Phosphoric acid activation of sugarcane bagasse for removal of *o-toluidine* and *benzidine*

M R M Adib, M H M N Attahirah and A R M Amirza

Faculty of Civil and Environmental Engineering, Universiti Tun Hussein Onn Malaysia (UTHM), 86400 Batu Pahat, Johor, Malaysia.

E-mail: adib@uthm.edu.my

Abstract. In the effort to find alternatives for low cost adsorbent, activated carbon using sugarcane bagasse (SBAC) has been introduced in this study that has undergo chemical treatment using phosphoric acid to determine the effectiveness of adsorption process in removing *o-toluidine* and *benzidine*. Throughout this study, 92.9% of *o-toluidine* has been successfully removed by SBAC at optimum value of 1.1 g of dosage with contact time of 10 minutes and concentration of 10 mg/L. While *benzidine* was remove by 83.1% at optimum dosage of 1.1 g with 60 minutes of contact time and at 20 mg/L concentrations. Testing of SEM proves that SBAC has high porosity and comparable to CAC. In FTIR results, shows that CAC has high number of double bond while SBAC shows no double bond at all. Presence of double bond in CAC lead to increase in percentage of removal of adsorbate. After considering other factor such as cost, energy and environmental friendly, it shows that SBAC was considerable to replaced CAC.

1. Introduction

Textile industry is among the chemical industries involved in water pollution wherein degree of pollution is characterized by its high water consumption and chemical usage [1, 2]. Dye and textile industries are always related to each other and it has been widely known all around the world. The release of textile wastewater inside natural source has been a major concern because it contain large amount of high metal, organic compound and toxic substance which will gives bad impact to human and environment [3-5]. Usually the discharge of textile wastewater inside the stream will cause significant problem such as high level of toxicity and reduce sun-rays penetrations into the stream and effects the photosynthesis process [6].

Colored wastewater is the direct result of the production of dyes and a consequence of their extensive use in the textile industries. The hazardous substances that contains in dyes are *o-toluidine* (OT) and *benzidine* (BZ). In fact, World Health Organization (WHO) had announce that *o-toluidine* and *benzidine* are one of the substance which have high amount of genotoxic and carcinogenic that are declared to be hazardous to human and environment [7-9]. *O-toluidine* (OT) are able to be adsorbed by skins and cause skin irritation and for long term effect may cause cancer. The exposure on health impacts due to *benzidine* (BZ) effects may cause bladder cancer. Other than that, it also will harm environment as it will lead to pollution of water and effect the aquatic life [10].

Nowadays, various physical-chemical techniques have been studied to access their applicability for the treatment of industrial effluents. Among these processes, may be included coagulation, adsorption, precipitation, flocculation and ozonation [11]. The adsorption is considered to be an effective method

for the dye removal due to its low maintenance, simple operation and removal effectiveness [12]. Activated carbon have shown great potential for dye removal due to its properties such as large surface area, microporous structure and high adsorption capacity. As a result, there is an increasing interest in the development and application of activated carbon produced from agricultural wastes [13].

Therefore, a method of removing *benzidine* and *o-toluidine* inside dyes of textile wastewater has been introduced throughout this study which is by using activated carbon prepared by sugarcane bagasse (SBAC) that has undergo chemical activation using phosphoric acid (H_3PO_4). Instead of using commercial activated carbon (CAC), this study will emphasis on using an agricultural waste to produce an activated carbon as it can cut cost and reduces the amount of waste in landfill [14]. Recently, Jiang *et al* has prepared *tetraethylenepentamine* modified sugarcane bagasse, and found that the adsorption capacity of sugarcane bagasse for anionic dye eosin Y increased to 399.04 mg/g at pH 6.0 [15]. In this study besides preparing SBAC to removes *benzidine* and *o-toluidine* are, by considering different factors, such as dosage, contact time and concentration in order to obtain the optimum value needed for SBAC to remove hazardous substances were investigated as well.

2. Materials and Methods

2.1. Sugarcane Bagasse Activated Carbon (SBAC) Preparation

The sugarcane bagasse was collected locally. The samples were initially washed under running tap water to remove contaminants and excess sugar and dried in dry oven at 105°C for 24 hours until constant weight achieved and stored in container for processing. Dried bagasse is impregnated with 30% of phosphoric acid (H_3PO_4) for another 24 hours. In impregnation process, raw bagasse is fully immersed in acid with the ratio of 30g bagasse to 900ml acid. After impregnation for 24 hours, impregnation bagasse is then carbonized at 500°C in furnace for two hours. The production of activated carbon is washed with pure water until the pH of activated carbon reached 4.00-4.99. Finally, the activated carbon is heated in dry oven at 70°C for 2 hours [16]. The SBAC produced was then sieved to 63µm by sieve analysis testing, referring to ASTM C136-06 Standard Test Method for Sieve Analysis of Fine and Course Aggregates.

Figure 1. Activated carbon from sugarcane bagasse.

2.2. Adsorbate Solution Preparation

The stock solution of 1000 ppm were prepared by dissolving appropriate amounts of 1 gm of powdered *o-toluidine* and *benzidine* in 1 litre of distilled water. Dilution were made with distilled water to make different concentrations range 10-100 ppm.

2.3. Characteristics of Sugarcane Bagasse Activated Carbon (SBAC) and Commercial Activated Carbon (CAC)

Sample of SBAC and CAC are taken and undergo proximate analysis testing which comprise of bulk density, moisture content and ash content. Proximate analysis is conducted to identify the characteristics

of the samples. Morphological view and pore size is measured using Scanning Electron Microscopy (SEM). SEM is microscope that works with electrons instead of light. SEM was used to visualize very small topographic details on the surface area of activated carbons. A range of pore size from selected surface area will be used to observe whether the pore is well-developed or raptured. While, the functional groups of the sample will be measured using Fourier Transform Infrared Spectroscopy (FTIR). For FTIR, the sample is tested to check the chemical composition contain inside the activated carbon that has related with the hazardous substance such as *o-toluidine* and *benzidine*.

2.3.1. Bulk Density. Bulk density is defined as the mass of a unit volume of the sample in air, including both the pore system and the voids among the particles. Generally, an adsorbent with bulk density need to be generated frequently because it can hold adsorbate per unit weight. It is expressed as g/cm^3. In this test, 8.0 g sample of SBAC and CAC are taken and placing in crucible and weight it. Then, placed the crucible in dry oven for 3 hours at temperature of 110°C. Let the samples cooling down before weight it to measure the mass after heated [17].

$$\text{Bulk Density} = \frac{M_o - M_i}{V} \; x \; 100 \qquad (1)$$

Where Mo is the initial mass of the sample (g), Mi is the final mass of the sample (g) and V is the volume of the sample (cm^3).

2.3.2. Moisture Content. 8.0 g of activated carbon sample weight are measured and then taken in a crucible. It was then heated in an oven at a temperature of 105°C for 90 minutes. The crucible is left open or not covered during heating process. After heating, crucible is removed and cooled in a desiccator. After cooling the weight of dried sample are measured [18].

$$\text{Moisture Content} = \frac{M_o - M_i}{M_o} \; \boldsymbol{x} \; \mathbf{100} \qquad (2)$$

2.3.3. Ash Content.
For ash content determination, 3.0 g of SBAC and CAC samples are placed in crucible and weighted. Then, the crucible was heated in a furnace under a temperature of 500°C for about 90 minutes inside the furnace. After that, the crucible was allowed to cool in a desiccator to room temperature and reweighed [19]. The ash content was calculated using the equation.

$$\text{Ash \%} = \frac{\textit{Ash weight}}{\textit{Oven dry weight}} \; \boldsymbol{x} \; \mathbf{100} \qquad (3)$$

2.3.4. Batch Experiment.
Batch experiment is performed to obtain the optimum condition get from the variable parameter that is set to remove *o-toluidine* and *benzidine* from aqueous solution through adsorption process. Parameter taken in this study; adsorbent dosage (0.1g-1.1g), contact time (10-120 minutes) and adsorbate concentrations (10-50 mg/L) was conducted using 50 ml of adsorbate solution measured in 250 ml conical flask. The sample were shaken at 135 rpm. At the end of each experiment conducted, the samples was filtered and the filtrate solution concentration was analysed using the UV-VIS Spectrometer at wavelength of 520 nm for *o-toluidine* and 497 nm for *benzidine*. The percentage adsorption of activated carbon toward adsorbates was calculated as

$$\text{\% Removal} = \frac{C_i - C_e}{C_i} \; x \; 100 \qquad (4)$$

Where C_i is the initial adsorbate concentration (mg/L), C_e is the equilibrium concentration of adsorbate (mg/L).

3. Result and Discussion

In this section, the textural and adsorption properties of the activated carbon produced were examined. Determination of optimal conditions in adsorption process would indicate a better modelling process for larger scale treatment. Thus, the result of major parameters that effect the adsorption process were discussed.

3.1. Characterization of SBAC and CAC

The proximate analysis results related to the SBAC and CAC are given in table 1.

Table 1. Results for proximate analysis of the adsorbents.

Parameter	SBAC	CAC
Bulk Density (g/cm^3)	164	316
Moisture Content (%)	50.5	28.5
Ash Content (%)	14.4	47.5

The determination of bulk density depends on the shape, size and density of adsorbent particles and is useful in estimating tank or packing volume [14]. The bulk density of SBAC is 164 g/cm^3, while 316 g/cm^3 for bulk density of CAC. According to Yakout and El-Deen indicates the increasing of carbon particle in activated carbon along with decreasing of bulk density [20]. The SBAC also possessed a low concentration of ash (14.4%) indicating a high-quality carbon adsorbent. Low ash content typically leads to superior adsorption of organic compounds from aqueous solution due to the hydrophobicity of the material [21]. Due to this feature of SBAC, the removal efficiency of dye is strengthened to be high.
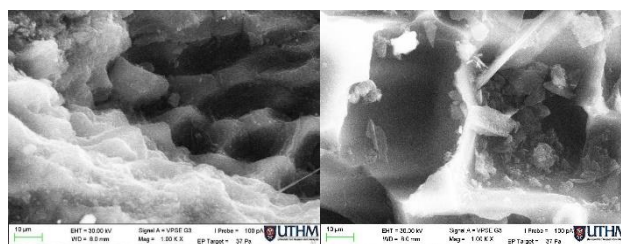

Figure 2. The morphology of SBAC (right) and CAC (left).

The sample of SBAC and CAC obtained from the batch experiment will be taken and tested using SEM to observe the pore structure of the activated carbon. Pores present in activated carbon act as the active sites, where adsorption take place. Figure 2 shown comparison of the morphology of SBAC and CAC.

During adsorption process, the morphology of CAC showed rough and uneven surface having irregular cavities with pores of different sizes. While, the SBAC has the smooth surface with less visible pores, indicating an adsorption on both the surface and within pores. The more micropores form in activated carbon, the bigger the surface area, hence the performance of activated carbon in adsorbing *o-toluidine* and *benzidine* are more efficient.
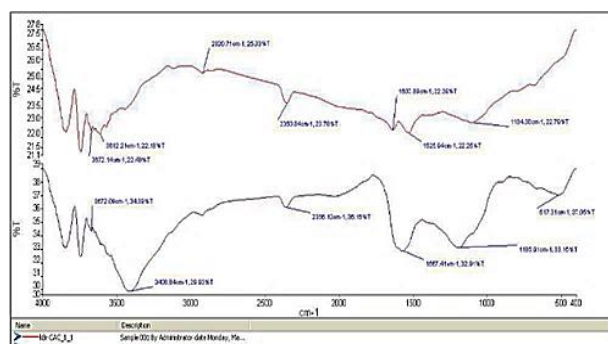
Figure 3. Spectrum of FTIR analysis for CAC and SBAC.

To determine which functional groups were responsible for substances uptake, an FTIR analysis of SBAC was performed using potassium bromide (KBr). The spectra displays a number of adsorption peaks, indicating the complex nature of the natural examined. At first peak, frequency for removal of OT and BZ consist of free hydroxide (-OH) at the range of 3612 cm^{-1} to 3840 cm^{-1}. These peaks that present in activated carbon may be caused of reducing of water content [22].

Besides that, at frequency of 1637 cm^{-1} and 1588 cm^{-1}, there is a presence of non-conjugated bond (C=C) and conjugated bond (C=N). Both double bond presence in SBAC will speed up the rate of removal of OT and BZ. Cecen and Yapsakli [23] in their research also stated that activated carbon which consist of double bond or halogen will increase the rate adsorption of the compound. This proven thorough the testing that SBAC has a potential in removal of *o-toluidine* and *benzidine*.

3.2. Effect of Dosage

The effect of adsorbent dose were conducted by varying dosage between 0.1 g to 1.1 g in fixed adsorbate concentration at 100 ppm and contact time of 60 minutes. The result in removal of *o-toluidine* and *benzidine* is shown in Figure 4. The figures show that increment of adsorption percentage occur along with the increase amount of adsorbent dose used. An increase in adsorption is due to the increase of surface area in the activated carbon which produce more sorption site to be able to adsorb the *o-toluidine* and *benzidine*. The results show that SBAC was efficient in adsorbing 83.1% of *benzidine* and 92.9% of *o-toluidine* at the dosage of 1.1 g. SBAC results is comparable with CAC results of 96% removal for *benzidine* and 99.1% for *o-toluidine*.
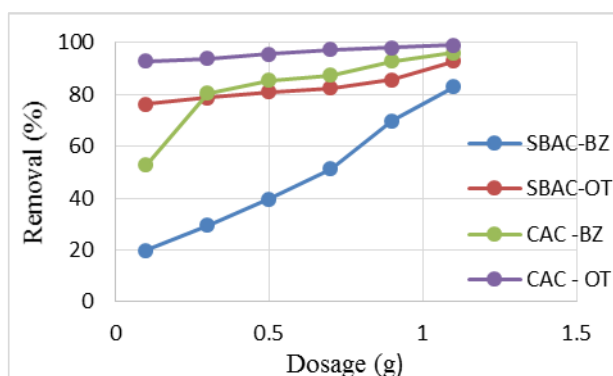

Figure 4. Effect of dosage of *benzidine* and *o-toluidine* on SBAC and CAC.

3.3. Effect of Contact Time

The effect of contact time on removal of adsorbate by SBAC and CAC is illustrated in figure 5. The value of optimum contact time was varied in the range of 10-100 minutes with fixed 100 ppm adsorbate

concentration and 1.1 g amount of adsorbent dosage. It was observed that a rapid adsorption of *benzidine* happen at the first hour process and optimum time for SBAC prove to be at 60 min with 86.7% removal, while CAC keep increase gradually and slowly continue to become constant at 120 min with 83.4% removal. As for removal of *o-toluidine* the graph showed almost 100% removal for both SBAC and CAC which the optimum time taken at 10 min of adsorption process.
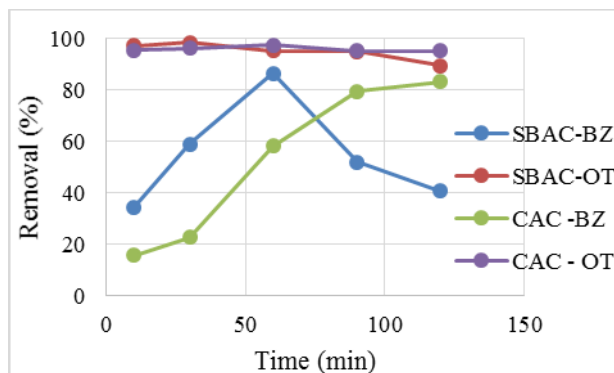

Figure 5. Effect of Time of *benzidine* and *o-toluidine* on SBAC and CAC.

3.4. Effect of Adsorbate Concentration

The adsorption of *o-toluidine* and *benzidine* was tested at different concentration (10, 20, 30, 40, 50 ppm) with a fixed 1.1 g amount of dosage in 1 hour for *benzidine* and 10 min for *o-toluidine*. The influent of adsorbent concentration was shown as in figure 6. The results show for increment in *benzidine* concentration that the removal percentage increase but after 20 ppm SBAC percentage in removing *benzidine* decrease due to reduce of surface area as the adsorption of *benzidine* saturated the active sites. Different result shown for CAC as the percentage of removal is still increase as the surface area is still available to saturated *benzidine*. For *o-toluidine* removal, both SBAC and CAC shown that almost 100% removal happen shown that the surface area and sorption site available is sufficient in removing *o-toluidine* even at 50 ppm of concentration.
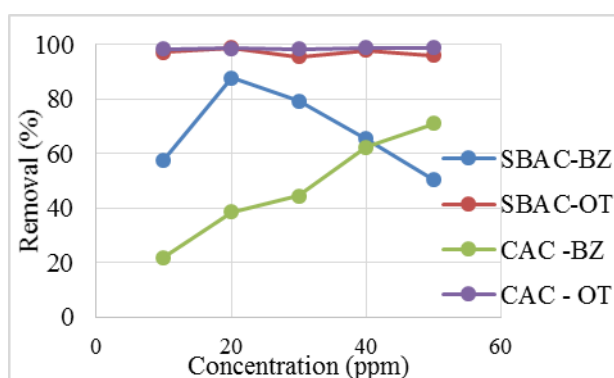

Figure 6. Effect of concentration of *benzidine* and *o-toluidine* on SBAC and CAC.

4. Conclusion

In this study, the removal of *o-toluidine* and *benzidine* in synthetic dye solution using activated carbon produce from sugarcane bagasse has been conducted by considering the effect of dosage, contact time and adsorbate concentration. Even though the adsorption percentage of activated carbon from sugarcane bagasse (agricultural waste) is less than the percentage removal of conventional activated carbon, however, SBAC considerable to use in removing *o-toluidine* and *benzidine*. In addition SBAC is an environmental friendly material which easily available and low cost to produce as activated carbon. Thus, it can be considered an effective adsorbent on the removal of *o-toluidine* and *benzidine* to substituted commercial activated carbon. It is also possible to be design for large scale of treatment process through optimization and modelling for removing industrial waste especially dye that contain *o-toluidine* and *benzidine*.

References
[1]   Brik M, Schoeberl P, Chamam B, Braun R, and Fuchs W 2006 Advanced treatment of textile wastewater towards reuse using a membrane bioreactor *Process Biochemistry* **41**(8) 1751
[2]   Khaled A, El-Nemr A, El-Sikaily A, and Abdelwahab O 2009 Removal of Direct N Blue-106 from artificial textile dye effluent using activated carbon from orange peel: Adsorption isotherm and kinetic studies *Journal of Hazardous Materials* **165** 100
[3]   Luongo G, Avagyan R, Thorsen G, and Ostman C, (2015) *Benzothiazole, Benzotriazole* and their derivates in clothing textiles- a potential source of environmental pollutants and human exposure. *Environmental Science and Pollution Research*. **22**(8) 5842
[4]   Njoku V , Foo K Y, Asif M, and Hameed B , (2014 Preparation of activated carbons from rambutan (*Nephelium lappaceum*) peel by microwave-induced KOH activation for Acid Yellow 17 dye adsorption *Chemical Engineering Journal* **250** 198
[5]   Djilani C, Zaghdoudi R, Modarressi A, Rogalski M, Djazi F, and Lallam A 2012 Elimination of organic micropollutants by adsorption on activated carbon prepared from agricultural waste *Journal of Chemistry Engineering* **189** 203
[6]   Namasivayam C, and Kanchana N, 2011 Waste banana pith as adsorbent for color removal from wastewaters *Chemosphere* **25**(11) 1691
[7]   Mostoni S, Pifferi V, Falciola L, Meroni D, Pargoletti E, Davoli E, and Cappelletti G, 2017 A chemistry tailored routes for home-made Bi-doped ZnO nano-particles: Photocatalytic performances towards *o-Toluidine*, a toxic water pollutant *Journal of Photochemistry and Photobiology* **40**(2) 800
[8]   Jung K W, Choi B H, Hwang M J, Jeong T U, and Ahn K H 2016 Fabrication of granular activated carbons derived from spent coffee grounds by entrapment in calcium alginate beads for adsorption of Acid Orange 7 and Methylene Blue *Bioresoruce Technology* **219** 185
[9]   Bedin K C, Martins A C, Cazetta A L, Pezoti O, and Almeida V C 2016 KOH-activated carbon prepared from sucrose spherical carbon: Adsorption equilibrium, kinetic and thermodynamic studies for Methylene Blue removal *Journal of Chemical Engineering* **286** 476
[10]   Ayman A I, Al-Degs Y S, Al-Ghouti M A, and Olimat A A M 2014 Studying competitive sorption behaviour of methylene blue and malachite green using multivariate calibration *Chemical Engineering Journal* **240** 554

[11]   Sun L, Chen D, Wan S, and Yu Z 2015 Performance, kinetics and equilibrium of methylene blue adsorption on biochar derived from eucalyptus saw dust modified with citric, tartaric and acetic acids *Bioresource Technology* **198** 300

[12]   Li G, Zhu W, Zhang C, Zhang S, Liu L, Zhu L, and Zhao W 2016 Effect of a magnetic field on the adsorptive removal of methylene blue onto wheat straw biochar *Bioresource Technology* **206** 16

[13]   Umar I A, Abdulraheem G, Bala S, Muhammad S and Abdullahi M 2015 Kinetics, equilibrium and thermodynamics studies of C.I. Reactive Blue 19 dye adsorption on coconut shell based activated carbon *International Biodeterioration and Biodegradation* **102** 265

[14]   Hameed B H, Din A T M and Ahmad A L 2007 Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies *Journal of Hazardous Materials* **141**(3) 819

[15]   Jiang G B, Lin Z T, Huang X Y, Zheng Y Q, Ren C C, Huang C K, and Huang Z J 2012 Potential biosorbent based on sugarcane bagasse modified with tetraethylenepentamine for removal of eosin Y *International Journal of Biological Macromolecules* **50**(3) 707

[16]   Adib M R M, Suraya W M S W, Hamdan R, Amirza M A R, Attahirah M H M N 2016 Effect of phosphoric acid concentration on the characteristics of sugarcane bagasse activated carbon. *IOP Conference Series: Materials Science and Engineering* **136** 1

[17]   Baseri J R, Palanisamy P N, and Sivakumar P 2012 Preparation and characterization of activated carbon from *Thevetia peruviana* for the removal of dyes from textile wastewater *Advances in Applied Science Research* **3**(1) 377

[18]   Siti Khadijah C O, Siti Fatimah C O, Misnon N A, and Hanim F K 2012 Utilization of sugarcane bagasse in the production of activated carbon for groundwater treatment *International Journal of Engineering and Applied Sciences* **1**(2) 76

[19]   Verla A W, Horsfall M, Verla E N, Spiff A I and Ekpete O A 2012 Preparation and characterization of activated carbon from fluted pumpkin (*Telfairia occidentalis hook f.*) seed shell. *Asian Journal of Natural and Applied Sciences* **1**(3) 39

[20]   Yakout S M, and El-Deen G S, 2012 Characterization of activated carbon prepared by phosphoric activation of olives stones *Arabian Journal of Chemistry* **9**(2) 1155

[21]   Saygili H, Guzel F and Onal Y 2015 Conversion of grape industrial processing waste to activated carbon sorbent and its performance in cationic and anionic dyes adsorption *Journal of Cleaner Production* **93** 84

[22]   Mokhlesur R, Thankachan R M, Sultana I, Glushenkov A M, Thomas S, Kalarikkal N, and Chen Y 2015 Enhanced lithium storage in $ZnFe_2O_4$-C nanocomposite produced by a low-energy ball milling *Journal of Power Sources* **282** 462

[23]   Cecen F, and Yapsakli K 2012 Effect of type of granular activated carbon on DOC biodegradation in biological activated carbon filters *Process Biochemistry* **45**(3) 355