others HCGAC design with 54.7%, 82.6% and 65% respectively. HGAC II showed the best result on the removal of BOD (61.8%) and Nitrate (60%) whereas HGAC III dominated on the removal of COD (50.1%) and colour (79.0%).

All the experiment were based on © Hach Company, 1999, 2001 all rights reserved procedure. Some of the procedure adapted from Standards Methods for the Examination of Water and Wastewater and some of them are equivalent to USEPA (U.S. Environmental Protection Agency) method.

The reasons to the variation in the results from all set experiment were:

a) Holding time- the long holding time applied the best result can be achieved.
b) Type of geometry- SGAC I appear to be the best geometry. Resistance or long bed time could be the factor.
c) Type of bacteria- *Escherichia sp* perform a good removal activity.

From Table 2-13, it was found that *Escherichia sp* in the SGAC I column were most effectively used to remove pollutant in textile wastewater. Increased in water quality was indicated by the removal of color and nutrient by *Escherichia sp* combination. The percentages of nutrient removal were nitrate (80.3%), phosphate (60.3%), sulphate (90.3%), colour (91.1%), TSS (98.8%), COD (96.4 %) and BOD (71.4%).

It can be concluded that SGAC I with the combination of *Escherichia sp* gave the best result on textile wastewater bioremediation treatment.

4.0 CONCLUSION

Overall remediation process results shown, textile wastewater treatment depends on the design and type of bacteria used for biofilm development. The more retention time for textile wastewater need the more effectiveness for the remediation process as well as the more holding time implemented in bioremediation treatment the best result will be accumulated. It can't be denied bacteria cooperated with activated carbon as their temporary house to remove pollutants in textile wastewater.

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