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Development of Adsorbent from Phytoremediation Plant Waste for Methylene Blue Removal

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ABSTRACT

Dyes are considered to be hazardous, have low biodegradability and can affect the human health as well as the aquatic life cycle. This research investigated the methylene blue (MB) removal using an activated carbon matrix of *Scirpus grouss* (waste that was initially used for phytoremediation of soil). The experiment was conducted in a flask containing 0.5 g AC-SC with MB concentrations of 5 and 15 mg/L. The adsorption was monitored for 120 sec. The results showed complete removal of MB within a contact time of 30 sec using 6-AC. The surface morphology analysis showed that at 6-AC, the structure was more porous. The ultimate potential of activated carbon prepared from the phytoremediation plant waste would be the best alternative for the water and wastewater treatment, while it provides an alternative to the phytoremediation waste management process.

Keywords: Methylene blue; dye removal; activated carbon; *Scirpus grossus*; phytoremediation

INTRODUCTION

There is an increasing trend of various industries using different dyes, leading to the accumulation of toxic pollutants in the environment. Dyes are considered to be dangerous pollutants and are released to the environment in large quantities from the textile, paper and pulp, tannery, and paint industries (Gupta & Suhas 2009; Muhamad et al. 2015). They are considered to be hazardous, have low biodegradability, and can affect the human health as well as the aquatic life cycle. Due to its wide usage in the textile industries for dyeing leather, cotton, printing, and tanning, methylene blue (MB) is one of the basic (cationic) dyes that is often found in the dye-based industrial wastewater (Gupta et al. 2004). Methylene blue has can have serious effects when consumed by humans; it can cause confusion, shortness of breath, vomiting, high blood pressure, many allergic reactions, and cancer.

Many studies have been conducted to examine various methods for the MB removal such as electrocoagulation (Golder et al. 2005; Mahmoud et al. 2013), ozonation (Al-Jibouri et al. 2015), electrolysis (Liu et al. 2020; Zhang et al. 2013), phytoremediation (Almaamary et al. 2017; Al-Badawi et al. 2018), photocatalyst (Kumar et al. 2002; Ahmed et al. 2016) and adsorption (Jawad et al. 2019; Somsesta et al. 2020; Sulizi et al. 2020). Several of these methods are expensive and have low removal efficiency. Moreover, physical-chemical methods are not effective for dye removal due to the low biodegradability of the dye itself. Some studies utilised clays, fly ash, activated carbon, and hydrogel for the dye removal (Bouatay et al. 2015; Basava Rao & Ram Mohan Rao 2006; Ahmad et al. 2020). Alternatively, phytoremediation is a process that uses different kinds of plants to remove contaminants, for example, a study conducted by Imron et al. (2019) showed successful phytoremediation of MB using duckweed (*Lemna minor*).

In general, plants consist of cellulose, hemicellulose, and pectin; they have different functional groups such as hydroxyl, carboxyl, and

carbonyl. This is beneficial because the functional groups of these plants interact well with the functional groups of dyes, leading to the binding of dyes to the biomass of the plants. Many studies demonstrated the tremendous potential of the *Scirpus grossus* plant for the removal of MB from the textile wastewater. The *S. grossus* plant is a plant which is extremely efficient at contaminant removal (Tangahu et al. 2019). It is also considered to be a less expensive source of biomass, although no suggestions regarding the disposal of the plant waste after it has been used in phytoremediation have been made.

This study investigates the possibilities for handling the phytoremediation plant waste and attempts to fabricate a novel biofilm carrier from the phytoremediation waste and cement to enhance the dye removal from industrial wastewater. *The grossus* plant waste was used in this research to be tested on the MB decolourisation.

METHODOLOGY

Plant collection

The *S. grossus* plant waste was collected from the greenhouses located in the Universiti Kebangsaan Malaysia (UKM). The plant waste was washed thoroughly with tap water to remove the dirt and was then cut into small pieces measuring 0.5 cm using scissors. The plant material was then dried for three days under the Sun. Lastly, the small pieces were washed three times with distilled water, spread into two aluminium foil trays and dried inside an oven (Protech, Model FAC-350, Malaysia) at 110°C for 24 hr. The dried plant material was stored in a sealed container for further use.

Impregnation process

The adsorbent was prepared using a modified chemical activation method as described by Collin et al. (2015). The dried plant waste (25 g) was impregnated with phosphoric acid (H_3PO_4) as a dehydrating agent at concentrations of 2 M (2-AC), 4 M (4-AC), and 6 M (6-AC). Each impregnation was conducted in a 500 mL conical flask. The conical flasks were covered with cotton wool, sealed with laboratory film, and transferred to a water bath at 80 °C for three days. The samples were shaken manually from time to time to ensure the plant material absorbed the reagent. After three days, the samples were transferred to a Petri dish and dried inside an oven at 110 °C for 24 hr. The samples were then cooled in a clean crucible covered with a lid and kept in a sealed container for the activation process.

Activation process

A two-step activation process was achieved using a muffle furnace. The samples were semi-carbonised at 200°C for 15 min. The furnace temperature was then adjusted to the desired activation temperature of 500°C and activated for 45 min. Lastly, the chemical *S. grossus* activated carbon (AC) was washed several times with distilled water to remove the residual acid from the adsorbent surface to obtain the final adsorbent.

AC matrix preparation

The *S. grossus* AC was mixed with cement to fabricate a heavier adsorbent to be used for the MB removal. Initially, AC was ground into powder using a mortar and was then mixed with cement powder at a fixed ratio of 1:1 for each type of AC at different impregnation concentrations. After mixing the cement with AC, approximately 2 mL of distilled water was added, the solution was mixed and dried completely under the sunlight. The AC matrices were crushed into small granules before being used for the MB adsorption.

Methylene blue adsorption

A stock solution of MB was prepared by dissolving MB (5 and 15 mg) in 1 litre of distilled water. The adsorption was conducted using a 50 mL conical flask. Approximately 15 mL of 5 mg/L and 15 mg/L MB solution were poured into the flask and then 0.5 g of the AC matrix was added to the solution. The flask was shaken at 50 rpm and 25°C for a variety of contact times (10, 20, 30, 60 and 120 sec). After the desired contact time was achieved, each solution was centrifuged for 15 min at 3000 rpm and the supernatants were filtered using a 0.45 μm syringe filter before being tested for the final concentration of MB using a UV spectrophotometer (HACH DR6000) at a wavelength of 665 nm.

AC Characterisation

The surface structure of *S. grossus* AC (SG-AC) was observed under field-emission scanning electron microscopy (FESEM), while the chemical elements were determined using energy dispersive x-ray (EDX). Chemical functional groups of AC were analysed using Fourier transform infrared spectroscopy (FTIR). This technique measures the sample absorption capability of infrared radiation versus wavelength.

RESULTS AND DISCUSSION

Surface structure analysis

FESEM analysis was performed to determine the physical characteristics of AC, in order to analyse the surface morphology. Figure 1 illustrates the FESEM imaging of AC at various impregnation concentrations. It was obvious from the results that increasing the H_3PO_4 concentrations increased the hexagonal layer size due to the agglomeration of the carbon particles. Thus, the treatment of H_3PO_4 could promote the bond cleavage reactions and the H_2PO^{4-} ions forming a hydrogen bond network with carbon through the Grotthuss mechanism (Abdulkreem-Alsultan et al. 2016). The chemical element composition of AC is shown in Figure 2. All EDX spectrums indicated the presence of peaks that corresponded to C, O, P and Si. The existence of P species confirms the successful phosphonation of activated carbon with H_3PO_4.

Chemical functional groups

Fourier transform infrared spectroscopy (FTIR) is a vibrational spectroscopy technique that provides distinct adsorption peaks which can be identified and apportioned to specific chemical bonds to qualitatively or quantitatively identify the functional groups present in a multifaceted sample. As shown in Figure 3, AC demonstrated a distinct broad peak from 3449 cm^{-1} region which refers to the stretching of the carboxylic acid O-H group. The AC absorption band was normalised by the intensity of the absorption band centred around 1578 cm^{-1}, attributed to C=C or the aromatic ring in the wood (De Mattos et al. 2012). All the samples were found to have absorption peaks at 1411 cm^{-1} (C=C), 1000 cm^{-1} (P=O), 692 cm^{-1} (C–C stretching) and 492 and 478 cm^{-1} (C–C bending). The disappearance of absorption band intensity at 3405 cm^{-1} (C-H) stretching vibration for AC when the H_3PO_4 was 6M indicated that the activation step successfully removed a significant amount of hydrogen after activation in the form of hydrogen gas (Heidari et al. 2014). The presence of a phosphate group was confirmed by clear and strong vibration bands at 1001 cm^{-1} assigned to the P=O stretching vibrations of the HPO_4^{2-} units, proving the presence of the $-PO_3H$ group covalently bonded to the polyaromatic carbon structure. The absence of C=O at absorption band 1615 cm^{-1} in AC indicated that the chemical activation broken between carbon and oxygen bonds in the aliphatic and aromatic species simultaneously eliminated many C=O from the parent material (Hesas et al. 2013). Increasing the H_3PO_4 concentrations from 0 to 6 M resulted in an increase in the absorption band intensity at 1553 cm^{-1} (C=C) and 545 cm^{-1} (C–C). This was due to the interaction between the phosphate groups and the carbon (De Mattos et al. 2012; Bi & He, 2013).

Physical observation

Adsorption of MB onto different AC matrices was investigated at time intervals of 0, 10, 20, 30, 60 and 120 sec with the concentrations of 5 and 15 mg/L of MB. As shown in Figure 4, for 5 mg/L of MB, the adsorption increased for the AC that was subjected to the impregnation process with H_3PO_4 at concentrations of 2, 4, and 6 M in comparison with the AC without impregnation.

Adsorption of MB

Figure 5(a) illustrates the results of the MB removal by the *S. grossus* AC matrix. The C-AC removed MB in 97–99% after contact times ranging from 10 to 30 sec. At 60 sec, MB was completely adsorbed onto the C-AC. The impregnation concentrations appeared to play a key role in the development of the morphology of the adsorbents which showed an excellent result by completely adsorbing MB after a contact time of 30 sec (2-AC, 4-AC and 6-AC). This explained the high porosity and surface area of the AC. During a comparison of the adsorbents, it was observed that the C-AC required more contact time.

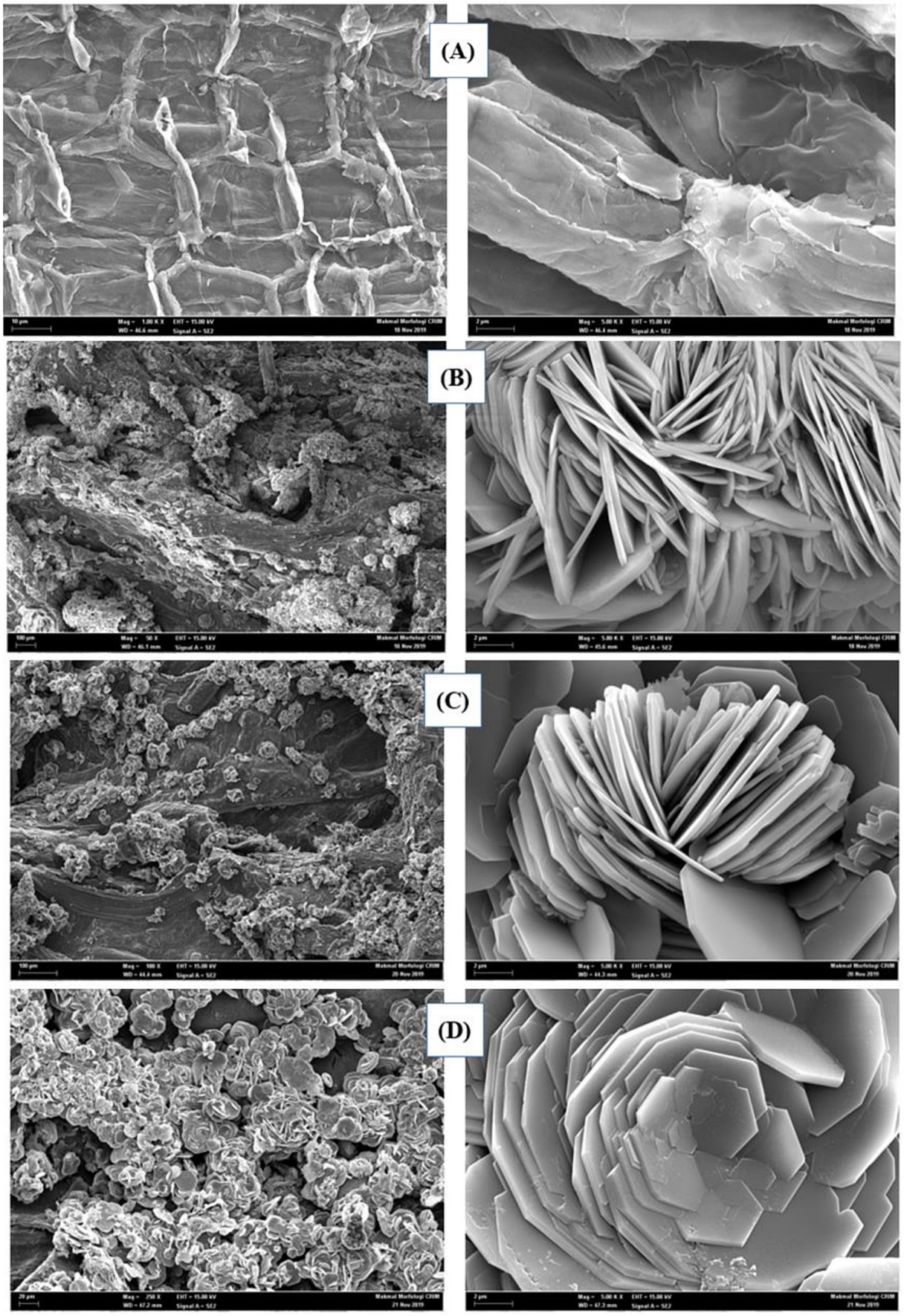

Figure 1. Surface structure of AC after impregnation with H_3PO_4 (a) control, (b) 2 M, (c) 4M, and (d) 6 M of H_3PO_4 without the addition of cement

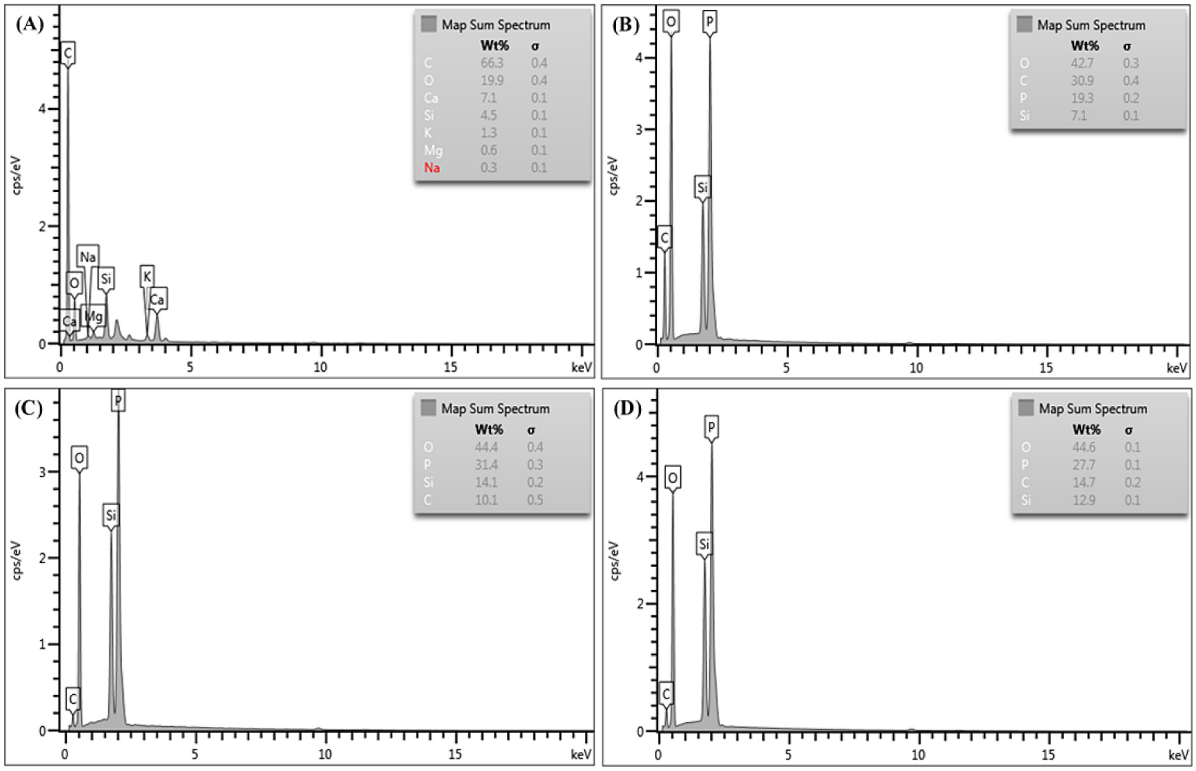

Figure 2. EDX results after impregnation with H_3PO_4 (a) control, (b) 2-AC, (c) 4-AC, and (d) 6-AC

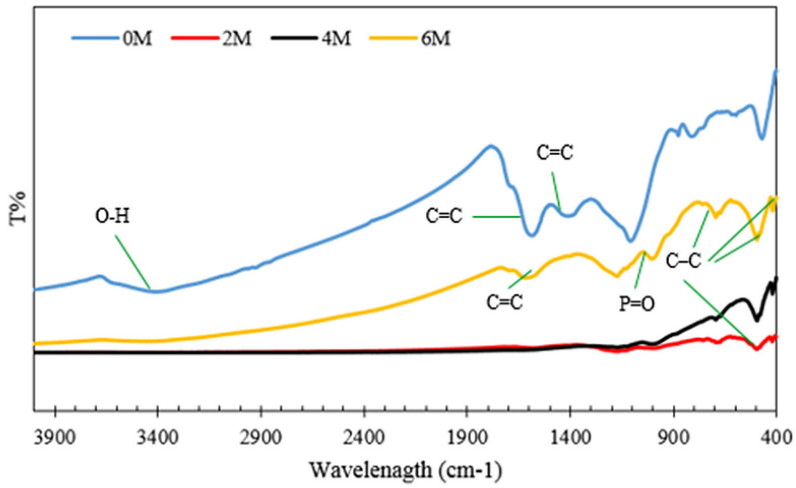

Figure 3. FTIR profile of prepared AC

The impregnation process and addition of cement appeared to influence the development of a porous structure and increased the surface area of AC, as confirmed by the FESEM results (Figure 6).

The adsorbents prepared without the addition of cement were also tested for the MB removal. The results showed a complete MB removal after a contact time ranging from 3 to 5 min. This finding showed that the addition of cement significantly enhanced the performance of the adsorbent, as it increased the porosity, consequently enhancing the adsorption of MB in shorter time. The efficiency of the 15 mg/L MB solution is illustrated in Figure 5(b). It was found that 4-AC and 6-AC were the most effective adsorbents as they almost completely removed MB in less than 60 sec compared to other AC. At 60 sec, the MB concentrations were measured at 1.2, 0.6, 0.005, and 0.001 mg/L for C-AC, 2-AC, 4-AC, and 6-AC, respectively.

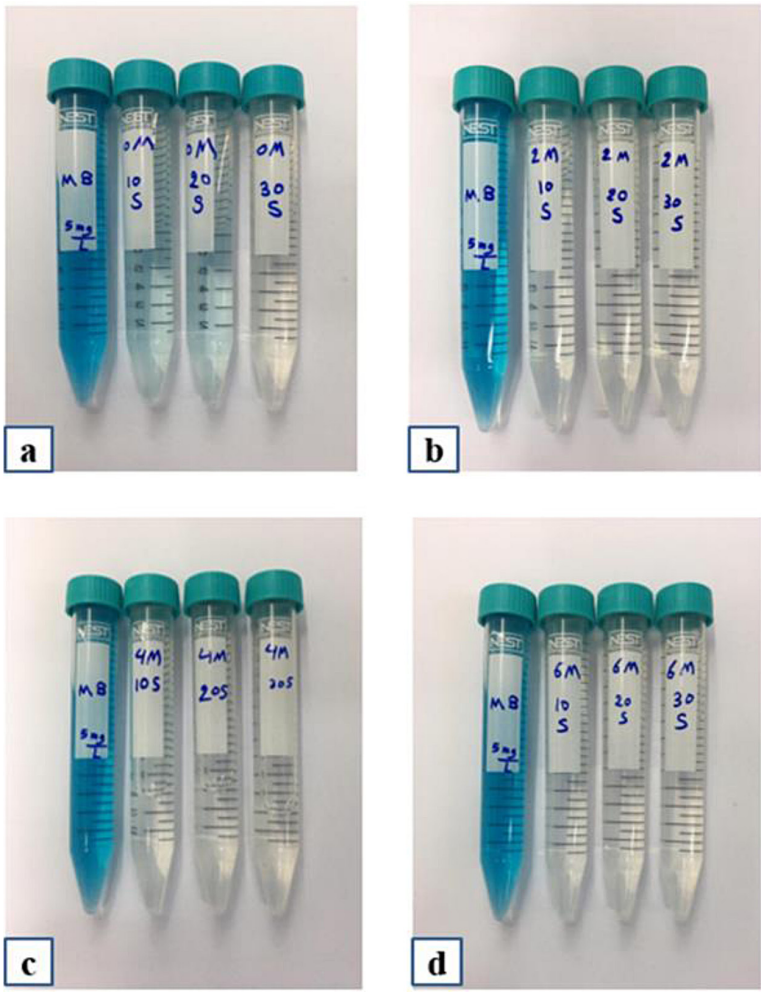

Figure 4 Observation of MB colour reduction for (a) C-AC, (b) 2-AC, (c) 4-AC, and (d) 6-AC

Comparison with other studies

The previous studies reported various types of adsorbent for MB removal such as corn husk, mango leaf, coconut shell, Fava bean peel, *Ficus carica* bast, and phytoremediation plant-based adsorbent such *S. grossus* as summarised in Table 1. Most studies utilised a synthetic MB solution at high concentrations (> 50 mg/L), whereas there is a lack of studies which used low concentrations of MB. Bayomie et al. (2020) developed a novel adsorbent using fava bean peel to adsorb low concentrations of MB (3.6–25 mg/L). In the study, researchers observed that within 20 min, 0.5 g of fava bean peel could adsorb 70 to 80% of MB. In comparison, in this study, with an MB concentration of 15 mg/L and 0.5 g SG-AC, 100% removal was achieved in only 30 sec. Another study using corn husk AC achieved more than 95% MB removal within 120 min under an acidic condition of pH 4 (Khodaie et al. 2013). Similar findings were obtained in a study by Khodaie et al (2013) in which mango leaf adsorbent in powder form removed MB at an initial concentration of 100 mg/L. However, in a study which used *Ficus carica* bast AC, the adsorption saturated after 60 min with removal at 60% (Pathania et al. 2017).

CONCLUSION

This study investigated the reuse of phytoremediation plant waste with the addition of cement as an adsorbent for the removal of MB in a solution. The tests showed that the adsorption of MB onto the adsorbent matrix was feasible and spontaneous due to the complete removal of MB within a short contact time of 30 sec. Moreover, the most effective impregnation was achieved at 6 M H_3PO_4. The analysis of characteristics showed that the adsorbent matrix at 6 M H_3PO_4 had a more porous structure. The findings indicated that phytoremediation plant waste could

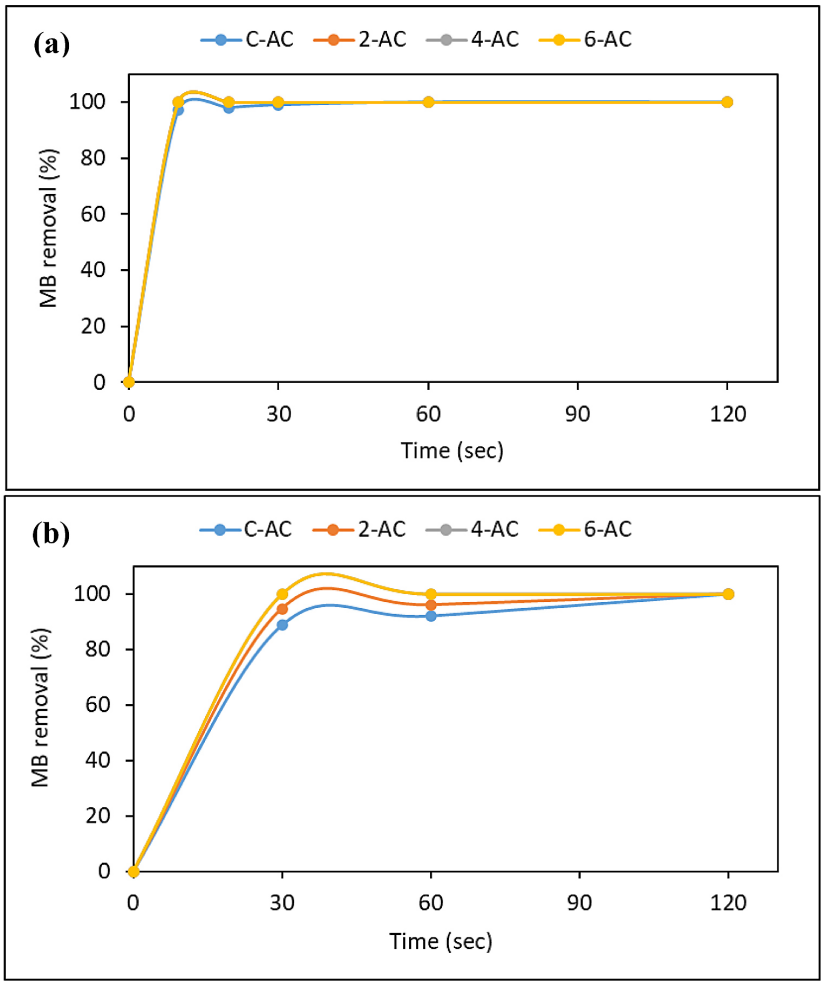

Figure 5. Removal of MB by AC based *S. grossus* (a) at 5 mg/L MB, and (b) at 15 mg/L MB

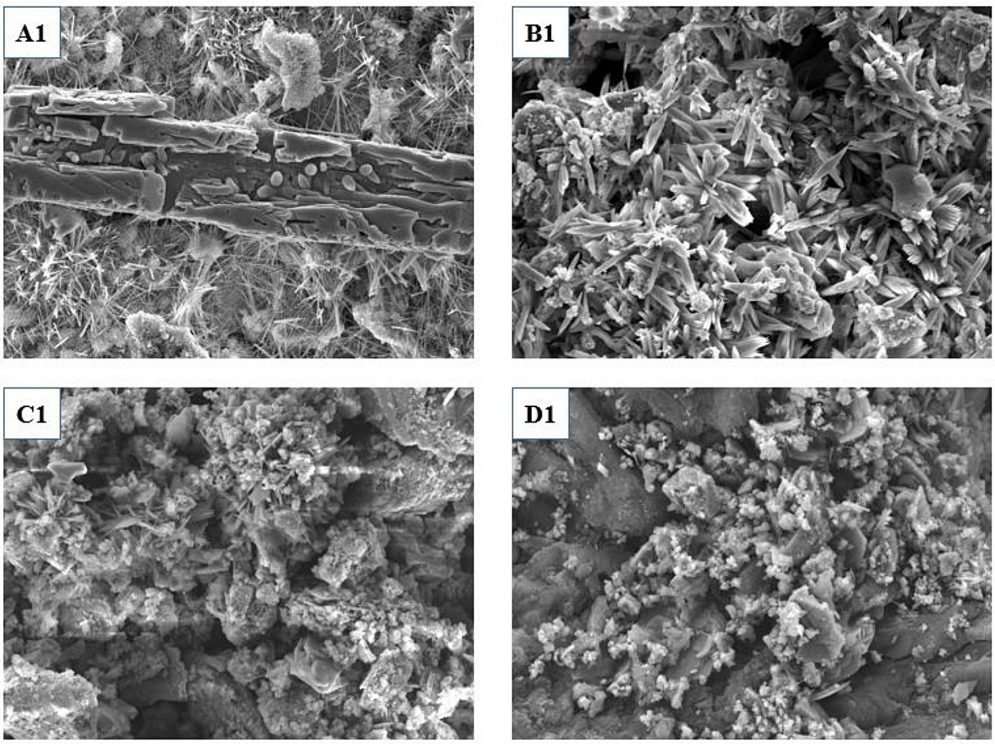

Figure 6. FESEM images of adsorbents after mixing with cement

Table 1. Comparison of MB removal using various sources of AC

Type of activated carbon	Initial concentration (mg/L)	Mass of adsorbent	Time	pH	Removal (%)	References
S. grossus	15 mg/L	0.5 g	30 sec	6.0	100	This study (2020)
Pea Shells Pea Shells Pea Shells Pea shells	250 mg/L	0.5 g	180 min	6.85	33.6	Geçgel et al. (2013)
Corn Husk	50 mg/L	0.5	120	4	> 95	Khodaie et al. (2013)
Mango leaf powder	100	0.5	120	-	> 95%	Uddin et al. (2017)
Typha orientalis *Typha orientalis* *Typha orientalis* *Typha orientalis* *Ficus carica* bast	100	0.5	60	7.8	60%	Pathania et al. (2017)
Coconut shell	200	0.1	450	5.6	83%	Jawad et al. (2020)
Fava bean peel waste Fava bean peel	3.6–25 mg/L	0.5	20	5.8	70–80%	Bayomie et al. (2020)

be processed to be reused as an adsorbent for the treatment of wastewater, thus creating a more sustainable process.

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