Sugarcane bagasse powder as biosorbent for reactive red 120 removals from aqueous solution

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Abstract. Reactive red 120 is used as a textile dye for fabric coloring. The dye waste is produced during textile finishing process subsequently released directly to water bodies which giving harmful effects to the environment due to the carcinogenic characteristic. Adsorption process becomes an effective treatment to treat textile dye. This research emphasizes the treatment of textile dye namely reactive red 120 (RR120) by using sugarcane bagasse powder. The batch study was carried out under varying parameters such as 60 minutes contact time, pH (1-8), dye concentration (5-25 mg/L), particle size (125-500 µm) and biosorbent dosage (0.01-0.2 g/L). The maximum adsorption percentage of RR120 was 94.62%. The adsorption of dye was increased with the decreasing of pH, initial dye concentration and particle size. Sugarcane bagasse powder as low-cost biosorbent was established using Fourier Transform Infrared (FTIR) and scanning electron microscopy (SEM). This locally agricultural waste could be upgraded into useful material which is biosorbent that promising for decolorization of colored textile wastewater.

1. Introduction
Dye is commonly applied in many industrial sectors such as food, paper, plastics, pharmaceuticals, cosmetics and widely used in textile industry [1-3]. However, the usage of dye upon urbanization giving rise to colored water pollution when the colored water discharge from the factory not properly treated. 10-15% dye is lost during textile finishing process which directly releases to water source [4]. The colored water imperils the environment since the dye is noted as among most hazardous pollutant [5]. As years past, many conventional methods have been used to treat textile effluent, for instance, ion exchange, Fenton-reagent method, electrochemical, precipitation, membrane separation, reverse osmosis, fungal decolorization and microbial degradation [6]. Since the dye is very stable and not degradable material it could not completely treat by a conventional method and will produce secondary pollutant as a by-product. In recent years, adsorption as a surface phenomenon has gained wide attention and popularly used in textile wastewater treatment [7]. Adsorption is a simple method, easy to handle, function able at very low concentration, safe and cost effective to remove pollutant in the textile wastewater compared to the previous methods [8]. Some of the adsorbents are proven as good dye remover precursors such as durian seed [9], coffee [10], rambutan peel [11, 12], rice husk [13, 14], egg shell [15, 16] including sugarcane bagasse [17, 18]. Sugarcane bagasse known as one of largest
agro-industrial waste in Malaysia which consists of lignin (18%), cellulose (45%) and hemicellulose (28%) [19]. Agricultural waste selected is free availability, easier to obtain including can solve the agricultural waste disposal problem. Sugarcane bagasse was used in removing safranin O with the adsorption capacity obtained 62.884 mg/g, 58.853 mg/g and 54.822 mg/g for base-treated SB, raw SB and acid-treated SB respectively [20]. It was known as an efficient adsorbent on the adsorption of Congo red with adsorption capacity 38.2 mg/g and followed pseudo-second order kinetic model [21]. A study reported adsorption capacity on methylene blue and acid orange II removal using sugarcane bagasse treated with propionic acid achieved were 59.5 mg/g and 25.5 mg/g respectively [22]. This research emphasizes the removal of reactive red 120 using sugarcane bagasse powder. The batch study was carried out under varying parameters such as contact time, pH, dye concentration, particle sizes and biosorbent dosage.

2. Experimental

2.1. Materials
Sugarcane bagasse was collected from roadside juice hawker in Tanah Merah, Kelantan. Modifying agents were 0.1-1.0 M of HCl and NaOH as pH adjustment and reactive red 120 (C_{44}H_{24}Cl_{2}N_{14}Na_{6}O_{20}S_{6}) was purchased from Sigma-Aldrich, USA.

![Molecular structure of reactive red 120](image)

Figure 1: The molecular structure of reactive red 120 [23].

2.2. Preparation of biosorbent
Sugarcane bagasse was collected, cut into small pieces (approximately 2 cm) and washed for three times with tap water followed by deionized water to remove the dust and any dirty, that would affect the analytical procedure. The wet sugarcane bagasse then dried under the sun and continued drying process in the oven at 60°C for 24 hours. The dried sugarcane bagasse was ground into powder, sieved at 125, 150, 300 and 500 µm and kept into powder jars for experimental usage and characterization purposes such as scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR).

2.3. Adsorption experiment
Biosorbent was added into the 100 mL of the dye solution at 15 mg/L of dye concentration and pH 3 in 250 mL Erlenmeyer flask. The experiment was carried out on a multi-channel shaker at 150 rpm and at room temperature. The sample was withdrawn at a determined contact time (10, 15, 30, 45 and 60 minutes) and filtered using filter paper. The optimum contact time was determined at minute 15th and used throughout further adsorption experiments. The absorbance of the supernatant was determined at maximum wavelength 514 nm using UV/VIS spectrophotometer. The result was reported on the basis of percentage dye removal. The efficiency of dye removal percentage was measured by following equation (1) [24].

\[
\text{Dye removal (\%) } = \frac{(C_i - C_t)}{C_i} \times 100
\]
Where $C_i$ and $C_t$ refers to initial dye concentration (mg/L) and dye concentration in the solution at contact time $t$.

2.4. Characterization

Fourier Transform Infrared FTIR (Thermo Scientific Nicolet iN10 Infrared Microscope) analysis was applied to the sugarcane bagasse powder and dye-loaded sugarcane bagasse powder to determine the surface functional groups and the spectra were recorded from 4000 to 500 cm$^{-1}$. Scanning electron microscopy (SEM) characterization is a technique to analyze morphology and topography of biosorbent surface material. It is also used to determine the particle shape and porous structure of biosorbent.

3. Results and discussion

3.1. Characterization of prepared biosorbent

3.1.1. Fourier Transform Infrared (FTIR).

Figure 2 showed a broad band at 3334.25 cm$^{-1}$ indicated the presence of hydroxyl group, O-H in cellulose, hemicellulose, and pectin. At 2894.62 cm$^{-1}$ peak showed stretching correspond to asymmetric and symmetric vibrations of $-\text{CH}_2$ group respectively [25]. The presence of peaks at 1728.25 and 1603.76 cm$^{-1}$ indicated carbonyl group, C=O and alkene group, C=C stretching vibration. The vivid absorption band of carboxylic acid group, C-OH stretch at 1033.91 cm$^{-1}$ might be presented in cellulose.

![FTIR spectrum of sugarcane bagasse powder](image)

Figure 2: FTIR spectrum of sugarcane bagasse powder.

3.1.2. Scanning electron microscopy (SEM).

The micrographs showed before and after dye adsorption. Based on the micrographs in Figure 3, micrograph (a) represented biosorbent before dye adsorption meanwhile micrograph (b) showed dye-loaded sugarcane bagasse powder for reactive red 120. There were significant differences between before and after dye adsorption of sugarcane bagasse powder morphological surface. Micrograph (a) clearly showed that sugarcane bagasse powder was porous and fibrous texture. Dye filled the empty pores of biosorbent surface vividly seen in the micrographs (b). The result was almost similar with safranin O adsorption using sugarcane bagasse [20].
3.2. Effect of contact time
The effect of contact time on the dye removal percentage of sugarcane bagasse was investigated at different contact times (1, 3, 5, 7, 10, 15, 30, 45 and 60 minutes) using 100 mL solution. Generally, the dye removal percentage was increasing with the increase of the contact time [26]. The result showed the dye percentage removal was increased rapidly at the initial stage of 10th-minute dye adsorption due to a large number of free surface sites of biosorbent were available [12]. After that, it was gradually increased from 28.23% to 37.10% at the 15th minute. After a 15th minute of dye adsorption, the percentage of dye removal showed no significant difference in the amount of removing dye in this state. This could be considered as equilibrium state since the active sites of biosorbent were fully occupied. Therefore, it was concluded that at 15th minute as an optimum time for reactive red 120 removal using sugarcane bagasse powder.

![Micrographs of reactive red 120 before adsorption (a) and dye-loaded sugarcane bagasse powder after adsorption (b).](image)

3.3. Effect of pH
The solution pH is an important factor in the adsorption process as it may affect the surface charge of adsorbent and the ionization degree of the dye. As shown in Figure 5 the percentage of dye removal was found to decrease with the increase of pH value. At pH 1 showed the highest percentage of dye removal (76.62%) which indicated as optimum pH. The dye removal percentage slowly decreased from 76.62 to 9.71% for pH 1 to 8 respectively. At low pH, the dye removal percentage higher because there was an electrostatic attraction between negative charges of anionic dye and positively charge biosorbent surface [27]. As going up the pH scale caused the number of positively charges surface site decreased and negatively charges increased [28]. This condition caused electrostatic repulsion between

![Graph showing percentage of dye removal vs. time.](image)
biosorbent and anionic dye which caused the decrement of the percentage of dye removal onto sugarcane bagasse.

![Figure 5: The percentage removal of various pH onto sugarcane bagasse powder for RR120 (Biosorbent dosage= 0.2 g/L, initial dye concentration= 15 mg/L, time= 15 minutes time interval, temperature= room temperature, particle size= 300 µm, agitation speed=150 rpm).]

3.4. Effect of dye concentration
The initial dye concentration parameter provides a vital driving force to encounter all mass transfer resistance of the dye between the dye molecules and solid phase adsorbent [29]. Figure 6 illustrated the percentage of dye removal decreased from 88.19 to 67.29% for RR120 with the increase of dye concentration (5-25 mg/L). The increased of dye concentration lead to decrease in adsorption process, suggesting the adsorption of this phenolic dye was highly dependent on dye concentration. This phenomenon was caused unoccupied active sites on the biosorbent surface were filled with dye molecules and saturation of biosorbent surface might be occurred when the dye concentration increased [30]. Saturation happened due to limited capacity of biosorbent surface which similar to the adsorption of methylene blue and crystal violet by sugar can stalks [31]. This finding agreed with the literature, the adsorption of methylene blue, bromophenol blue and coomasive brilliant blue by α-chitin nanoparticles could be removed using very low dye concentration which were 6, 10 and 5 mg/L referred to methylene blue, bromophenol blue and coomasive brilliant blue respectively [32]. In recent study, low dye concentration which 10 mg/L applied to remove methylene blue using activated orange peel resulted maximum dye percentage 88% compared to 50 mg/L which just 82% [33].

![Figure 6: The percentage removal of various initial dye concentration onto sugarcane bagasse powder for RR120 (Biosorbent dosage= 0.2 g/L, pH=1, time= 15 minutes, temperature= room temperature, particle size= 300 µm, agitation speed=150 rpm).]
3.5. Effect of particle size

Figure 7 presented the highest percentage of dye removal (95.20%) obtained by using smallest particle size (125 µm) which as expected. The maximum dye removal followed by other particle sizes such as 150, 300 and 500 µm which resulted to 87.02, 80.88 and 79.42% of dye removal respectively. The decreasing of particle size of sugarcane bagasse powder have increased the adsorption rate of RR120. Low particle size would increase the surface area availability which increased the active sites of sugarcane bagasse [34]. This was agreed with previous study onto reactive red 120 dye removal using Chara Contraria [35]. In the study found the dye uptake increased with decreasing particle sizes. The optimum particle size evaluated was 125-250 µm.

![Figure 7: The percentage removal of various particle sizes onto sugarcane bagasse for RR120 (Biosorbent dosage = 0.2 g/L, pH = 1, contact time = 15 minutes, temperature = room temperature, dye concentration = 5 mg/L, agitation speed = 150 rpm).](image)

3.6. Effect of biosorbent dosage

The effect of various biosorbent dosage was studied at room temperature by using the biosorbent amount from 0.01 to 0.2 g/L. Figure 8 showed the adsorption of RR120 percentage increased from 73.57 to 94.62% with the increase in the amount of sugarcane bagasse (0.01-0.05 g/L). This was due to greater availability of the surface area and more binding sites at a higher amount of the biosorbent dosage [36, 37]. The dye removal percentage was maintained 94.62% after 0.1 g/L of biosorbent dosage added. This was because there were no binding sites existing for dye molecule to attach on its surface sites.

![Figure 8: The percentage removal of various biosorbent dosage onto sugarcane bagasse for RR120 (particle size= 125 µm, pH=1, contact time= 15 minutes, temperature= room temperature, dye concentration= 5 mg/L, agitation speed=150 rpm).](image)
4. Conclusion

Sugarcane bagasse powder was used as an alternative biosorbent to remove reactive red 120 as textile dye. The maximum dye removal percentage was 94.62% at optimum conditions studied were pH 1, 15th minutes contact time, 5 mg/L, 125 µm size and 0.1 g/L dosage which was considered high for untreated material. Recent literatures found dyes could be removed using very low dye concentration. The need of market is to produce green technology biosorbent and limit the procedure costs. Sugarcane bagasse powder has been proven to be good alternative and low-cost biosorbent for the removal of RR120 from aqueous solution and could solve the agriculture disposal problem.

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