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Removal of Crystal Violet from Aqueous Solution using Post-Treated Activation Biochar Derived from Banana Pseudo Stem

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The removal of crystal violet (CV) dye from wastewater using biochar derived from various agricultural wastes increased interest among researchers. In this study, banana pseudo stem (BPS) waste was used as the feedstock for preparing biochar through slow pyrolysis at temperatures 300 °C, 500 °C, 700 °C and 900 °C. The adsorption screening results revealed that BPS biochar optimized at a pyrolysis temperature of 300 °C (denoted as BC300) exhibited the highest removal and amount of CV adsorbed with 96.4 % and 48.2 mg/g, respectively. Activation by chemical treatment with H_2SO_4, HCl, NaOH and KOH was then applied to the BC300 and the efficient removal of CV from the aqueous solution was investigated. The adsorption experiment showed that the removal percentage and amount of CV adsorbed with BC300 were significantly improved in the range of 14.0 % – 17.8 % and 0.7 mg/g – 1.2 mg/g, respectively, after chemical activation. In comparison to the other three activated biochar, BC300 biochar with H_2SO_4 treatment achieved the highest removal rate (98.4 %) and the highest quantity of CV adsorbed (9.8 mg/g). The findings preliminary indicate the potential of biochar derived from banana pseudo stem to be used as a promising adsorbent for removing CV. Activation by chemical treatment, preferably with H_2SO_4 enhanced the adsorption capability of the biochar thus resulting in a higher removal percentage of CV from the aqueous solution.

1. Introduction

Human, aquatic life, and the environment are negatively impacted by dye effluents discharged from various dye industries such as textile, plastic paper and leather industries. Approximately 100,000 commercially available dyes are used to produce an estimated 700,000 tons of different colouring per year (Abdi et al., 2017). Crystal violet (CV), also known as gentian violet, basic violet 3 and methyl violet 10B, is one of the common synthetic dyes used in the dyeing of clothing, paper printing, leather, cosmetics, food processing, pharmaceuticals, and fertilizers industries. CV is made up of a variety of functional groups, many of which are hard to decompose due to their complex and stable aromatic character (Alsenani, 2013). Although at low concentrations (< 1 ppm), the presence of this undesirable dye in water bodies is extremely noticeable because it interferes with sunlight transmission, impairs photosynthesis, reduces oxygenation throughout the water bodies, and ultimately has an adverse effect on aquatic life and the ecosystem (Ahmad et al., 2014). Due to its toxicity, long exposure to this carcinogenic dye causes various health problems like skin irritation, allergy and cancer and mutation in humans (Shoukat et al.,2017). Therefore, it is necessary to remove this dye from wastewater effluents before releasing it into the water stream to minimize its negative impacts on the environment and living things.

Dye-containing effluents can be treated using various treatment methods. Amongst, the adsorption technique with activated carbon as the adsorbent is the most frequently employed method due to its excellent adsorption capacity, high porosity, and large surface area properties (De Gisi et al., 2016). However, the high production costs of commercialized activated carbon restrict its use in a variety of technologies. Thus, researchers are giving great attention on exploring the use of biochar from various agricultural waste as an alternative adsorbent. Biochar is a porous carbonaceous solid material that is prepared by the pyrolysis of biomass from plants, such

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as agricultural waste, and aquatic plant or animal waste under limited oxygen and anoxic conditions (Lehmann & Joseph, 2009). Besides the easy availability factor, studies reported biochar derived from agricultural wastes is less expensive, and more economic yet able to give excellent adsorption efficiency (like activated carbon) in removing pollutants from aqueous effluent (Abd-Elhamid et al., 2020; Aminuddin & Baharim 2021; Baharim et al., 2022; Yu et al., 2019).

Bananas are tropical, herbaceous and perennial crops belonging to the Musaceae family. The banana pseudo stem is particularly the major agricultural waste left in the field or plantation after harvesting the banana fruit. The stem is a potential waste that can be converted and utilized as an adsorbent since it is rich in carbon organic compounds, such as cellulose, hemicellulose pectin substances and lignin (Mahopatra et al., 2010). The presence of numerous active functional groups including hydroxyl, carboxyl, amino and carboxyl on the stem surface, provides the adsorption capacity towards dyes, heavy metals and other water-soluble pollutants (Zhou et al., 2019). The previous study used banana pseudo stem derived biochar successfully removed 98.0 % methylene blue (Liu et al., 2019), 87.0 % remazole red RGB (Kumar et al., 2021) and 91.2 % congo red (Jadhav & Thorat, 2022). There are no works reported on the removal of CV using biochar with modification, prepared from the banana pseudo stem. Chemical modification enhances the adsorption capabilities of biochar. Therefore, in this preliminary study, the banana pseudo stem was utilized as the starting material to produce biochar, which was then chemically activated with acid and alkali solutions after being pyrolyzed at various temperatures. The modification was a simple and straightforward procedure by using less concentrated acid and alkali solutions with a short activation time to prevent other contamination from the procedure. The post-treated activation biochar was then used as an adsorbent to remove CV from an aqueous solution. Comparisons on the removal efficiency and adsorption capacity of CV on different chemical activation banana pseudo stem biochar were evaluated.

2. Materials and methods

2.1 Chemicals

All of the reagents utilized in this study were high purity and analytical grade. CV dye (Molecular formula, $C_{25}H_{30}N_3Cl$; Molecular weight 407.98 g/mol) was purchased from Bendosen Laboratory Chemicals (Malaysia). The hydrochloric acid (HCl) and sodium hydroxide (NaOH) were obtained from R & M Chemicals (Malaysia). Distilled water was used throughout the work and preparation of all chemical solutions.

2.2 BPS biochar preparation

In this study, banana pseudo stem (BPS) of *Musa paradisiaca* (locally known as Pisang Berangan) species were collected from Bestari Jaya, Selangor, Malaysia. The stems were thoroughly washed with distilled water to remove dirt and impurities, chopped into small pieces (5 cm × 2 cm) and followed with air drying for three days. Then, the samples were dried in an oven (Venticell 55, USA) at a temperature of 105 °C for 24 h. After cooling, the oven-dried BPS was placed in a stainless-steel sample holder and pyrolyzed at four different temperatures of 300 °C, 500 °C, 700 °C and 900 °C for 1 h in a furnace (PROTHERM, Turkey). The produced biochar (denoted as BC300, BC500, BC700 and BC900) was ground, sieved to a uniform size (< 100 μm) and kept in an airtight container for the screening of the biochar optimization experiment.

The optimized biochar was treated with 1.0 M of sulfuric acid (H_2SO_4), 1.0 M of hydrochloric acid (HCl), 1.0 M of sodium hydroxide (NaOH) and 1.0 M potassium hydroxide (KOH) (1 g biochar : 5 mL solution) for 24 h at room temperature. After cooling to room temperature, the biochar was washed with plenty of distilled water to remove excess acid/alkali, filtered and dried in an oven at 105 °C for 24 h. Finally, the treated biochar was kept in an airtight container for further use. The cleaned, dried BPS and ground BPS biochar are shown in Figure 1.

(a) (b) (c)

Figure 1: BPS samples after (a) cleaned; (b) dried; (c) ground and sieved

2.3 Characterization of BPS biochar

The proximate analysis for BPS biochar was carried out to determine the moisture content, ash content and volatile content according to ASTM D1762. The fixed carbon content for both adsorbents was measured from the following equation:

$$FC = 1 - M - VM - ASH \quad (1)$$

where M, VM and ASH stand for moisture, volatile matter, and ash content respectively. The pH of the BPS biochar was measured using a pH meter (Sartorius, China) following the ASTM D3838-80.
The calculation of the BPS biochar yield can be expressed as:

$$\text{Percentage of biochar yield, \%} = \left(\frac{\text{mass of biochar (g)}}{\text{mass of dry feedstock (g)}}\right) \times 100\% \quad (2)$$

2.4 Crystal violet-adsorbate preparation

CV stock solution with 1000 ppm concentration was firstly prepared by dissolving 1 g of CV dye powder (Bendosen, Malaysia) in 1000 mL of distilled water in a 1000 mL of volumetric flask. The stock solution was later diluted to 100 ppm and 20 ppm for the adsorption experiment. The pH of all prepared CV solutions was adjusted to the required pH by using 0.1 M HCl or 0.1 M NaOH.

2.5 Adsorption experiments

The adsorption experiments were carried out at room temperature to determine the removal efficiency and the amount of CV adsorbed onto the prepared biochar. For the biochar with different pyrolysis temperatures optimization, the experiments were conducted using 100 mL of 100 ppm CV solution in 250 mL Erlenmeyer flasks with an agitation speed of 120 rpm for 60 min. The pH of the CV solution remained in its original condition (pH 5.5) with 0.2 g of biochar dosage added to each flask containing dye solution. Then the mixtures were filtered and the absorbance of the CV solution was determined using a UV-Vis spectrophotometer (Hitachi, Japan) at a maximum absorbance wavelength (λ_{max}) of 583 nm. For the post-treated BPS biochar adsorption experiment, the concentration of CV solution was fixed at 20 ppm while other parameters remain the same as the previous procedure. All experiments were carried out in triplicate to minimize errors. The percentage removal of CV (R%) and the amount of CV adsorbed (Qe) were defined as:

$$\text{Removal of CV, R\%} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (3)$$

$$\text{Amount of CV adsorbed, Qe} = \left(\frac{C_0 - C_e}{m}\right) V \quad (4)$$

Where, C_o and C_e are the CV concentration (ppm) at initial and equilibrium, V is the volume of solution and *m* is the mass of the dosage (g).
Validation of the significance differences in the effect of biochar pyrolysis temperature and types of chemical treatment in the removal percentage and amount of CV adsorbed were statistically analyzed through the Variance analysis (ANOVA) and Tukey's test for mean comparison at 95 % reliability ($p < 0.05$) using the IBM SPSS Statistics 27 software.

3. Result and discussion

3.1 Characteristics of BPS biochar

The proximate analysis result and characteristics of the BPS biochar produced at four pyrolysis temperatures are tabulated in Table 1. The biochar yield, moisture content and volatile content decreased with the increasing temperature due to the greater thermal decomposition of the biomass and the release of water and volatile matter compounds (H_2, CO_2 and CH_4) at higher temperatures (Fernandes et al., 2020). The pH values increased with higher pyrolysis temperature, following the trend observed in the literature (Conz et al., 2017). Increasing biochar pH with the pyrolysis temperatures could be associated with the increase of the ash content and the release of volatile matter composed of acid functional groups with the increment in pyrolysis temperature (Enders et al., 2012). An increase in ash content with the rise in temperature is attributed to the concentrations of the pyrolyzed minerals and organic matter products (Fernandes et al., 2020). The fixed carbon increased with increasing pyrolytic temperature, signifying the biochar's level of carbonization increased. Other studies have noted similar findings in biochar with the increasing pyrolysis temperature (Peng et al., 2016).

Table 1: Characteristics of banana pseudo stem biochar produced at different temperatures

Parameters	BC300	BC500	BC700	BC900
Biochar yield (%)	47.46 ± 0.5	34.87 ± 0.8	32.75 ± 0.8	32.18 ± 1.1
pH	6.10 ± 0.1	10.43 ± 0.1	10.87 ± 0.1	11.15 ± 0.1
Moisture content (%)	9.90 ± 0.3	8.55 ± 0.5	7.31 ± 1.0	6.23 ± 0.9
Ash content (%)	26.76 ± 0.6	33.95 ± 0.5	38.89 ± 0.7	41.42 ± 0.8
Volatile content (%)	40.73 ± 0.2	31.54 ± 0.6	23.55 ± 0.3	18.62 ± 0.5
Fixed carbon (%)	22.61 ± 0.3	25.96 ± 0.4	30.25 ± 0.4	33.73 ± 0.7

Values represent mean (n = 3) ± standard deviation

3.2 Standard calibration curve of crystal violet solution

The concentration of CV solution at equilibrium was calculated using a standard calibration curve, where the measured absorbance from the UV Spectrophotometer was plotted versus the prepared series of known CV solution concentrations. The equilibrium CV solution concentration was adjusted from the calibration curve in Figure 2. The graph followed Beer's Law in the range of concentration 0 – 6 ppm, with a linear equation of $y = 0.1285x + 0.0522$ and an excellent correlation coefficient, $R^2 = 0.9991$.

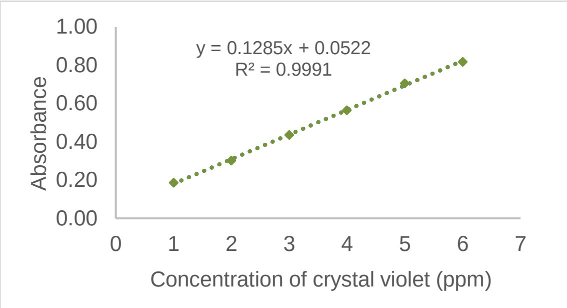

Figure 2: Calibration curve of CV solution

For the optimization of biochar at different pyrolysis temperatures screening experiment, the percentage removal and amount adsorbed of CV using dried raw BPS and pristine biochar are presented in Figure 3. The pyrolysis at 300 °C significantly improved the adsorption capabilities of BC300, with higher removal and amount adsorbed (4.8 % and 2.3 mg/g) than dried BPS. This is explained by the fact that BC300's porosity was greatly increased by carbonization, creating additional surface adsorption sites. However, the removal and amount of CV adsorbed gradually decreased and was lower than dried BPS when the pyrolysis temperature increased from 500 °C to 900 °C. Increasing pyrolysis temperature caused the specific surface area to decrease. This condition is attributed to the collapse of the pore structure at a high temperature. Zhao et al., (2021) reported a similar observation when biochar derived from pulp and paper sludge at different temperatures was used to remove colours from wastewater. Therefore, the highest removal and amount of CV adsorbed of 96.4 % and 48.2 mg/g using pristine BPS biochar was optimized at a pyrolysis temperature of 300 °C. Statistical analysis using one-way ANOVA and Tukey Test at the significance level of 0.05 ($p < 0.05$) showed that the removal and amount of CV adsorbed using different pyrolysis temperatures were different from the dried raw. However, there was no significant statistical difference between BC500 and dried raw.

BC300 was then employed for the chemical treatment activation with different acids and alkali solutions; H_2SO_4, HCl, NaOH and KOH. Figure 4 shows the CV adsorption capacities using post-treated BC300 with a different chemical solution and dried BPS are also provided for comparison. In comparison to untreated biochar, the removal percentage of biochar treated with H_2SO_4, HCl, NaOH and KOH increased by 17.8 %, 17.5 %, 14.8 % and 14.0 % respectively.

The amount of CV adsorbed was also improved by 1.2 mg/g, 1.1 mg/g, 0.8 mg/g and 0.7 mg/g corresponding to the chemical treatments. In comparison to alkali-treated biochar, the removal percentage and amount of CV adsorbed with acid-treated biochar increased by 4.7 % and 0.5 mg/g, respectively. Amongst all the studied adsorbents, biochar treated with H_2SO_4 exhibited the highest 98.4 % removal and 9.8 mg/g of CV adsorbed. Mahdi et al., (2019) also reported that biochar with acid modification increased the surface acidities, and enhanced the porous structure by adding more heterogeneous pores.

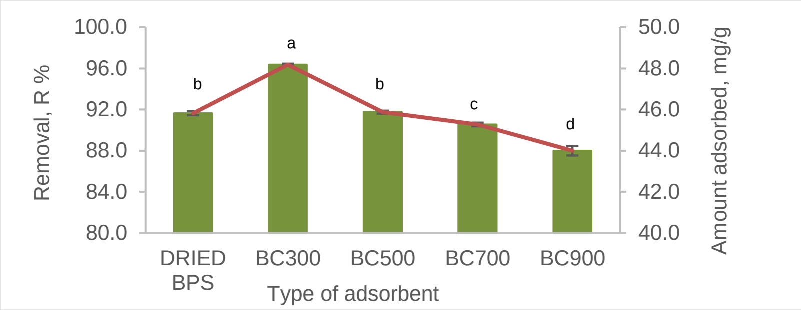

Figure 3: Influence of biochar at different pyrolysis temperature on the CV adsorption (Dosage : 0.2 g in 100 mL, CV concentration: 100 ppm, pH : 5.5; contact time : 60 min, stirring speed : 120 rpm). Error bars represent the standard deviation between three replicates (n = 3). Values represent mean. Value with the same letter does not statistically differ from one another according to Tukey's test at a 5 % significant level.

Thus, improving the adsorption capacity of the biochar than the alkali treatment biochar. The statistical analysis confirmed that the chemical-treated biochar was significantly different ($p < 0.05$) from the untreated biochar. Nevertheless, the differences in the removal and amount of CV adsorbed between two acids and two alkalis were not statistically significant. Since H_2SO_4-treated biochar was the highest improvement and removal percentage, thus investigation on the adsorption effects on this biochar is recommended for future works.

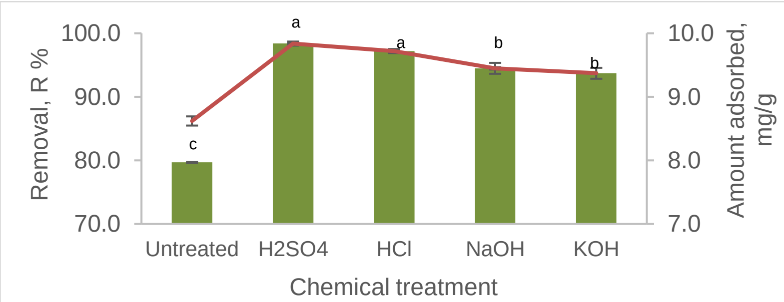

Figure 4: Adsorption capabilities of post-treated biochar 300℃ with different chemical activation (Dosage : 0.2 g in 100 mL, CV concentration: 20 ppm, pH : 5.5; contact time : 60 min, stirring speed : 120 rpm). Error bars represent the standard deviation between three replicates (n = 3). Values represent mean. Value with the same letter does not statistically differ from one another according to Tukey's test at a 5 % significant level.

4. Conclusions

This study demonstrated the potential of banana pseudo stem biochar in removing CV from an aqueous solution. Initially, the biochar was prepared via slow pyrolysis at four different temperatures and the adsorption results found that biochar prepared at 300 °C (BC300) was the highest removal percentage and amount of CV adsorbed. Biochar BC300 was then activated by chemical treatment with different acid and alkali solutions. The removal percentage of biochar treated with H_2SO_4, HCl, NaOH, and KOH was enhanced by 17.8 %,17.5 %, 14.8 %, and 14.0 %, respectively, in comparison to untreated biochar. Moreover, the chemical treatments increased the quantity of CV adsorbed by 1.2 mg/g, 1.1 mg/g, 0.8 mg/g, and 0.7 mg/g, correspondingly. H_2SO_4-treated biochar had the highest removal rate of 98.4 % with the highest amount of CV adsorbed (9.8 mg/g). This preliminary study confirmed that banana pseudo stem biochar by acidic post-treated activation significantly improved the removal percentage and adsorption amount efficiency of CV. The characterization analysis of the post-treated activation biochar and the influence of adsorption parameters; like pH solution, adsorbent dosage, contact time, initial concentration, temperature and stirring speed on the CV removal and adsorption capacity can be conducted for further investigation.

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