

CARBON-SILICA COMPOSITE AS ADSORBENT FOR REMOVAL OF CATIONIC DYE (METHYLENE BLUE)

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Abstract

The aim of this research was to synthesize carbon-silica composite (CSC) as an adsorbent for cationic dye removal from wastewater. Molasses, a by-product of the sugar industry, was successfully utilized to prepare CSC by sol-gel method with tetraethoxysilane (TEOS) as silica source. The physicochemical properties of the composites were studied by N₂ adsorption, FTIR and TGA. The highest specific surface areas of CSC was 144 m²/g at a molasses/TEOS ratio of 0.8, with a mesopore volume of 83% and average pore width of 9.71 nm. This optimal CSC was evaluated for methylene blue (MB) adsorption using batch experiments under varying adsorption times and initial MB concentrations. Adsorption equilibrium was reached within 14 h and the pseudo-second order equation provided the adequate fit for the kinetic studies, suggesting that dye adsorption was limited by chemisorption. The equilibrium data were best described by the Sips model with a maximum adsorption capacity of 180.22 mg/g. The CSC derived from molasses is considered a potentially promising adsorbent for cationic dye removal in wastewater.

Keywords: Dye removal; Methylene blue; Adsorption; Carbon-silica composite; Wastewater treatment

Introduction

Treatment of wastewaters containing hazardous substances such as dyes from the textile, paper, plastic, cosmetic and food industries is of great importance because of their harmful and potential carcinogenic effects on living beings (Geçgel *et al.*,

2013). Methylene blue (MB) is a basic or cationic dye that is most often used and can cause eye burn by direct contact, nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia by ingestion (Valliammai

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et al., 2017). To efficiently remove such contaminants, adsorption technology is highly regarded because of its economic feasibility, simplicity in design and operation, ability to remove a large variety of contaminants, and possibility of adsorbent recovery and reuse (Gong *et al.*, 2013; Falsafi *et al.*, 2020). The selectivity of an adsorbent towards a specific adsorbate greatly depends on the adsorbent properties (Falsafi *et al.*, 2020), and thus adsorbent selection plays a vital role in the performance of toxic substance adsorption. Adsorbents containing carbon such as activated carbon, biochars or carbon nanotubes are widely used to remove hazardous substances from aqueous solutions. Moreover, composites of carbon with inorganic oxides (such as SiO_2 , Al_2O_3 and TiO_2) have also received great interest for their efficiency in effluent treatment. For example, Santos *et al.* (2015) prepared carbon composites from a mixture of coffee waste and clay (mainly composed of SiO_2 (66.2%) and Al_2O_3 (21.0%)) and considered the application of this adsorbent for removal of anionic dyes.

Owing to the microporous structure of carbon materials and the high thermal stability and mesoporous structure of silica (Valle-Vigón *et al.*, 2013; Wu *et al.*, 2022), carbon-silica composites (CSC) are composite materials that combine these advantages of both materials. Various methods can be used to prepare CSC, including hybrid pyrolysis carbonization, hydrothermal carbonization, and sol-gel method (Wu *et al.*, 2022). Particularly the sol-gel method has been widely used due to convenient operation, low reaction temperature and low cost (Wu *et al.*, 2022). In recent years, activated carbon powder (Fu *et al.*, 2020) and resorcinol (Goudria *et al.*, 2020) have been used as carbon source in CSC, while the most commonly used silica source is tetraethoxysilane (TEOS) (Fu *et al.*, 2020).

In this study, the sol-gel method was employed to synthesize CSC by simple mixing of molasses and TEOS. Molasses is a by-product of sugar production and presents an inexpensive and widely available source of sucrose (29-40%), and glucose (4-14%) that can be used as carbon source with other non-sugar compounds and mineral such as potassium (4-51%), magnesium (1-14%), calcium (0.8-15%), sodium (0.09-9%), protein (0.5-4.5%), sulphates (2.2-9.9%) and amino acids (0.3-1.5%) (Jamir *et al.*, 2021). The influence of the ratio between molasses and TEOS on the surface area of the composites was investigated. The material with the highest surface area was further characterized using N_2 adsorption, FTIR, TGA and was tested for its MB adsorption capacity.

Materials and Methods

Molasses (Figure 1 (a)) was obtained from Mitr Phol Innovation & Research Center, Chaiphum, Thailand. The carbon-silica composites (CSC) were synthesized by mixing molasses with 4.4 g of tetraethoxysilane (TEOS, $\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$). Next, 20 mL of 50% H_2SO_4 and 5 mL of deionized water were added. The mixture was stirred at 35°C for 4 h and further stirred at 80°C for 18 h. The resulting gel was washed several times with distilled water followed by drying at 120°C for 7 h, after which the resulting CSC solid was obtained. Figure 1(b) shows the photo of the as-prepared CSC. The amount of molasses was varied from 1.32 g to 7.92 g, corresponding to molasses to TEOS ratios of 0.3, 0.5, 0.7, 0.8, 1.0, 1.3, 1.4, 1.5 and 1.8. For comparison, an adsorbent using only molasses (without addition of TEOS) was also prepared.

N_2 adsorption-desorption isotherms were measured at 77 K using ASAP2460 (Micromeritics). The specific surface area, S_{BET} , was determined by using the Brunauer-Emmett-Teller (BET) equation in the range of P/P° from 0.05 to 0.3. The micropore volume (V_{mic}) was calculated via the Dubinin-Radushkevich (DR) equation and the single point total pore volume (V_{T}) was measured at $P/P^\circ = 0.995$. The difference between the total pore volume and micropore volume corresponds to the mesopore volume (V_{meso}). The average pore width, D_{p} , was calculated from $(4 \times \text{total pore volume}) / \text{specific surface area}$. The FTIR spectra were collected on a TENSOR 27 FTIR spectrometer (Bruker) by KBr pellet method. Thermogravimetric analysis (TGA) was performed on a TGA-50H (Shimadzu) with a heating rate of 10°C/min under 10 mL/min of continuous N_2 flow. The temperature was increased from 25°C to 700°C.

The CSC prepared at optimum conditions (i.e., with the highest surface area) was used for methylene blue (MB) adsorption at room temperature. Batch adsorption experiments were performed by shaking 10 mg of CSC with 50 mL of 6 mg/L MB solution for 1-22.5 h. The effect of initial concentration (2-200 mg/L) was also studied to measure the adsorption isotherm. After the adsorption experiments, the CSC was separated from the mixture by centrifugation. The residual MB concentrations were measured with a UV-vis spectrophotometer (Analytik Jena AG) with a maximum absorbance wavelength at 664 nm. The adsorbed amount of MB onto CSC at time t (q_t , mg/g) was calculated using equation (1):

$$q_t = \frac{V(C_o - C_t)}{m} \quad (1)$$

where C_o and C_t are the concentrations of dye at initial and time t (mg/L), respectively, V is the volume of dye solution (L) and m is the mass of CSC used (g).

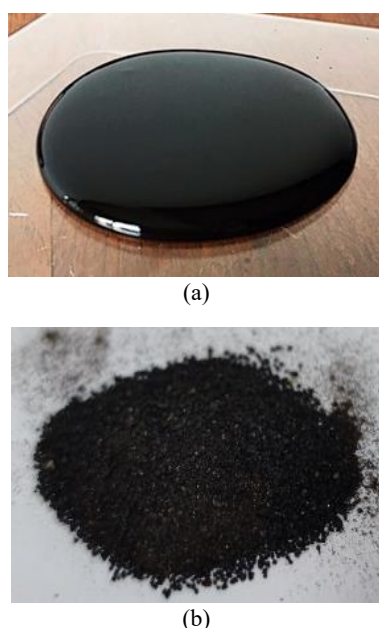


Figure 1. (a) Molasses used as carbon source and (b) as-prepared CSC

Results and Discussion

The relationship between the molasses to TEOS ratio and surface area is given in Figure 2. The surface area of CSC increased with increasing this ratio from 0.3 to 0.8, whereas a further increase resulted in a lower surface area. Table 1 presents the porous properties of CSC for all preparation ratios. The adsorbent prepared without TEOS had a very low surface area and porosity that could not be measured. This indicated that using only molasses as carbon source without silica source could not produce a porous material. At ratio 0.8, the CSC had a specific surface area of 144 m²/g. The micropore volume, mesopore volume, total pore volume and average pore diameter were 0.06 cm³/g, 0.29 cm³/g, 0.35 cm³/g and 9.71 nm, respectively. Due to highest surface area and high mesoporosity (83%)

that are capable of dye adsorption, therefore, the composite prepared at the molasses to TEOS ratio of 0.8 was selected for further characterization of its physicochemical properties with other techniques and was used as adsorbent for MB adsorption.

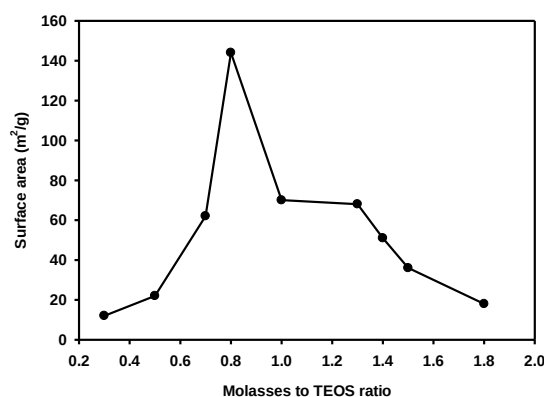


Figure 2. Effect of molasses to TEOS ratio on specific surface area of CSC

Table 1. Porous properties of CSC for different molasses to TEOS ratios

Ratio	S_{BET} (m ² /g)	V_{mic} (cm ³ /g)	V_{meso} (cm ³ /g)	V_T (cm ³ /g)	D_p (nm)
0.3	12	0.01 (20%)	0.04 (80%)	0.05	15.00
0.5	22	0.01 (12%)	0.07 (88%)	0.08	14.91
0.7	62	0.02 (11%)	0.16 (89%)	0.18	11.32
0.8	144	0.06 (17%)	0.29 (83%)	0.35	9.71
1.0	70	0.03 (15%)	0.17 (85%)	0.20	9.49
1.3	68	0.03 (19%)	0.13 (81%)	0.16	9.51
1.4	51	0.02 (14%)	0.12 (86%)	0.14	9.31
1.5	36	0.01 (11%)	0.08 (89%)	0.09	9.80
1.8	18	0.01 (25%)	0.03 (75%)	0.04	9.74

The nitrogen adsorption-desorption isotherm of the CSC obtained at molasses to TEOS ratio of 0.8 is shown in Figure 3. The composite presented a Type IV isotherm that is typical for mesoporous materials which was confirmed by the average pore diameter (pores with diameter 2-50 nm).

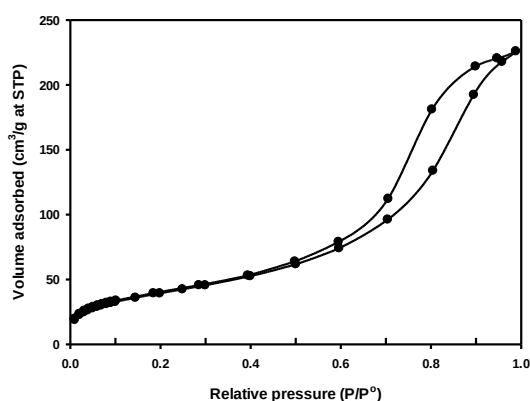


Figure 3. Nitrogen adsorption-desorption isotherm of the CSC obtained at the optimum molasses to TEOS ratio of 0.8

The FTIR technique was used to investigate the functional groups present in CSC (Figure 4). The broad absorption band at 3383 cm^{-1} was attributed to the carboxylic acid O-H stretching vibrations (Pang *et al.*, 2017). The carbonyl (C=O) stretching band at 1705 cm^{-1} was also observed (Taşdelen *et al.*, 2017). The absorbance band at 1624 cm^{-1} was attributed to the O-H stretching vibration of surface hydroxyl groups (Qin *et al.*, 2018), and the characteristic intensity of the band at 1055 cm^{-1} was assigned to the asymmetric stretching vibrations of Si-O-Si groups (Yu *et al.*, 2018). The peak that arose from Si-OH bonds on the composite surface was observed at 893 cm^{-1} (Ye *et al.*, 2010) and the peak at 783 cm^{-1} was due to symmetric vibrations of SiO_2 (Givianrad *et al.*, 2013). Moreover, the band at 594 cm^{-1} corresponding to O-Si-O groups (Eyssa *et al.*, 2019) was observed. These results indicated that Si interacted with the carbon structure.

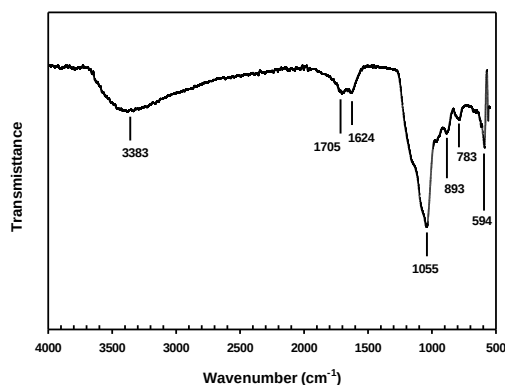


Figure 4. FTIR spectrum of CSC obtained at optimum molasses to TEOS ratio

Figure 5 presents the thermogravimetric profiles of CSC. The TGA curve is divided into three parts based on the three endothermic peaks (at 86, 189 and 430°C) in the differential thermogravimetric (DTG) curve. The first part from 25 to 120°C with a mass loss of 30% was ascribed to the loss of loosely bound water molecules. The second mass loss region from 120 to 220°C of 19% could be attributed to loss of water molecules that were more tightly bound in the carbonaceous matrix (Santos *et al.*, 2015). From 220 to 450°C , the mass loss was 20% and could be attributed to the partial decomposition of the carbon skeleton (Santos *et al.*, 2015). A residual mass of 29% at 700°C represented the inorganic fraction of the composite and undecomposed organic compounds (Santos *et al.*, 2015) and suggested that CSC has a moderate content of inorganic matrix.

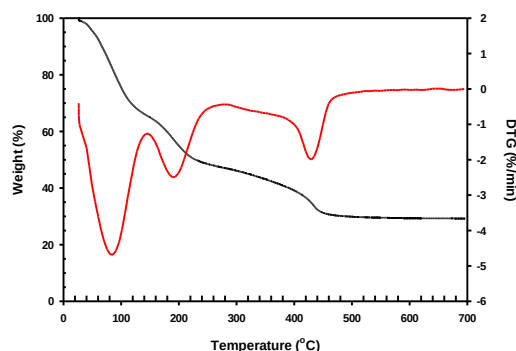


Figure 5. TGA and DTG analysis of CSC obtained at optimum molasses to TEOS ratio

The effect of adsorption time on MB removal was investigated as shown in Figure 6. The adsorption capacity increased rapidly in the first stage, then slowed down and finally reached equilibrium after 14 h. The surface of the composite may contain a number of active sites, and the high adsorption rate at the initial period was likely due to the vacant sites available for MB uptake as a result of high concentration gradients between adsorbate in solution and adsorbate on the adsorbent surface. As time proceeded, this gradient was reduced due to the accumulation of MB molecules onto the vacant sites leading to a decrease in the adsorption rate. The equilibrium time of 14 h was chosen for the adsorption isotherm study.

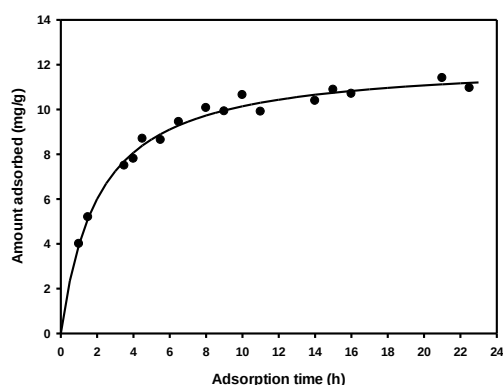


Figure 6. Effect of adsorption time on the amount adsorbed of MB dye

In order to investigate the adsorption mechanism, the adsorption kinetics were modeled with pseudo-first order and pseudo-second order equations. The non-linear form of these models is given in Equations (2) and (3), respectively:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (2)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (3)$$

where q_e is the amount of MB adsorbed at equilibrium (mg/g), q_t is the amount of MB adsorbed at time t (mg/g), k_1 is the pseudo-first order adsorption constant (min^{-1}) and k_2 is pseudo-second order constant ($\text{g/mg} \cdot \text{min}$).

The fitting of both kinetic equations is shown in Figure 7(a) and the model parameters are summarized in Table 2. The correlation coefficient (R^2) obtained from the pseudo-second order kinetic equation was greater than that of the pseudo-first order kinetic model and was close to 1. The adsorption of MB onto CSC was better described by the pseudo-second order than the pseudo-first order kinetic equation, even though the calculated adsorption capacity of the pseudo-first order was closer to the experimental adsorption capacity (q_e (exp)) than that of the pseudo-second order equation. The fitting that correlated with the pseudo-second order model indicated that the adsorption process of MB by using CSC was of chemical nature, involving electron donation or exchange between the adsorbate and the adsorbent (Carvalho *et al.*, 2018).

The adsorption of adsorbate molecules from the liquid phase onto the solid adsorbent surface involves three stages: (1) mass transfer of the

adsorbate molecules across the external boundary layer, (2) intra-particle diffusion within the pores of the adsorbent, and (3) adsorption at an active site on the adsorbent surface (Nyankson *et al.*, 2020). Therefore, the rate-limiting step is a crucial factor in the adsorption process. Both the pseudo-first order and pseudo-second order models cannot identify the rate-limiting step of dye adsorption because they include all three stages (Alharby *et al.*, 2021). For this reason, the intraparticle diffusion model was applied. The intra-layer diffusion depends on several factors such as the physical properties of the adsorbent, the initial adsorbent concentration, the rotation speed in batch mode and the temperature (Nyankson *et al.*, 2020). The intraparticle diffusion model is given by:

$$q_t = k_i t^{1/2} + C \quad (4)$$

where k_i is the rate constant of the intraparticle diffusion ($\text{mg/g} \cdot \text{min}^{1/2}$) and C is the intercept corresponding to the boundary layer thickness (mg/g). If intraparticle diffusion occurs, a linear plot is obtained. Moreover, intraparticle diffusion is a rate-limiting step if the plot passes through the origin.

Figure 7(b) shows the plot of the intraparticle diffusion model for the removal of MB by using CSC and the parameters are summarized in Table 2. The linear plots in this figure did not cross the origin, indicating that intraparticle diffusion played a significant but not rate-limiting role in the adsorption of MB onto CSC surface, which took place as a multistep process. The intraparticle diffusion model indicated the rate-determining steps of the adsorption in two stages.

The first stage with a steeper slope ($k_{i,1} = 0.465 \text{ mg/g} \cdot \text{min}^{1/2}$) represented a faster adsorption due to the electrostatic interaction between adsorbate in solution and solid adsorbent. This also confirmed that the adsorption process was chemisorption, as a result of the pseudo-second order kinetics. The second stage with slope $k_{i,2}$ ($0.092 \text{ mg/g} \cdot \text{min}^{1/2}$) represented a slow diffusion process indicating that the active sites and pores were being occupied by the MB molecules. Similar results were reported for MB adsorption onto Brazil nut shell (Brito *et al.*, 2010), *Vigna Trilobata* pod (Kandisa *et al.*, 2018), iminodiacetic acid functionalized magnetic peanut husk (Aryee *et al.*, 2020) and crosslinked O-CM-chitosan hydrogel (Alharby *et al.*, 2021).

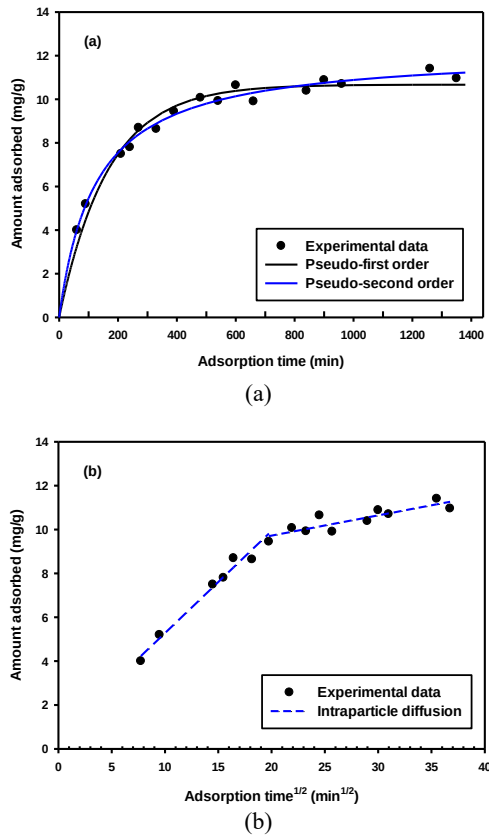


Figure 7. Kinetic fitting of (a) pseudo-first order and pseudo-second order and (b) intraparticle diffusion models

Table 2. Kinetic parameters for MB adsorption

Model	Parameter	Unit	Value
—	q_e (exp)	(mg/g)	11.40
Pseudo-first order kinetic	q_e	(mg/g)	10.67
	k_1	(min ⁻¹)	0.00604
	R^2		0.979
Pseudo-second order kinetic	q_e	(mg/g)	12.23
	k_2	(g/mg·min)	0.00066
	R^2		0.992
Intraparticle diffusion	Stage 1		
	$k_{i,1}$	(mg/g·min ^{1/2})	0.465
	C	(mg/g)	0.632
	R^2		0.975
	Stage 2		
	$k_{i,2}$	(mg/g·min ^{1/2})	0.092
	C	(mg/g)	7.883
	R^2		0.772

In general, an adsorption equilibrium isotherm test can be utilized to optimize the design of adsorption system for the removal of a target contaminant from solution. Several isotherm equations have been employed to describe the adsorption process. The Langmuir isotherm model assumes that adsorption occurs at specific sites and no further adsorption occurs after monolayer adsorption is complete. In contrast, the Freundlich isotherm model assumes infinite multilayer adsorption on a heterogeneous surface. A combination of the Langmuir and Freundlich isotherms is the Sips isotherm. Due to the problem of the continuing increase in the adsorbed amount of adsorbate with an increase in solution concentration in the Freundlich model, the Sips model has a finite limit when the concentration is high (Húmpola *et al.*, 2013). The non-linear forms of the Langmuir, Freundlich and Sips equations are presented in equations (5), (6) and (7), respectively:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

$$q_e = K_F C_e^{1/n} \quad (6)$$

$$q_e = \frac{q_{ms} K_S C_e^{1/n}}{1 + K_S C_e^{1/n}} \quad (7)$$

where C_e is the concentration of MB solution at equilibrium (mg/L), q_e is the equilibrium amount adsorbed (mg/g), q_m and q_{ms} are maximum amount adsorbed of Langmuir and Sips isotherm (mg/g), respectively, and K_L , K_F and n and K_S are Langmuir, Freundlich and Sips constants, respectively.

Experimental and fitted model adsorption isotherm data are shown in Figure 8 and the calculated adsorption equilibrium parameters are collected in Table 2. According to the R^2 values, the Sips model satisfactorily described the experimental data. The maximum adsorption capacity from Sips equation was 180.22 mg/g. The value of exponent $1/n$ for the Sips model was close to unity (1.183), indicating that adsorption was on a homogeneous adsorbent surface corresponding to the Langmuir equation (the greater the $1/n$ value is the more heterogeneous system). This was confirmed by the high R^2 value of the Langmuir model.

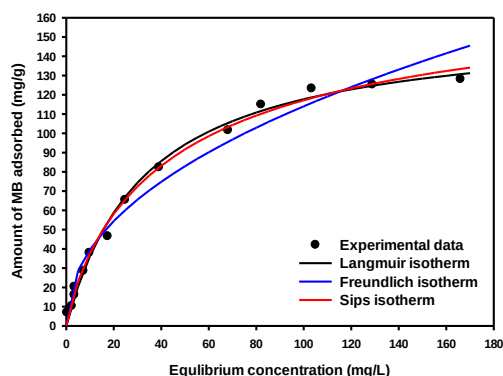


Figure 8. Non-linear Langmuir, Freundlich and Sips isotherms for the adsorption of MB onto CSC

Table 3. Model parameters and correlation coefficients of the various isotherm models

Adsorption isotherm	Parameter	Unit	Value
Langmuir	q_m	(mg/g)	156.92
	K_L	(L/mg)	0.030
	R^2		0.990
Freundlich	K_F	(mg/g) (L/mg) ^{1/n}	13.72
	$1/n$		2.175
	R^2		0.972
Sips	q_{ms}	(mg/g)	180.22
	K_S	(L/mg) ^{1/n}	0.038
	$1/n$		1.183
	R^2		0.993

The maximum MB adsorption capacity values (q_{max}) on several adsorbents reported in the literature are summarized in Table 4. The adsorption capacity of CSC obtained in this study revealed that this composite is a potential adsorbent for the removal of MB from wastewater. This may be due to the higher surface area of CSC than other adsorbents such as fig leaf-activated carbon (surface area 18.30 m²/g). Some adsorbents exhibited a lower adsorption capacity than CSC, even though the surface area was higher. This was attributed to the smaller average pore diameter of those materials that was within micropore range, such as activated carbon/cellulose composite film (surface area 1165 m²/g, pore width 2.52 nm). The mesoporous structure of the CSC adsorbent favors dye adsorption. It should be noted that the studies that presented the preparation of adsorbents like montmorillonite/CoFe₂O₄ composite, multi-walled carbon nanotube, crosslinked chitosan/bentonite composite and chitosan-immobilized magnesium oxide nanoparticle did not characterize porous properties. In addition, CSC also had higher adsorption capacity than Fe₃O₄/activated

montmorillonite which had higher surface area (147.92 m²/g) and larger pore size (46.39 nm). This indicated that the surface chemistry of the adsorbent also plays a key role in dye adsorption performance. The mechanism of surface adsorption of cationic dye methylene blue involves electrostatic attraction with negative functional groups (hydroxyl, carbonyl and carboxylic acid groups) on the CSC surface.

Table 4. A Comparison of MB adsorption capacity with the previously report

Type of adsorbent	q_{max} (mg/g)	Model	Reference
Fig leaf-activated carbon	41.7	Langmuir	Al-Asadi <i>et al.</i> (2023)
Montmorillonite/CoFe ₂ O ₄ composite	97.75	Langmuir	Ai <i>et al.</i> (2011)
Activated carbon/cellulose composite film	103.66	Langmuir	Somsesta <i>et al.</i> (2020)
Fe ₃ O ₄ /activated montmorillonite	106.38	Langmuir	Chang <i>et al.</i> (2016)
Multi-walled carbon nanotube	132.61	Sips	Shahryari <i>et al.</i> (2010)
Crosslinked chitosan/bentonite composite	142.86	Langmuir	Bulut and Karaer <i>et al.</i> (2015)
Chitosan-immobilized magnesium oxide nanoparticle	163.87	Langmuir	Myneni <i>et al.</i> (2020)
Carbon-silica composite	180.22	Sips	This study

Conclusions

This study presents the sol-gel process for the synthesis of carbon-silica composite based on molasses as carbon source and TEOS as silica precursor. The desired composite material with the highest specific area was obtained at a molasses to TEOS ratio of 0.8. The surface area of this composite was 144 m²/g with a high mesopore fraction of 83%. The removal of methylene blue on this mesoporous composite was investigated under different times and concentrations. The adsorption isotherm was best described by the Sips isotherm model, achieving a maximum adsorption capacity of 180.22 mg/g. The adsorption kinetics followed the pseudo-second order model, suggesting that the adsorption process was controlled by a multistep mechanism involving chemisorption. Considering that the carbon-silica composite derived from molasses favors the removal of contaminants such as methylene blue, the challenge for future work is to modify the resulting CSC (e.g., heat treatment or chemical impregnation) to achieve a higher

porosity. In addition, the adsorption test with real wastewater from industrial and fixed-bed operation should also be investigated.

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