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Removal of methylene blue from aqueous solution by a carbon-microsilica composite adsorbent

Deyi Zhang*,,†, Ying Ma**, Huixia Feng*, Heming Luo*, Jiao Chen*, and Yuan Hao****

*College of Petrochemical Technology, Lanzhou University of Technology, Lanzhou 730050, China
**State Key Laboratory of Gansu Advanced Non-ferrous Metal Materials,
Lanzhou University of Technology, Lanzhou 730050, China
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Abstract–Microsilica, one kind of industrial solid waste material, was utilized firstly to prepare a carbon-microsilica composite adsorbent (CMS). The prepared adsorbent was characterized with XPS, SEM and Gas sorption experiments. The results indicated the SO_3H groups, which are very effective in capturing cationic organic dye, were introduced onto the surface of CMS; the Brunauer-Emmett-Teller (BET) surface area (S_{BET}) and total pore volume (V_{total}) of CMS reach 51 m^2/g and 0.045 cm^3/g, respectively. Meanwhile, the possibility of the utilization of the adsorbent for removal of methylene blue (MB) from aqueous solution was investigated. The effect of pH, contact time and initial MB concentration for MB removal were studied. Equilibrium data were modeled using the Langmuir, Freundlich and Dubinin-Radushkevich equations to describe the equilibrium isotherms. It was found that data fit to the Langmuir equation better than the Freundlich equation. Maximum monolayer adsorption capacity was calculated at different temperatures (298, 308, and 318 K) reach 251.81, 283.76 and 309.70 mg/g, respectively. It was observed that adsorption kinetics obeys the pseudo- first-order equation.

Key words: Carbon, Microsilica, Methylene Blue, Adsorption

INTRODUCTION

Dyes and pigments are widely used to color many industrial products, especially in the textile, paper, plastics, leather, food and cosmetic industries [1]. The amount of dyes and pigments consumed commercially every year is estimated to be more than 100,000 tons and at least 10% of them enter the environment as wastes [2]. These industrial effluents may present an eco-toxic hazard and introduce the potential danger of bioaccumulation, which may be extremely injurious to humans through the food chain [3]. Due to complicated and stable chemical structures, dyes and pigments, especially some synthetic dyes, are inert and biodegradably difficult; removing them from colored wastewater by conventional physical and chemical processes is often inefficient and/or cost disadvantageous [4]. The adsorption method was found to be more effective and attractive due to the higher efficiency for removing dyes in wastewater [5]. The adsorption of acid dyes has been studied using different adsorbents, such as active carbon [6], polyelectrolyte impregnated mesoporous silica [7], tripoli [2], musa spp. waste [8], gypsum [9], sugarcane bagasse [10], bentonite [11], chitosan [12], rice husk [13], and sawdust [14].

Microsilica is an industrial waste of the production silicon metal or ferrosilicon alloys with particle size in the range of 30-300 nm. The dominant constituent of microsilica is amorphous silicon dioxide. At present, microsilica mainly is recycled as an additive in Portland cement concretes and fireproof material to improve material properties due to extremely high surface area and amorphous nature [15]. However, microsilica recycling is still not sufficient and novel applications have to be explored. In the past years, utilization of microsilica as an adsorbent for removal of pollutants such as dyes, heavy metals, and phenolic compounds in wastewater has not been reported in the literature.

Microsilica is not an operative adsorbent, and in our previous work [16] we found that carbonization and sulfonation of microsilica produces an adsorbent with excellent adsorption capacity for dyes and heavy metal ions.

EXPERIMENTAL

1. Materials

Microsilica (SiO_2>68%) was provided by Jiuquan Iron & Steel Group Co., Ltd. Sucrose of chemical purity was purchased from Shanghai Experiment Reagent Co., Ltd. Sulfuric acid (AR) was used as carburetant. Other chemicals used are analytical reagents (AR). Methylene blue (MB), a basic dye, is a cationic dye that was used for evaluating the potential of the adsorbent to remove dyes from wastewater (Fig. 1).

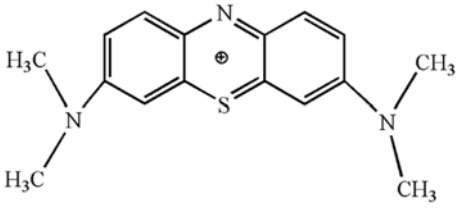

Fig. 1. The molecular structure of MB.

†To whom correspondence should be addressed.
E-mail: lzdeyizhang@yahoo.cn

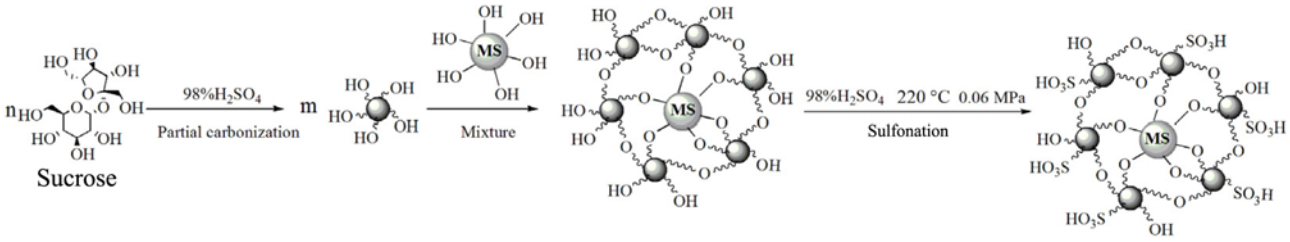

Fig. 2. Scheme of the synthesis route of CMS.

2. Preparation of Adsorbent

The carbon-microsilica composite adsorbent (CMS) was prepared via a partial carbonization, mixture, and sulfonation process (as shown in Fig. 2). Briefly, 2 g of sucrose was dissolved in 1 ml H_2O, after which 4 ml 98% H_2SO_4 was added dropwise at ambient temperature to obtain carbon precursor, and then 5 g microsilica was immediately added in this precursor, and stirred to a mash, which was then heated to 150 °C to form a bread shape in thermostatic drying oven. Thereafter, the bread-shaped substance was sulfonated and desulfurized at 220 °C in 0.06 MPa for 5 hours in vacuum drying oven, and then was cooled to ambient temperature in vacuum. A black carbon-microsilica composite adsorbent powder then was obtained.

3. Characteristics of the Adsorbent

X photoelectron spectra (XPS, Escalab210, Vg Scientific Ltd., UK) analyses were utilized for surface chemistry determination. Scan electron microscope (SEM, JSM-6701F, Japan Electron Optics Laboratory Co., Ltd., Japan) was used for structure analysis. Nitrogen adsorption/desorption isotherms were determined by Surface area and porosimetry analyzer (Tristar 3000, Micromeritics Ltd., USA) in 77 K to characterize the textural properties. BET surface area was determined by means of standard BET equation applied in the pressure ranging from 0.05 to 0.3. Total pore volume was calculated at relative pressure of approximately 0.98, and at this relative pressure all pores were completely filled with nitrogen gas [17].

4. Batch Adsorption Experiments

Adsorption experiments were performed in a shaking thermostatic gas bath at 298, 308 and 318 K for a period of 6 h at 160 rpm using 100 ml Erlenmeyer flasks. A stock solution of MB was prepared (1,000 mg/L) by dissolving the required amount of MB in distilled water. The stock solution was diluted with distilled water to give the appropriate concentration of the working solutions. Batch adsorption experiments were performed by contacting 0.1 g of CMS samples with 50 ml of an aqueous solution of MB of the desired concentration, temperature and pH. The residual MB after adsorption was measured with a UV/visible spectrometer (U-2001, Hitachi, Japan) at a λ_{max} corresponding to the maximum absorption for MB (λ_{max}=661 nm); the MB amount retained in the adsorbent phase was calculated according to

$$q_e = \frac{(c_0 - c_e)V}{W} \quad (1)$$

where q_e (mg/g) is the amount of MB adsorbed per unit mass of CMS, c_0 and c_e are the initial and equilibrium concentrations (mg/L) of MB solution, respectively; V is the volume (*l*); and W is the weight (g) of CMS.

The percent removal of MB from aqueous solution was calculated by the following equation:

$$\%\text{Removal} = \frac{c_0 - c_e}{c_0} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

1. Characteristics of CMS

XPS was employed to determine the surface elemental composition and functional groups of CMS. XPS survey spectra, as is shown in Fig. 3(a), indicates that carbon, oxygen, silica and sulfur elements are main elements on CMS surface, thereinto, carbon and oxygen elements are dominant superficial elements. The atomic ratio of O/C reaches 2.3 : 1, which implies that abundant of oxygen functional groups existed on CMS surface. The XPS survey spectra of CMS exhibits a single S2p peak attributable to SO_3H groups at 168 eV (see Fig. 3(b)) [18]. Toda et al. [19] reported that incomplete carbonization of sugar can result in a rigid carbon material that is composed of small polycyclic aromatic carbon sheets in a three-dimensional sp^3-bonded structure and sulfonation of this material would generate -SO_3H groups on the surface of CMS. In our experiment, sucrose is partially carbonized by 98% H_2SO_4, and then was sulfonated by concentrated sulfuric acid, and -SO_3H groups were successfully introduced onto the surface of CMS. These functional groups are very effective in capturing cationic organic dyes from aqueous

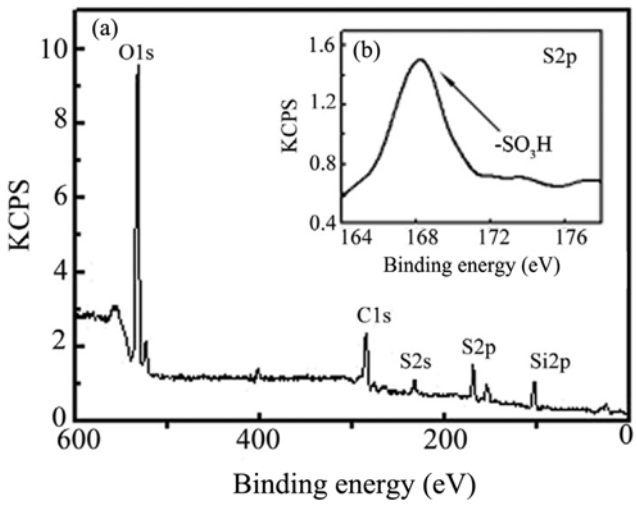

Fig. 3. The XPS survey spectra of CMS ((a) XPS survey spectra; (b) The high-resolution XPS S2p spectra).

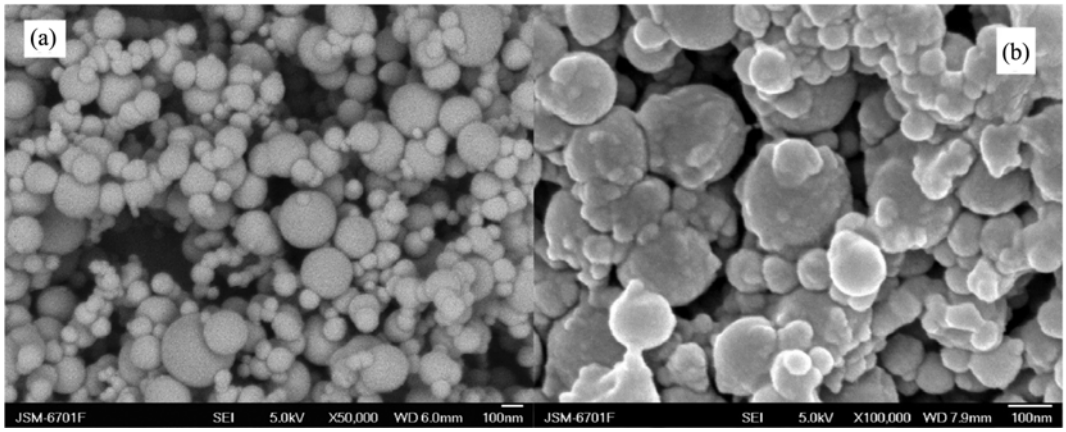

Fig. 4. The SEM photos of microsilica and CMS ((a) The SEM photo of microsilica; (b) The SEM photo of CMS).

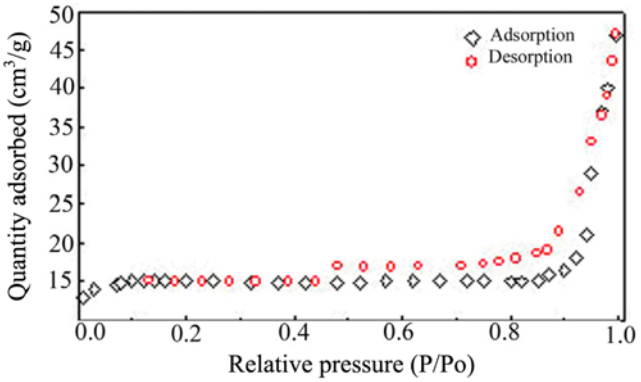

Fig. 5. The nitrogen adsorption/desorption isotherms of CMS.

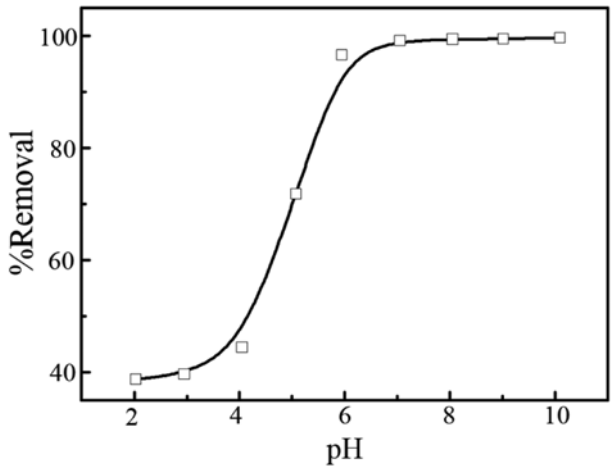

Fig. 6. Effect of pH on the removal of MB.

solution.

Fig. 4 shows the SEM photos of microsilica and CMS. As shown in Fig. 4(a), microsilica exhibits regular spherical structure with particle size in the range of 30-300 nm. The CMS, Fig. 4(b), exhibits evident core-shell structure of carbon covered microsilica. The structure of microsilica changed from homogeneously dispersed sphere with regular interface to steric continuous network with abundant slit-like mesopores, which average width was about 30 nm when microsilica was coated by carbon particles.

Fig. 5 shows the nitrogen adsorption/desorption isotherms of CMS. As shown, the nitrogen adsorption/desorption isotherms of CMS exhibit type IV isotherm with H3 type hysteresis loop at relatively high pressure P/P_0, which is always given by many mesoporous industrial adsorbents, indicating the mesoporous characteristics of CMS [20]. The BET surface area and total pore volume are 51 m^2/g and 0.045 m^3/g, respectively.

2. Effect of pH on the Removal of MB

The effect of pH on the removal of MB for 200 mg/L MB solution by CMS was investigated in the pH range of 2-10 (which was adjusted with HCl or NaOH at the beginning of the experiment and not controlled afterwards) at 298 K. As shown in Fig. 6, the removal efficiency was found to be highly dependent on hydrogen ion concentration of solution. When initial pH value of the MB solution was increased from 2 to 6, the removal efficiency increased from 39.2 to 97.5%. With increase in pH value up to 10, the removal efficiency was more than 99%.

The pH value of the system is very effective on the adsorption capacity of MB onto CMS, presumably due to its influence on the surface properties of CMS and ionization/dissociation of the adsorbate molecules. Lower removal efficiency of MB, one cationic dye, at acidic pH is probably due to the presence of excess H^+ ions competing with the dye cations for the adsorption sites. At the alkaline pH, the number of negatively charged sites on CMS surface increase, which favors the adsorption of the cationic dye due to electrostatic attraction between them [21].

3. Effects of Contact Time

The relation between removal efficiency of MB and contact time was investigated to identify the rate of dyes removal at 298 K. Fig. 7 shows the removal efficiency of MB for 200 mg/L MB solution at pH 6.0. As shown in Fig. 7, the removal efficiency increases with increasing contact time. More than 95% removal of dyes concentration occurred in the first 240 min, and thereafter the rate of adsorption was found to be slow. Equilibrium reached after nearly 5 h. During initial stage of adsorption, a large number of vacant surface sites are available for MB molecules. Then, a decrease in the number of adsorption sites and repulsion between free and adsorbed MB molecules slows down the rate of adsorption. This process slows down the rate of MB adsorption during the later period of adsorp-

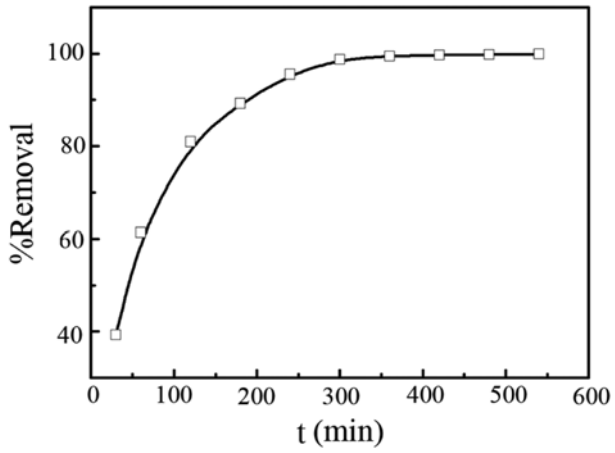

Fig. 7. Effect of contact time on the removal of MB.

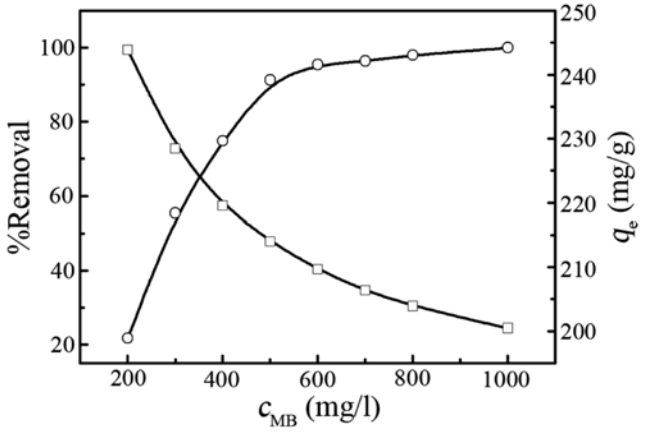

Fig. 8. Effect of initial MB concentration on the removal of MB.

tion [22].

4. Effect of Initial MB Concentration

The effect of initial MB concentration on the removal of MB from aqueous solution by CMS is shown in Fig. 8; these data have been obtained over an MB initial concentration range of 200-1,000 mg/L at 298 K. The procedure outlined in the experimental section was followed with 0.1 g of CMS and 50 ml of MB solution of the desired concentration at pH 6.0.

The removal efficiency of MB decreased from 99.0 to 24.5% as the initial MB concentration increased from 200-1,000 mg/L; meanwhile, the adsorption amount of MB increased from 198.1 to 244.9 mg/g. The result indicated that the adsorbent has an excellent potential for removal of dyes from colored wastewater. At lower MB concentrations, sufficient adsorption sites are available for adsorbing MB molecules. However, adsorbent is saturated at higher MB concentration.

5. Adsorption Kinetics

To investigate the controlling mechanism of the adsorption process, the experimental data of MB adsorption onto CMS, from 30 to 550 min were modeled by the pseudo-first-order [23] and pseudo-second-order kinetics equations [24].

5-1. Pseudo-first-order Model

A pseudo-first-order model can be expressed in a non-linear form as

$$q_t = q_e - \frac{q_e}{e^{\frac{k_1}{2.303}t}} \tag{3}$$

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

5-2. Pseudo-second-order Model

The adsorption kinetics may also be described by a pseudo-second-order kinetic model. The non-linear form of the model is

$$q_t = \frac{q_e}{\frac{1}{k_2 q_e}\frac{1}{t} + 1} \tag{4}$$

where k_2 is the pseudo-second-order rate constant of adsorption.

The adsorption kinetic studies were conducted using initial MB concentrations of 600 mg/L. Kinetic parameters obtained from two models at different temperatures are listed in Table 1. The fitted data to the pseudo-first-order model gave higher values of correlation coefficients than those for the pseudo-second-order kinetic model at all temperatures. The results showed that the pseudo-first-order model fit better the experimental data than the pseudo-second-order model.

Table 1. The pseudo-first-order and second-order kinetic parameters for adsorption of MB at different temperatures

T/K	Pseudo-first-order kinetics			Pseudo-second-order kinetics		
	q_e (mg/g)	k_1 (L/min)	R^2	q_e (mg/g)	k_2 (g/mg·min)	R^2
298	251.79	2.4×10^{-3}	0.992	266.56	9.77×10^{-6}	0.979
308	283.85	2.7×10^{-3}	0.976	397.84	1.504×10^{-5}	0.956
318	303.63	3.5×10^{-3}	0.983	311.47	2.95×10^{-5}	0.975

6. Adsorption Isotherms and Thermodynamic Parameters

Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms. The adsorption isotherm is important from both a theoretical and a practical point of view. Isotherm data should accurately fit to different isotherm models to find a suitable model that can be used for the design of adsorption process. The experimental data obtained in the present work were tested by the Langmuir [25], Freundlich [26] and Dubinin-Radushkevich models [27]. The linear form of the Langmuir is represented by the following equation:

$$\frac{1}{q_e} = \left(\frac{1}{K q_m}\right)\frac{1}{c_e} + \frac{q}{q_m} \tag{5}$$

where c_e (mg/L) is the equilibrium concentration of the MB, q_m is the maximum adsorption at monolayer coverage and K (L/mg) is the constant related to the extent of adsorption, respectively.

The Freundlich isotherm is written as follows:

$$\log q_e = \log K_F + \frac{1}{n_F}\log C_e \tag{6}$$

where K_F and n_F are Freundlich constants with n_F giving an indication of how favorable the adsorption process and K_F (mg/g) related

Table 2. Parameters of the Langmuir, Freundlich and Dubinin-Radushkevich isotherms for adsorption of MB at different temperatures

T (K)	Langmuir			Freundlich			Dubinin-Radushkevich		
	q_m (mg/g)	K (L/mg)	R^2 (n=8)	K_F (mg/g)	$1/n_F$	R^2 (n=8)	q_D (mg/g)	E (kJ/mol)	R^2 (n=8)
298	251.81	0.0781	0.990	174.48	0.0547	0.939	245.3	1.96	0.92
308	283.76	0.1049	0.985	198.86	0.0451	0.936	277.13	2.56	0.90
318	309.70	0.1308	0.991	253.64	0.0296	0.948	302.05	4.88	0.86

to the bonding energy [28].

The Dubinin-Radushkevich is given by:

$$\ln q_e = \ln q_D - B_D\left(RT\ln\left(1+\frac{1}{c_e}\right)\right)^2 \quad (7)$$

where B_D (mol^2/J^2) is related to the free energy of adsorption per mole of the adsorbate and q_D is the theoretical monolayer saturation capacity. The apparent energy of adsorption from Dubinin- Radushkevich isotherm, E, (kJ/mol) that gives information about chemical and physical adsorption can be computed using the relationship (Eq. (8)).

$$E = \frac{1}{\sqrt{2B_D}} \quad (8)$$

Parameters obtained from the Langmuir, Freundlich and Dubinin-Radushkevich are shown in Table 2. As seen from the results, R^2 values of the Langmuir isotherm at all temperatures were greater than those of the Freundlich isotherm. This shows that MB molecules adsorb onto the prepared adsorbent as monolayer. The maximum monolayer adsorption capacity was calculated at 298, 308, and 318 K were 251.81, 283.76 and 309.70 mg/g, respectively. It is proposed that the $-SO_3H$ groups of the prepared adsorbent act as its adsorption sites. The apparent energy of adsorption computed by Eq. (8) was 1.96, 2.56 and 4.88 kJ/mol at 298, 308, and 318 K, respectively, which indicates that the nature of adsorption of MB onto CMS is physisorption.

Thermodynamic parameters such as free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) of adsorption can be evaluated from the following Equations:

Table 3. Thermodynamic parameters for adsorption of MB onto CMS

T (K)	Thermodynamic parameters		
	ΔG/(J/mol)	ΔH/(J/mol)	ΔS/(J/mol·K)
298	91.00		
308	84.18	294.24	0.682
318	77.36		

$$\ln K_a = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (9)$$

$$\Delta G = \Delta H - T\Delta S \quad (10)$$

where R (8.314 J/mol·K) is the universal gas constant, T (K) is the absolute solution temperature and K_a (L/mg) is the Langmuir isotherm constant.

The values of ΔH and ΔS can be calculated, respectively, from the slope and intercept of the van't Hoff plot of lnK versus 1/T. ΔG can then be calculated using Eq. (10). The values of these parameters are recorded in Table 3. The value of ΔH (294.24 J/mol) indicated that the adsorption is physical in nature involving weak forces of attraction. The positive values of ΔS obtained showed increasing randomness at the solid0solution interface [22].

In aqueous solutions, $-SO_3H$ groups would dissociate to $-SO_3^-$, meanwhile, the dissociation degree would increase with increase in pH. MB molecule adsorbs on CMS surface by electrostatic attraction between the positive charge center of MB and the $-SO_3^-$ formed by dissociation of $-SO_3H$ groups on CMS surface. Adsorption mechanism of CMS for MB is shown in Fig. 9.

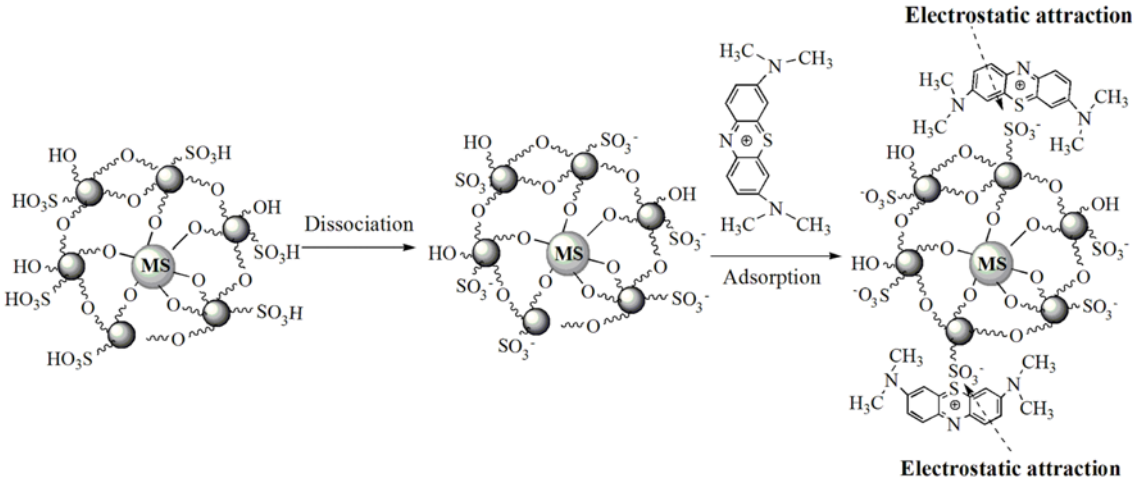

Fig. 9. The possible adsorption mechanism of MB onto CMS.

Table 4. Comparison of adsorption capacity of different adsorbents for MB reported in the literature

Adsorbent	Max adsorption capacity (mg/g)	Reference
Tripoli	16.6	[2]
Activated carbon	294.14	[6]
Bentonite	75.2	[11]
Rice husk	40.58	[13]
Sawdust	142.36	[14]
Microsilica	37.82	This paper
Carbon-microsilica	251.81	This paper

Finally, The adsorption capacities of the prepared adsorbent for removal of MB are greater than those of microsilica and a number of adsorbents [2,6,11,13,14] (Table 4).

CONCLUSIONS

The present study shows that carbon-microsilica composite adsorbent prepared from microsilica as raw material is an efficient adsorbent for removal of MB from aqueous solutions. The characterization results indicated the BET surface area and total pore volume of CMS were 51 m^2/g and 0.045 m^3/g, respectively. SO_3H groups of the surface of adsorbent act as adsorption sites. The adsorption of MB is a function of pH, contact time and initial MB concentration. The adsorption isotherm studies showed that the Langmuir adsorption isotherm fits well with the experimental data. Maximum monolayer adsorption capacity (q_m) calculated at different temperatures (298, 308, and 318 K) was 251.81, 283.76 and 309.70 mg/g, respectively. Kinetic data of the adsorption process obey the pseudo-first-order kinetic model.

ACKNOWLEDGEMENTS

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