SORPTION OF MALACHITE GREEN (MG) BY CASSAVA STEM BIOCHAR (CSB): KINETIC AND ISOTHERM STUDIES

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ABSTRACT

Cassava stem biochar (CSB) was produced by pyrolyzing CS at 500°C for 2 hours at nitrogen environment. Proximate and ultimate analyses were conducted on CS and CSB. Batch sorption experiment on synthetic MG wastewater was optimized for the sorbent dosage, MG solution pH and contact time. Sorption data was analysedwith linearized sorption kinetic and linearized isotherm models. Pyrolysis of CS produced carbon-rich and stable CSB with a yield of 11.94%. The optimum sorption sorbent dosage, MG solution pH and contact time are 1.67 g/L, > pH 7.4 and 10 minutes respectively. The sorption of MG by CSB was best described by the pseudo-second-order kinetic model and the Langmuir isotherm model. The Langmuir sorption capacity of CSB was 40.5 mg/g. Monolayer of MG molecules formed chemical bonds on the homogenous surface of CSB.

Keywords: Manihotesculenta Crantz; charcoal; black carbon; adsorption.

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1. INTRODUCTION

Dyes are organic or inorganic molecules used in large mount in the textile industry, producing a considerable amount of coloured wastewater in the waterways [1]. Malachite green is one of the common textile dyes also used in the aquaculture for controlling parasite, fungus and protozoan infections on aquatic organisms[2]. However, MG is highly toxic to aquatic fauna, flora and human beings. Moreover, MG may also increase the level of Chemical Oxygen Demand in wastewater and decrease Dissolved Oxygen in aquatic environments [3]. Hence, its removal from the effluent streams is highly needed [2].

Conventionally, dyes may be managed by chemical oxidation. However, these methods of wastewater treatment may not be feasible in long run due to the rising cost of chemicals and the possibility of creating secondary pollutant. Removal of MG from water treatment may be a cheaper option, especially when utilizing waste biomass [4-5]. To enhance the performance of biomass sorbent, dry carbonization or pyrolysis produces carbon materials called biochar that possesses large surface area due to its porous structure. The benefit of using waste biomass for biochar production compared to other types of biomass is that it is cost-effective [6].

Cassava (ManihotesculentaCrantz) is a food crop that has high biomass yield and is resilient to environmental stresses. Apart from the tuber peel, the cassava stem (CS) is the major waste biomass produced from harvesting this crop and most are abandoned or burned on the fields. Only 10-20% of CS are used for propagation [7]. Cassava stem may be converted to biochar for sorption of MG. To the best of our knowledge, cassava stem based carbon has been produced and studied but none has been focussed on its sorption of pollutants from aqueous phase. The objectives of this study are:

  i. To characterize the physical and chemical properties of CS and CSB.

  ii. To determine the optimum sorption parameters (i.e., such as pH, contact time, sorbent dosage and initial concentration) of CSB for the removal of MG from aqueous system.

 iii. To identify the maximum sorption capacity and sorption mechanism of MG by CSB using isotherm and kinetic models.

2. RESULTS AND DISCUSSION

2.1. Proximate Analysis of CS

Fig.1 shows the percentages of moisture, volatile, fixed carbon and ash in CS. The moisture content of CS was 53.41%, the volatile matter content was 32.84%, the fixed carbon content was 11.94% and the ash content was 1.82%. Cassava stem consists primarily moisture and volatile contents. The fixed carbon and ash contents were similar to those reported by [8].
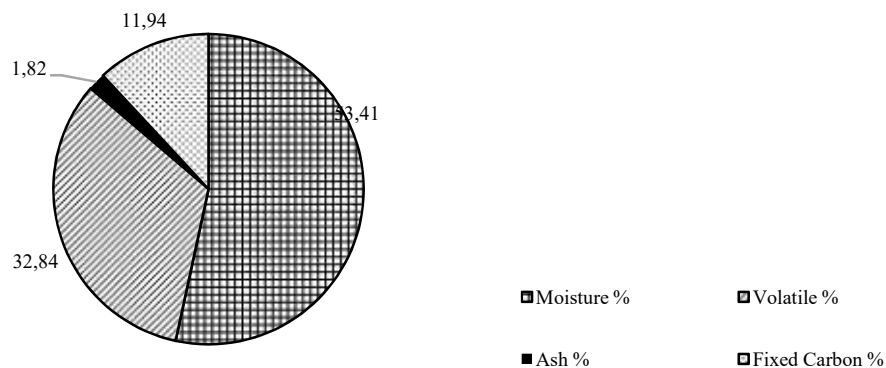

Fig.1. The percentages of moisture, volatile, ash and fixed carbon for CS

2.2. Ultimate Analysis for CS and CSB

Table 1 shows the percentages of C, H, N, O and S for CS and CSB. Pyrolysis process increased the percentage for C, but decreased that of O. The high C/O ratio for CSB implies a high stability [9]. Cassava stem contains no N nor S. Therefore, pyrolysis of CS will not release environmentally non-friendly gaseous emission, such as NO_x and SO_2.

Table 1. Percentages of C, O, H, N and S for CS and CSB

| Element	Percentage (% w/w)	
	CS	CSB
C	44.78	74.45
O	49.66	23.38
H	5.56	2.17
N	0	0
S	0	0
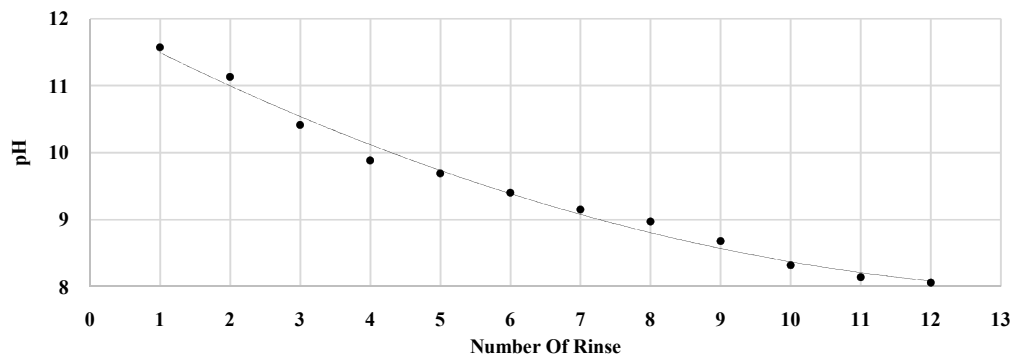
Fig.2.pH values for CSB as a function of rinsing frequency

Fig.2 shows the pH of CSB as a function of rinsing frequency. The high pyrolysis temperature has cause high pH of CSB [10]. The initial pH value of the quenched CSB (i.e., 11.57) decreased (to about pH 8) with increasing frequency of rinsing. The ash in the quenched CSB is alkaline and its removal from rinsing with deionized water has gradually decrease the pH value of CSB.

2.3.Optimization of Batch Sorption Parameters

Fig. 3 shows the removal percentage (%) of MG from the aqueous solutions as a function of CSB sorbent dosage (g/L). The removal percentage increased to reach the plateau at 90.4% MG removal, and at 1.67g/L of CSB dosage. After that, there is no significant difference in the removal percentage of MG. The upward trend of the percentage removal is due to the increase of available surface area from higher CSB sorbent dosage [11]. The slight increase of MG removal percentage at an elevated CSB dose (i.e., ≥1.67g/L) may be due to the competition among sorbent molecules and the splits present in the concentration gradient [12-13].
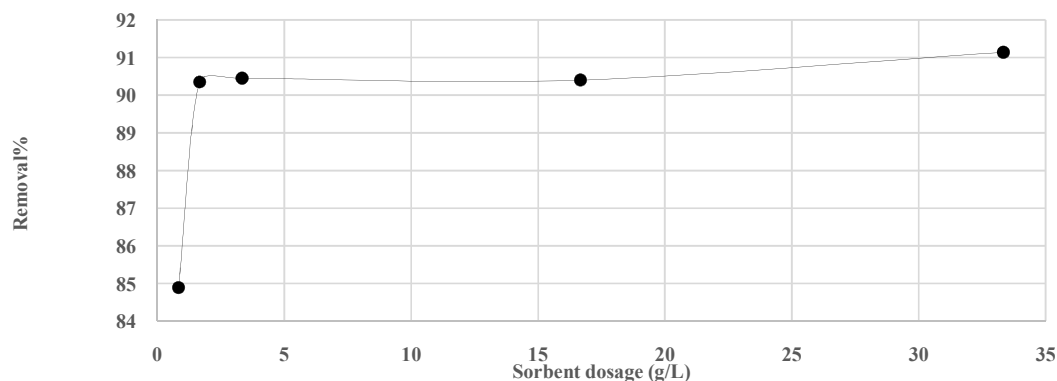
Fig.3. Removal percentage (%) of MG from aqueous solution as a function of CSB sorbent

dosage (g/L) [Constant variables: agitation (100 rpm), contact time (10 minutes), initial
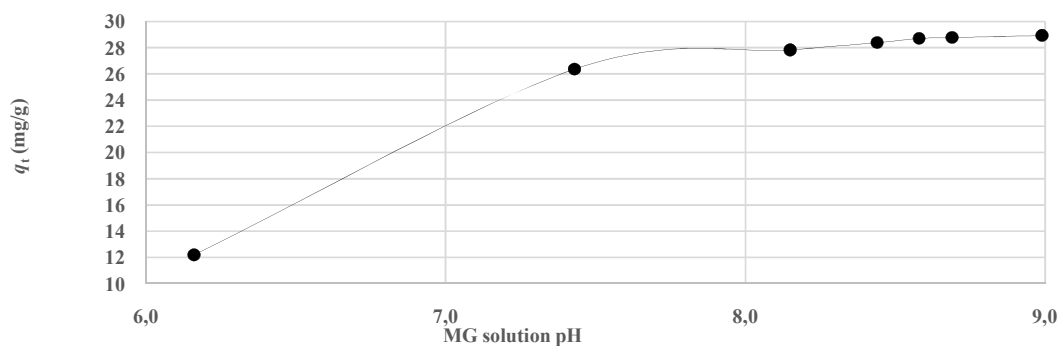
concentration (50 ppm)]

The sorption capacity of CSB, q_t (mg/g)as a function of contact time (minute) was illustrated in

Fig.4. Rapid uptake of MG occurred from the beginning until the 10th minute, whereby the

sorption capacity was 23.7 mg/g. Then, the q_t value increased slightly until 26.8 mg/g at the 60th

minute. At the beginning of the experiment, free binding sites were present on the surface of

CSB. But after the 10th minute, the surface of CSB may have been saturated with MC. The

optimum contact time for sorption of MG from aqueous solution is 10 minutes.
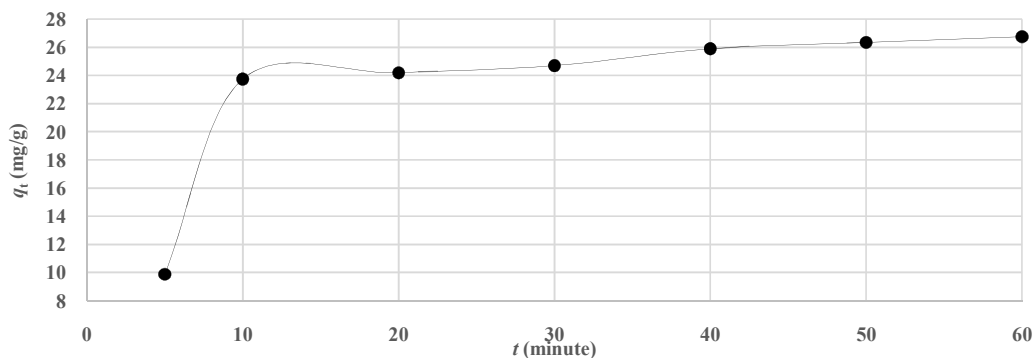
Fig.4. Sorption capacity of CSB, q_t (mg/g) as a function of contact time, t (minute) [Constant

variables: CSB sorbent dosage (1.67 g/L), agitation (100 rpm), initial MG concentration (50

mg/L)]

Generally, the pH of MG solution was increased by 0.5-2.0 pH unit upon contact with CSB.

The initial, unadjusted pH for MG solution (i.e., 3.9) was increased to 7.2 and 8.2 after agitation

with CSB for 5 and 120 minutes respectively. Fig.5 shows the sorption capacity of CSB, q_t

(mg/g) as a function of equilibrium MG solution pH. The q_t values increased rapidly from 12.2

to 26.4 mg/g when the equilibrium pH of the MG solution increased from 6.2 to 7.4 respectively. The q_t values were increased slightly between pH 7.4 and pH 9.0. Low amount of MG was adsorbed onto CSB at <pH 7.4. The excessive amount of hydronium ion in acidic MG solution may cause protonation of MG and functional groups on CSB surface. Malachite green molecules may form positively-charge MG derivatives and remain soluble due to the electrostatic repulsion [14]. Moreover, the hydronium ion may compete with the positively-charged MG derivative for sorption sites on CSB surface [15]. The protonation of CSB surface sites may cause deactivation of the carboxylate and phenolate groups [16-17]. However, at high MG solution pH (i.e., >7.4), MG molecules were deprotonated to form neutrally-charged MG derivative (i.e., carbinol) [18]. Consequently, electrostatic repulsion between the MG and the negatively charged surface of CSB decreased, resulting in the increase of q_t values [19].

Fig.5. Sorption capacity of CSB, q_t (mg/g) as a function of equilibrium MG solution pH [Constant variables: CSB sorbent dosage (1.67 g/L), contact time (10 minutes), agitation (100 rpm), initial MG concentration (50 mg/L)]

2.4.Sorption Kinetic and Isotherm

Table 2 shows the parameters for pseudo-first-order and pseudo-second-order kinetic models for sorption of MG by CSB. The sorption kinetic were best described by the pseudo-second-order model (R^2= 0.988), compare to the pseudo-first-order model (R^2= 0.867). This indicates that the rate-limiting step for sorption of MG was possibly controlled by a chemical process on the CSB surface [20].

Table 2. Parameters of pseudo-first-order and pseudo-second-order kinetic models for sorption of MG by CSB

Model	Parameter	
Pseudo-first-order	$q_{e(exp)}$ (mg g^{-1})	26.8
	$q_{e(cal)}$ (mg g^{-1})	12.2
	k_1 (min^{-1})	0.0677
	R^2	0.867
Pseudo-second-order	$q_{e(exp)}$ (mg g^{-1})	26.8
	$q_{e(cal)}$ (mg g^{-1})	29.6
	k_2 (g mg^{-1} min^{-1})	0.0057
	R^2	0.988

Fig.6 shows the plot for q_t value (mg/g) as a function of equilibrium MG concentration (mg/L). The q_t value for CSB increased with increasing C_e value. In general, q_t values increased with increasing C_e values. High initial concentration for MG may have contributed toa high driving force for the transfer of MG molecule onto CSB surface[21].
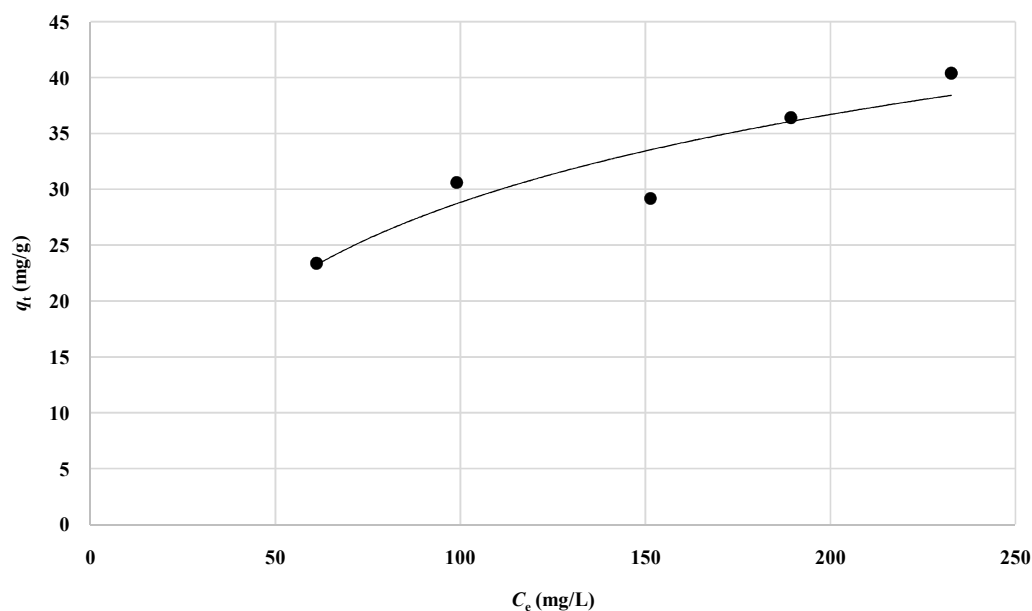
Fig.6. Sorption capacity of CSB, q_t (mg/g) as a function of equilibrium MG concentration, C_e (mg/L) [Constant variables: CSB sorbent dosage (1.67 g/L), contact time (10 minutes), agitation (100 rpm)]

Table 3 shows parameters of Langmuir and Freundlich isotherm models for sorption of MG by CSB. The sorption data was best described by the Langmuir isotherm (R^2= 1.00), compare to the Freundlich isotherm (R^2= 0.284). This indicates that sorption occurred where MG molecules occupy one active site on the homogeneous surface of CSB [22]. The value of R_L is 1.61 x 10^{-15}, indicating that the sorption of MG by CSB is unfavourable.

Table 4 shows the sorption capacities of MG by bagasse fly ash, walnut shell, Oil palm trunk fibre, Casuarinaequsetifolia needle, chitin and CSB. Sorption capacity of CSB is comparable to that of bagasse fly ash and higher than chitin but is still lower than those of walnut shell, Oil palm trunk fibre, Casuarinaequsetifolia needle. However, CSB is a stable, carbon-rich sorbent. Even with an inferior sorption capacity for MG, CSB and may be more resistant to degradation and is more suitable to be regenerated and reused.

Table 3. Parameters of Langmuir and Freundlich isotherm models for sorption of MG by CSB

Model	Parameter	
Langmuir	K_L (L mg^{-1})	1.24 x 10^{13}
	q_{MAX} (mg g^{-1})	40.5
	R^2	1.00
	R_L	1.61 x 10^{-15}
Freundlich	n	14.6
	K_F (mg g^{-1})	22.9
	R^2	0.284

Table 4. Langmuir sorption capacities forMB by CSB andothervarious sorbent materials

Sorbent	Langmuir Sorption Capacity (mg g^{-1})	Reference
Bagasse fly ash	42.2	[23]
Walnut shell	90.8	[24]
Oil palm trunk fibre	149.3	[25]
Casuarinaequsetifolia needle	77.6	[26]
Chitin	29.6	[27]
CSB	**40.5**	**This study**

3. EXPERIMENTAL

3.1. Sampling of CS and Preparation of CSB

Cassava stem with an average diameter of 5 cm was collected at KampungDamai, Kuang, Selangor. Cassava stem was sun-dried for 7 days, and oven-dried further in the oven at 70°C for 5 days. Then, the septum was removed and the bark was crushed, pulverized and sieved to ≤2 mm of particle diameter. For the preparation of CSB, pyrolysis of CS was conducted using a muffle furnace at 500°C in nitrogen gas ambient for 2 hours [28]. Hot CSB was quenched and rinsed thoroughly with deionized water to remove ash. Then, it was oven-dried at 100°C for 24 hours, and sieved to particle size of ≤150 μm.

3.2.Characterization of CS and CSB

Proximate analysis (% w/w) was conducted by gravimetric method to determine the contents of moisture, ash, volatile matter and fixed carbon for CSB [29]. The weights of fresh and oven-dried CS were used to determine moisture content. Ash content was determined from combustion of the oven-dried CS at 750°C for 1 hour using a furnace to produce ash, fixed carbon was determined from W_c and volatile matter was determined by difference. The pH for CSB was determined using a calibrated pH meter. Ultimate analysis was conducted using CHNS elemental analyzer (Thermofinnigan Flash EA2000, UK) and the oxygen was calculated by difference.

3.3.Optimization of Batch Sorption Parameter

Malachite green stock solution (100mg/L) was prepared by diluting MG chloride salts with deionized water, and stored at 4°C in an amber reagent bottle. The stock MG solution was

diluted to 50 mg/L and was used for all sorption optimization experiments except for sorption isotherms. All solution was filtered using centrifuged at 40000 rpm for 30 minutes and filtered with 0.45 μm millipore syringe filter and the concentration of residual MG solution was analyzed by colorimetric method using a series of MG standards and a spectrophotometer [30].

3.3.1. CSB Sorbent Dosage

Thirty milliliters of MG solution (50 mg/L) was agitated with various amount of the CSB (i.e., 0.025, 0.050, 0.100, 0.500 and 1.000 g). The solutions were shaken at 100 rpm for 120 minutes using a Multi-Function Rotator.

3.3.2. Contact Time

Thirty milliliters of MG solution (50 mg/L) was agitated with 0.050g CSB at 100 rpm using a Multi-Function Rotator at 6 contact times (i.e., 10, 20, 30, 40, 50 and 60 minutes).

3.3.3. MG Solution pH

Thirty milliliters of MG solution (50 mg/L) was agitated with 0.050g CSB at 100 rpm for 10 minutes, using a Multi-Function Rotator at various initial pH of the MG solutions (i.e., 3, 4, 5, 6, 7, 8, 9). The solution pH was adjusted using 0.1 M sulfuric acid (H_2SO_4) and 0.1 sodium hydroxide (NaOH).

3.4. Sorption Kinetic and Isotherm

For sorption isotherm experiment, the MG stock solution (100 mg/L) was diluted into 5 concentrations (i.e., 100, 150, 200, 250 and 300 mg/L). The diluted MG solutions were agitated with 0.050g CSB at 100 rpm for 10 minutes, using a Multi-Function Rotator. The sorption data for contact time optimization was analyzed with linearized kinetic models (i.e., pseudo-first-order and pseudo-second-order) and the sorption isotherm data was analyzed with Langmuir and Freundlich models (Table 5). Malachite green removal percentage (%) and sorption capacity, q_t (mg/g) for CSB were calculated using Equation (1) and (2) respectively.

$$\text{Re}moval\% = \frac{[MG]_i - [MG]_f}{[MG]_i} \times 100 \qquad (1)$$

$$q_t = \frac{[MG]_i - [MG]_f}{m_{CSB}} \times V_{MG} \qquad (2)$$

Table 5. Linearized kinetic models (pseudo-first-order andpseudo-second-order) and isotherm

models (Langmuir andFreundlich)

Kinetic/Isotherm Models	Linearized Equation
Pseudo-first-order	$\log(q_e - q_t) = \log q_e - \dfrac{k_1 t}{2.303}$
Pseudo-second-order	$\dfrac{t}{q_t} = \dfrac{1}{k_2 q_e^2} + \left(\dfrac{1}{q_e}\right) t$
Langmuir	$\dfrac{C_e}{q_e} = \dfrac{C_e}{q_{max}} + \dfrac{1}{K_L q_{max}}$
Freundlich	$\ln q_e = \dfrac{1}{n}\left(\ln C_e\right) + \ln K_F$

where $[MG]_i$ and $[MG]_f$ are the initial and final concentrations for MG (mg/L) respectively,m_{CSB} is the mass for CSB (g); V_{MG} is the volume for MG solution (L), t is the contact time between CSB and MG solution (minute),q_e is the equilibrium sorption capacity (mg/g), k_1 (min^{-1}) and k_2 (g/mg min) are the rate constant for the pseudo-first-order and pseudo-second-order equation respectively. The parameters for the pseudo-first-order and pseudo-second-order kinetic models were obtained by the linear regression of the $\log(q_e - q_t)$ versus t plot and t/q_t versus t plot respectively. q_{max} is the maximum sorption capacity of CSB in the Langmuir model (mg/g),n is the empirical constant for Freundlich model (L/mg),K_L and K_F are the constants for Langmuir (L/mg), Freundlich (mg/g) respectively. The parameters for Langmuir isotherm model were obtained by linear regression of the C_e/q_e versus C_e and $\ln q_e$ versus $\ln C_e$ plots respectively. The separation factor (R_L) was determined with Equation (3).

$$R_L = \frac{1}{1 + K_L C_o} \qquad\qquad (3)$$

The R_L value indicates whether the sorption is either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [31]. The R_L value

4. CONCLUSION

There is potential in using CS for producing CSB for removing MG from aqueous solution. Sorption of MG by CSB is optimized at sorbent dosage of 1.67 g/L, contact time of 10 minutes and MG solution at >pH 7.4. Linear regression of the batch sorption data with kinetic and isotherm models indicated that MG molecules may have formed monolayer, and chemically bound to the homogenous surface of CSB. The Langmuir sorption capacity of CSB is lower to other biomass, but may offer greater stability when being regenerated to reuse. Further studies on the desorption behaviour of MG from CSB, and MG sorption performance by CSB in actual wastewater is needed to understand the potentials of CSB as sorbent for MG from polluted wastewater.

5. ACKNOWLEDGEMENTS

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