*Asian Journal of Fundamental and Applied Sciences*
*e-ISSN: 2716-5957 | Vol. 2, No. 1, 1-10, 2021*
*http://myjms.mohe.gov.my/index.php/ajfas*

# Characterization and Adsorption Study of Raw Sugarcane Bagasse for Bromophenol Blue Removal

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Accepted: 15 February 2021 | Published: 1 March 2021

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**Abstract:** *To date, sugarcane bagasse has been used as an ideal precursor for the formulation of cost-effective biosorbent for dye degradation for example bromophenol blue. This adsorption analysis contributes to new research data, possibly for the first time, as no similar previous studies have been reported. In this study, adsorption factors which influence the efficacy of dye removal, for instance, contact period (60 minutes), pH (1-6), initial dye concentration (5-25 mg/L), particle size (0.125-0.5 mm) and biosorbent dose (0.01-0.2 g/L) were evaluated. The raw and BPB treated biosorbents were analysed using FTIR and SEM. Findings from this study suggest that 15 mins of the contact period, pH 1, dye concentration at 5 mg/L, sugarcane particle size at 125 microns and biosorbent dose at 0.1 g/L were optimum conditions for removal of bromophenol blue at 99.97% efficiency. The FTIR results showed variations between raw and dye treated sugarcane bagasse. Alkene, hydroxyl, carboxylic acid and carbonyl were presented in the IR spectra as vital chemical moieties of sugarcane bagasse. The SEM findings showed that sugarcane bagasse has peculiar pores and a fibrous texture. This raw agricultural waste is therefore strongly recommended as an efficient biosorbent for dye adsorption.*

**Keywords:** Adsorption, Bromophenol blue, Sugarcane bagasse

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## 1. Introduction

Over the years, the use of artificial dyes was risen and being preferred over natural dyes derived from insects and plants, including their leaves, roots, shells and flowers. The cheaper cost of production, ease of use and the speed of artificial dyes are among the key reasons for its high demand in industries (Katheresan *et al.*, 2018). Although the use of artificial dyes is essential nowadays, these dyes have significant disadvantages, particularly regarding environmental issues. The formation of dye wastes from industries causes significant environmental harm if not properly handled, as these dye wastes are often intentionally disposed directly into rivers. Additionally, the presence of complex aromatic rings in artificial dyes make them mutagenic, teratogenic and carcinogenic, which can result in serious health complications, for example, skin cancer, skin irritation and allergies (Jain & Gogate, 2017). Furthermore, the coloured wastewater will cover the surface of the river and reduce light penetration, which inhibits photosynthesis in phytoplankton (Khuluk *et al.*, 2019). Hence, waste from the use of artificial dyes is considered one of the environmental challenges that need to be urgently curbed.

Nowadays, treatment methods used to treat coloured dye wastewater include physical, chemical and biological techniques (Aljeboree & Alkaim, 2019). As years passed, methods for dye removal and degradation such as membrane filtration (Zhao *et al.*, 2019) electrolysis, chemical coagulation (Dalvand *et al*., 2017), Fenton oxidation (Ertugay & Acar, 2017) and fungal decolourization have been introduced (Abd El-Rahim *et al*., 2017, Tochhawng *et al*., 2019 and Zhang *et al*., 2020). Although alternative dye wastewater treatments are plenty, the adsorption method is the method of choice for combating coloured wastewater, especially for small-scale industries. Besides, the essential criteria of adsorption that makes it the most preferred mechanism for dye wastewater treatment are its low-cost, operational friendliness especially for small and medium industries, being harmless and able to be handled at very low concentrations, and high colourant degradation efficiency (Holkar *et al*., 2016 and Tagade *et al*., 2019).

In this dye adsorption research, we propose the use of sugarcane bagasse, which is an agricultural waste, likely a potential alternative biosorbent for dyes adsorption from coloured effluent because of its potential which meets the adsorption criteria. The most significant aspect of this adsorption precursor is being cost-free and readily accessible as a leftover from any operation (Anastopoulos *et al*., 2017). Sugarcane bagasse is known to be high in hemicellulose (28%), cellulose (42%) and lignin (21%) (de Moraes Rocha *et al*., 2015). Moreover, the dye would be attracted on its surface through the functional chemical groups on the cellulosic material surface. This study highlights the degradation of bromophenol blue (BPB) onto raw sugarcane bagasse under various adsorption parameters, i.e., contact period, pH, dye concentration, sugarcane particle size and sugarcane dosage.

## 2. Experimental

### *2.1.Materials*

Sugarcane bagasse was piled up from roadside sugarcane hawkers in Tanah Merah, Kelantan. The modifying materials used for pH adjustment were 0.1-1.0M HCl and NaOH. Bromophenol blue dye ($C_{19}H_{10}Br_4O_5S$) was purchased from Sigma-Aldrich, USA.

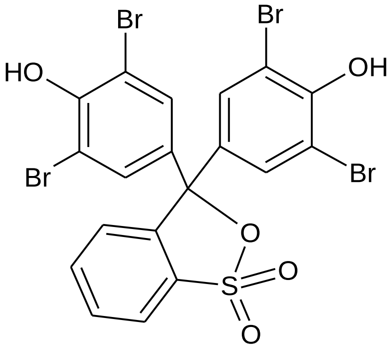

**Figure 1: The proposed molecular structure of bromophenol blue (Abdel-Khalek *et al*., 2018)**

### *2.2.Preparation of biosorbent*

The bagasse sample was piled up from sugarcane juice hawkers and processed to smaller pieces (approximately 2 cm). After that, the cut pieces were cleaned three times using tap water continued with deionized water to eliminate any dirt and dust which may influence subsequent experiments. The wet sugarcane bagasse was desiccated in a drying oven for 24 hours at 60$^{o}$C. The dried biosorbent was pulverized and sieved at 125, 150, 300 and 500 µm and kept in glass jars for experimental usage and characterization purposes such as scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR).

### *2.3.Adsorption experiment*

The biosorbent was added into dye mixture containing 15 mg/L of the dye in 100 mL mixture volume at pH 3 using 250 mL Erlenmeyer flasks. This adsorption study was conducted at room temperature and flasks were agitated at 150 rpm on a multi-channel shaker. Samples were tested at predetermined contact periods (1, 3, 5, 7, 10, 15, 30, 45 and 60 minutes) and followed by sorbent-sorbate filtration. The optimum contact period was determined to be 15 minutes and this duration was used throughout further adsorption experiments. The absorbance of the adsorbate was determined at the maximum wavelength at 590 nm using a UV/VIS spectrophotometer. The result was discussed in terms of dye removal percentage. The competency of dye removal was calculated by using the equation depicted below (Mahmoodi *et al*., 2019):

$$\text{Dye removal (\%)} = \frac{(C_i - C_t)}{C_i} \, x \, 100$$

where $C_i$ and $C_t$ refer to the initial dye concentration (mg/L) and amount of dye solution in the mixture at contact period t respectively.

### *2.4.Characterization*

Fourier transform infrared spectroscopy (FTIR) analysis was investigated on the sugarcane bagasse and bromophenol blue loaded sugarcane bagasse using an infrared microscope (Thermo Scientific Nicolet iN10) to determine the exterior functional chemical groups. The spectra were reported from 4000 to 500 $cm^{-1}$. The topology, shape, porous structure and size of the biosorbent surface material was analysed and characterized using scanning electron microscopy (SEM).

## 3. Results and Discussions

### *3.1. Characterization of sugarcane bagasse*

### *3.1.1. Fourier Transform Infrared (FTIR)*

The presence of a broad absorption band noticed at 3332.25 $cm^{-1}$ shifted to the left at 3333.28 $cm^{-1}$ in Figure 2 is indicative of the presence of hydroxyl groups, O-H, commonly present in cellulosic materials (Oyenkami *et al*., 2019). At 2895.55 $cm^{-1}$, the presence of a stretching peak corresponds to the asymmetric and symmetric vibrations of $-CH_2$ groups shifted to 2896.10 $cm^{-1}$. The existence of peaks at 1728.19 and 1603.70 $cm^{-1}$ indicated the stretching vibration of carbonyl groups, C=O (Fideles *et al.*, 2018) and alkene groups, C=C (Brahmi *et al*., 2019). There were no changes in these functional groups before and after dye adsorption. A peak was vividly stretched at 1033.74 $cm^{-1}$ and shifted to 1033.19 $cm^{-1}$ after dye adsorption corresponds to the presence of the carboxylic acid group, C-OH in cellulose (Veloo & Adam, 2017). Besides, it was observed that no significant changes between both spectra bromophenol blue adsorption which suggests the absence of chemical bonding between dye and biosorbent. This finding is in agreement with results reported by Haji Azaman *et al*., (2018), Yang *et al*., (2018) and Tongpoothorn, *et al*., (2019) However, results from SEM characterization in the next section revealed the presence of pores filled with dye, which suggests that interactions had occurred between the sorbent and sorbate during dye adsorption.

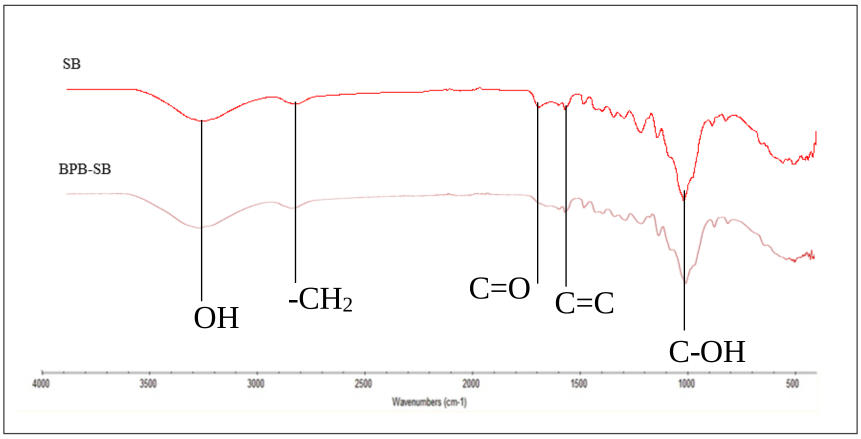

**Figure 2: FTIR spectrum of SB and BPB-SB**

### *3.1.2. Scanning electron microscopy (SEM)*

Figure 3 depicted SEM micrographs of SB and BPB-SB. The micrographs (a) and (b) represented raw biosorbent and the bromophenol blue loaded-sugarcane bagasse respectively. There were significant differences between these micrographs. Micrograph (a) demonstrated the presence of a rough base, fibrous texture and irregular pores on the sugarcane bagasse. The dye is trapped within these cavities as these pores play a significant role in the adsorption system (Da Fontoura *et al.*, 2017). Moreover, the empty pores which were presumably partly filled with dye are clearly shown in micrograph (b) which is nearly identical to micrographs depicting dye-filled pores in previously reported research (Shakoor & Nasar, 2017, Taqui *et al.*, 2017 and Ahmad *et al.*, 2018). According to Sing, 2017, the existence of interaction and chemical bonding between the sorbent and sorbate during adsorption allowed the dye trapped in the sorbent's voids.

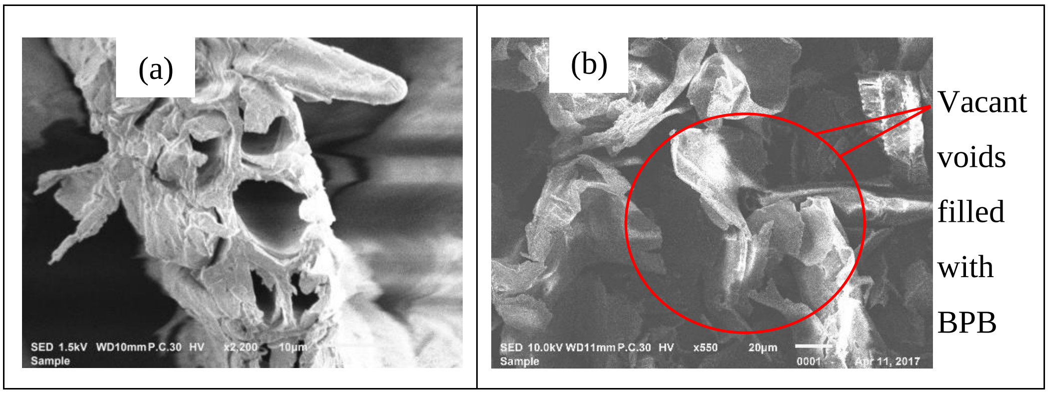

**Figure 3: Micrographs of sugarcane bagasse before adsorption, SB (a) and bromophenol blue loaded sugarcane bagasse after adsorption, BPB-SB (b)**

## *3.2 Results from Adsorption Study*

### *3.2.1 Effect of contact period*

The percentage of bromophenol blue removal on various of contact period (1, 3, 5, 7, 10, 15, 30, 45 and 60 minutes) was evaluated using 100 mL of dye mixture. It found that the rate of dye removal was rapid over the first 10 minutes and gradually increased in the next 5 minutes before reaching a plateau (Figure 4). Within the first 10 minutes, 89.86% of BPB was removed, which then increased to 91.63% at 15 minutes. High accessibility of adsorption sites in the vacant voids is the factor of the rapid dye adsorption during the first 10-15 minutes (Piri *et al.*, 2019). After that, the percentage of dye degradation plateaued until the 45th minute. This stagnant pose could probably be due to saturation of the cavities within the biosorbent with dye molecules and hence the reduced availability of free cavities for dye adsorption. However, after 45 minutes of contact time, the removal of BPB was reduced from 91.63% to 88.95%, possibly due to the weakening of sorbent-sorbate interaction forces, causing dye molecules to detach from the biosorbent exterior into the mixture. Thus, this observation might imply desorption, which is similar to the observations made by Sahu *et al*., (2020) in methylene blue removals.

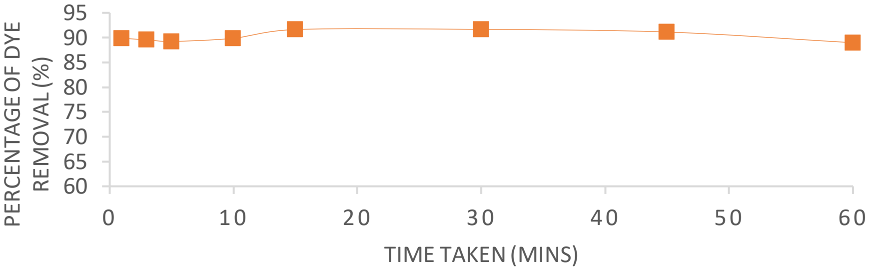

**Figure 4: Effect of contact period on BPB adsorption**

### 3.2.2 *Effect of pH*

The solution's pH plays a vital role in dye removal as it can influence the external charge of the biosorbent and the degree of ionization of the dye. The isoelectric point of sugarcane bagasse was 4.85, as remarked in a previous study (Cueva-Orjuela *et al*., 2017). In general, the removal of BPB declined with increasing pH (Figure 5). The removal of BPB was reduced from 99.67% at pH 1 to -16.61% at pH 6. BPB removal was only slightly reduced between pH1 to pH3. However, starting from pH 3 onwards the BPB adsorption was dramatically reduced to -16.61%. Dye degradation was higher at acidic form due to the electrostatic attraction between the positive charge of the sugarcane bagasse surface and negative anionic charge of BPB (Abidi *et al*., 2018). The rise in pH induced a decrease in electrostatic forces between the sugarcane bagasse surface and BPB, due to the deprotonation of -OH and $-SO_3^-$ (Li *et al*., 2018). Therefore, the percentage of dye removal was decreased. However, BPB removal was greatly impeded at pH5 and pH6 resulting in -7.45% and -16.61% of removal respectively. This phenomenon may involve the exchange of ions between the surface of sugarcane bagasse and BPB at pH 5 and above. Furthermore, the extravagance of OH- ions in a basic dye solution could induce a reduction in the percentage of dye removal (Jain *et al*., 2020). Since BPB is a pH indicator, the change in colour due to the increase in pH could result in a higher absorbance value, thus causing the final concentration value to be much higher than the initial concentration, which in turn translates into negative values. This condition is similar to previous research in the Coomassie Brilliant Blue R-250 removals (Ngoh *et al*., 2015).

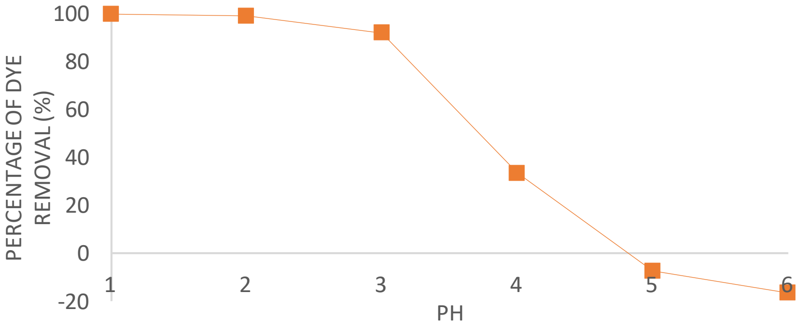

**Figure 5: Effect of pH on BPB adsorption**

### *3.2.3 Effect of dye concentration*

This parameter relies on the association between the available active sites in the biosorbent and dye concentration (Etim *et al.*, 2016). Increasing the dye concentration from 5 to 25 mg/L resulted in a slight decline in the percentage of BPB removal from 99.97% to 99.54%. The pores were filled with dye molecules promotes the adsorption saturation due to the overload of the free active sites on the sugarcane bagasse (Elijah *et al.*, 2020). This phenomenon could be due to natural limitations in the surface ability of sugarcane bagasse to absorb BPB, as reported in a previous study on papaya wood (Rangabhashiyam *et al.*, 2018). As reported in previous research, dye removal by adsorption is possible at very low dye concentrations (Ahmad et al., 2015, Dhananasekaran *et al.*, 2016 and Muhammad Farhan *et al.*, 2020).

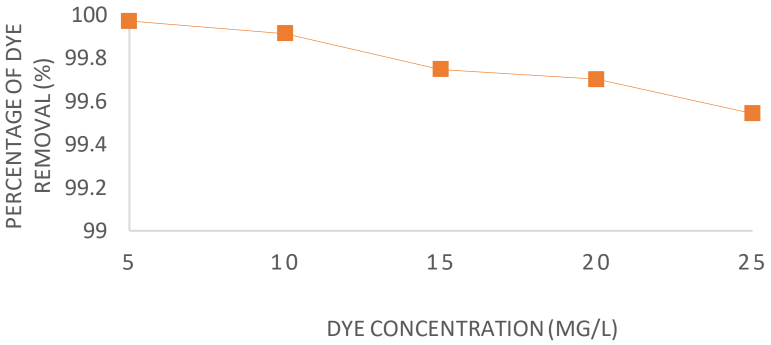

**Figure 6: The effect of dye concentration on BPB adsorption**

### *3.2.4 Effect of sugarcane particle size*

Figure 7 presented the effect of various sugarcane bagasse particle sizes on BPB dye adsorption. The tested sizes were 0.125, 0.150, 0.300 and 0.500 mm. Overall, the percentage of BPB removal decreased from 99.90 to 99.53%. The greater the biosorbent particle size, the lower the dye removal ability. Increasing the biosorbent particle size caused a reduction in the number of active sites and resulted in a smaller sugarcane bagasse surface area (Daneshvar *et al.*, 2017). Similar studies have documented the effect of sugarcane particle size on dye adsorption with results in line with observations from our study (Dhaih-Allah *et al.*, 2020).

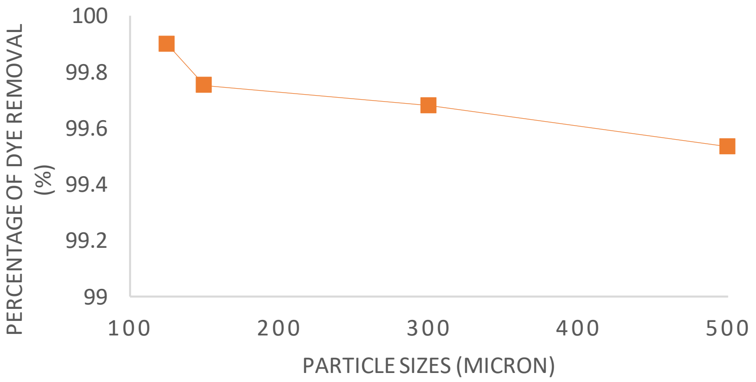

**Figure 7: The effect of sugarcane particle sizes on BPB adsorption**

### *3.2.5 Effect of sugarcane dosage*

Figure 8 revealed the effect of various sugarcane dosage ranging from 0.01 g/L to 0.2 g/L. As depicted in Figure 8, BPB elimination efficiency increased from 99.68% to 99.97% as the precursor dosage increased from 0.01 g/L to 0.1 g/L. Increasing the amount of sugarcane bagasse increases its surface area and the accessibility of dye binding sites, which translates into higher BPB adsorption (Arabi *et al*., 2019). Nonetheless, the adsorption of BPB noticed reaching a plateau at biosorbent dosages higher than 0.1 g/L. No improvement observed in terms of dye removal at 0.15 g/L and 0.2 g/L. This situation may be due to binding sites remaining unsaturated during adsorption with increasing biosorbent dosages.

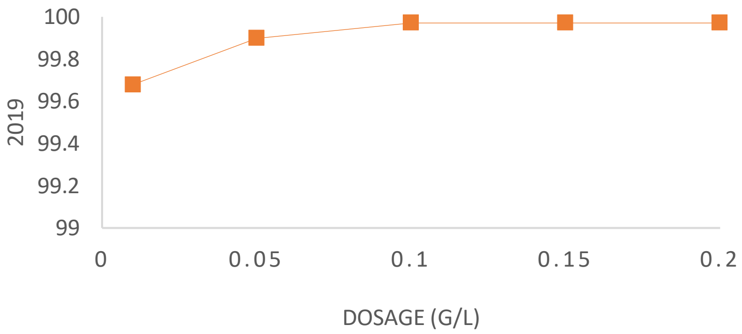

**Figure 8: The effect of sugarcane dosage on BPB adsorption**

## 4. Conclusion

The alternative cost-effective agricultural waste, raw sugarcane bagasse selected as a precursor for the elimination of BPB in wastewater. The limit achievable of BPB dye removal was 99.97%. Findings from this study suggest that 15 minutes of contact time, pH 1, dye concentration at 5 mg/L, particle size at 0.125 mm and 0.1 g/L biosorbent as the ideal parameters for removal of BPB. As it is essential to produce green, low cost and safe biosorbents, the biosorbent used in this study could be utilized as a better alternative for the BPB dye adsorption. The use of sugarcane bagasse which is in itself low in cost could also help reduce and minimize the amount of waste generated from the sugarcane industry.

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