Adsorption Efficiency, Adsorption Isotherms and Kinetic Study for Methylene Blue Removal in Aqueous Solution of Thiol-Functionalized Mesoporous Silica Nanospheres

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Abstract

Thiol-functionalized mesoporous silica nanospheres material was synthesized by co-condensation method under biphasic system. Structural characterization comfirmed the mesoporous structure and the content of adsorbents by transmission electron microscopy, N_2 adsorption-desorption and Fourier transform inferred spectroscopy. The adsorbent were nanosphere with particle diameter lower than 50 nm. A batch adsorption study was carried out with variable pH, adsorption time, adsorbent dose, shaking rate, temperature and adsorbate concentration. Methylene blue could be removed by 0.05 g of MSN and MSN-SH at pH 10 and 30 min of adsorption time. The adsorption process followed pseudo-second-order kinetics. The experimental adsorption isotherm was found to be best fitted with the Langmuir model, which implied that the adsorption of MB as a monolayer.

Keywords: Adsorption; Thiol-Functionalized Mesoporous Silica; Methylene Blue; Adsorption Isotherm; Kinetic Adsorption

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Introduction

Organic and inorganic substances in wastewater are a main source of environmental pollution. Organic dyes are major pollutants of wastewater [1]. Many dyes and pigments have toxic as well as carcinogenic, mutagenic and teratogenic effects on aquatic life and also on humans. Dyes and pigments are widely used in textile, leather, paper, plastic and other industries [2]. One of the highly consumed materials in the dye industry is methylene blue which is used for cotton and silk painting [3]. Methylene blue has been studied as dye pollution not only because of its toxicity but also because of us color its color. Methylene blue has very wide applications which makes it one of the most common pollutants or constituent of color effluents [4]. Different methods have been developed to remove colored pollutants from wastewater such as coagulation, adsorption, chemical oxidation, biological treatment and flotation. Adsorption has been found to be superior to other techniques for water treatment in terms of initial cost, simplicity of design, ease of operation and insensitivity of toxic substances. Adsorption technology is rapidly gaining prominence as a technique for removing organic and inorganic micropollutants from aqueous effluent [5]. For analytical purposes, functionalized silica particles with organic functional groups are commonly used since the material silica provides many advantages such as good adsorption, easy to prepare with chemical compound and particular impregnate medium to create several modified silica surfaces, high mechanic and thermal stability [6]. Thiol-functionalized mesoporous silica appears to be particularly promising due to large adsorption capacities and high uptake rates for dyes. In this research, we reported an easy and simple method for fabrication of silica in nanometer range via surfactant template assisted and functionalized with thiol groups. In present study, the synthesis of thiol-functionalized mesoporous silica nanospheres (MSN-SH) is demonstrated by co-condensation of precursor solution in biphasic system. The MSN-SH was applied as a adsorbent for methylene blue removal from aqueous solution under various conditions. The adsorption isotherm and kinetic studies were conducted to evaluate the adsorption behaviors of MSN-SH

Materials and method

1. Materials

All chemicals were analytical grade. Tetraethyl orthosilicate (TEOS), 3-mercaptopropyl trimethoxysilane (MPTES) and l-arginine were supplied by Sigma Aldrich. Cetyltrimethylammonium bromide (CTAB) was purchased from Unilab. Cyclohexane (CHX) and ethanol were provided by Qrec. Methylene blue (MB) and glycerol were purchased from Carlo Erba.

2. Preparation of MSN and MSN-SH

0.25 g of CTAB and 0.18 g of l-arginine were dissolved in 110 mL of deionized water. Subsequently CHX phase was formed afloat on the aqueous phase by adding drop-wise of CHX. The bi-phase layer was then heated to 60 °C for 30 min. A mixture 9.2 mL of TEOS and 4.4 mL MPTES was added drop-wise into CHX phase to start the reaction which was allowed to proceed for 20 h. The reaction was terminated by quenching the reaction vial in cooled water. CHX phase was decanted using a syringe prior to centrifugation of the aqueous phase at 6,000 rpm to collect MSH-SH particles. The MSN-SH particles were washed with water then dried in an oven. Finally, the extracted MSN-SH particles were dried overnight at 60 °C. Mesoporous silica nanosphere (MSN) without functionalization with thiol was also synthesized using the same method described above except MPTES.

3. Characterization

The morphology and particle sizes of the synthesized particles were examined with transmission electron microscopy (TEM) technique from FEI Tecnai G2 operated at an accelerating voltage of 200 kV. Pore characteristic of the synthesized MSN and MSN-SH was examined by Nitrogen adsorption-desorption method performed on Autosorb-1, Quantachrome Instrument. Pore volume and specific surface area were determined according to the standard Brunauer Emmett Teller (BET) method. Functionalization of MSN and MSN-SH was confirmed by Fourier transform inferred spectroscopy (FT-IR) using Bruker FT-IR Spectrometer, Tensor II.

4. Adsorption studies

Batch adsorption experiments were performed in a set of Erlenmeyer flask (125 mL) each one containing 25 mL of different initial concentrations of MB (1 - 40 mgL^{-1}) together with adsorbent (0.01 - 0.2 g). A magnetic stirrer was used at desired temperature (30, 45 and 60 °C) and pH (2 - 11). The different contact times (5 - 120 min) and shaking rate (0 - 200 rpm) were studied. The mixture was centrifuged at 6,000 rpm for 10 min and finally separated into liquid and solid. The solution was measured by the UV-Vis spectrophotometer (T92 + PG instrument) with wavelength 665 nm to determine the concentration of MB. The adsorbed amount of MB at equilibrium was calculated by the following equation (1) [7]:

$$q_e = \frac{C_o - C_e}{W} \times V \tag{1}$$

where q_e is the adsorbed amount of MB at equilibrium (mgg^{-1}), C_o and C_e are the initial and equilibrium MB concentrations (mgL^{-1}) respectively, V is the volume of the used solution containing the MB (L) and W is the weight of the used adsorbent (g).

5. Adsorption isotherm

An adsorption isotherm describes the relationship between the amount of adsorbate taken up by the adsorbent and the adsorbate concentration remaining in solution. Langmuir isotherm determines the adsorption of MB on the surface of the adsorbent on the monolayer and equivalent sites on the surface. The Langmuir adsorption is given below equation (2) [8]:

$$\frac{C_e}{q_e} = \frac{1}{(K_L q_m)} + \frac{C_e}{q_m} \tag{2}$$

where q_m represents the maximum adsorption capacity ($\mathrm{mgg^{-1}}$) and K_L is the Langmuir constant ($\mathrm{Lmg^{-1}}$)

Freundlich isotherm is based on the multilayer adsorption with heterogeneous surface and can be define as below equation (3) [9]:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{3}$$

where n represents the Freundlich exponent which is related to the adsorption intensity and K_F is the Freundlich constant ($(\mathrm{mgg^{-1}})(\mathrm{Lmg^{-1}})^{1/n}$)

6. Adsorption kinetics

Two simplified kinetic models were adopted to examine the mechanism of the adsorption process. First, the kinetics of adsorption were analyzed by the pseudo first order equation given by [10] as equation (4) :

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{4}$$

On the other hand, the pseudo second order equation based on equilibrium adsorption [10] is expressed as equation (5) :

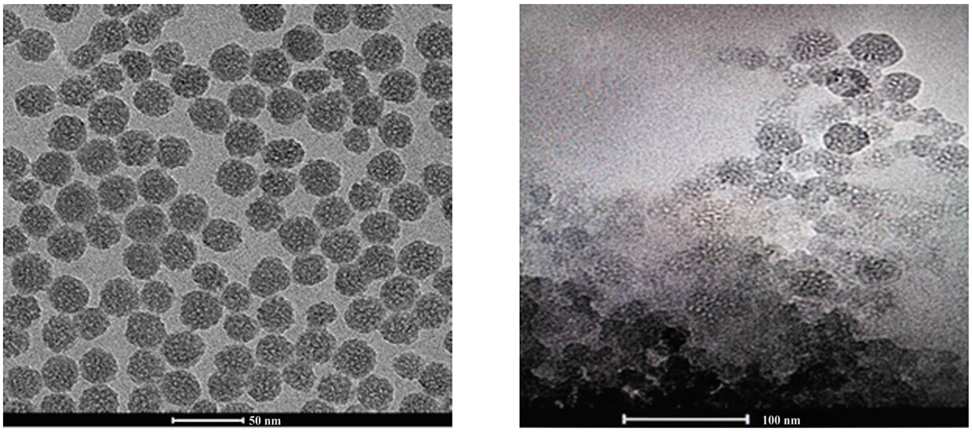
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{5}$$

where q_e is the amount of adsorbate adsorbed at equilibrium ($\mathrm{mgg^{-1}}$), q_t is the amount of adsorbate adsorbed at time ($\mathrm{mgg^{-1}}$), t is the time (min), k_1 is the rate constant of pseudo first order equation ($\mathrm{min^{-1}}$) and k_2 is the rate constant of pseudo second order equation ($\mathrm{g(mgmin)^{-1}}$).

Results and Discussion

1. Characterization of MSN and MSN-SH

The morphologies and structural features of the supported material MSN and MSN-SH can be observed directly through TEM in Figure 1. As can be noticed, both TEM image revealed the porous structure with the pore size in meso range. MSN-SH possessed spherical particles with an average 42.67 nm however some particle showed irregular shapes due to particle agglutinate during the synthesis.



(a) MSN (b) MSN-SH

Figure 1 TEM image of MSN and MSN-SH

In order to obtain the structure information about the MSN-SH on a nanoscopic scale, N_2 adsorption-desorption was used to characterize the particles. The MSN-SH had a specific surface area of 404.75 m^2g^{-1}, pore volume of 0.99 cm^3g^{-1} and mean pore diameter of 1.69 nm. Calculated results obtained from the adsorption-desorption isotherms are summarized in Table 1.

Table 1 Textural properties of MSN and MSN-SH particles.

Adsorbent	Average particle diameter from TEM (nm)	Specific surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	Mean pore diameter (nm)
MSN	33.93	509.80	1.40	2.10
MSN-SH	42.67	404.75	0.99	1.69

Figure 2 Shows the FT-IR spectra of the synthesized MSN and MSN-SH samples. Characteristic peaks of silica were observed for MSN at 1,063.35 cm^{-1} and 801.43 cm^{-1} belonging to asymmetric vibrations and symmetric stretching of Si-O-Si. Surface modification was verified by FT-IR spectroscopy as characteristic S-H functional group frequencies were readily detected. The peak at around 2,500 cm^{-1} corresponded to the thiol group. This confirmed the presence of thiol functional group in MSN-SH particles.

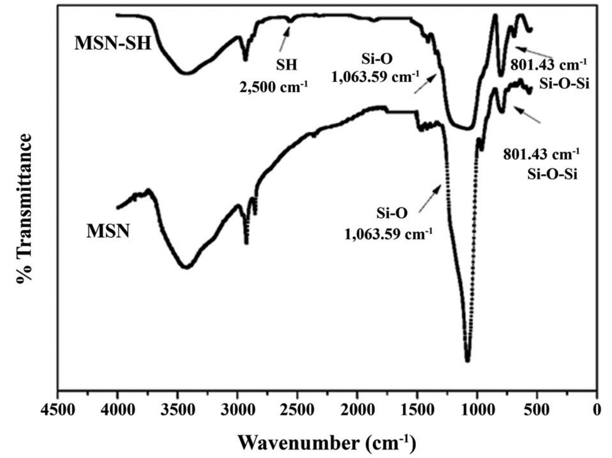


Figure 2 FT-IR spectra of MSN and MSN-SH

2. Effect of variables on MSN and MSN-SH adsorption performance

2.1 Effect of solution pH on MB uptake

The effect of initial pH of the MB solution on the adsorbed amount at equilibrium was studied by varying the initial pH in the range of 2 - 11 under constant parameter (3 mgL^{-1} initial MB concentration, 0.05 g adsorbent dose and 30 min adsorption time). The results are shown in Figure 3. The low adsorption efficient of MB on MSN and MSN-SH observed in acidic solution was due, probably, to the positive charge of the surface, causing ions (H^+) to compete effectively with dye cation causing a decrease in the adsorbed amount. The increasing pH, the positive charge on the interface of the solution decreased and the adsorbing surface appeared to be negatively charged [10] - [11]. Thus, more adsorption site was exposed at higher pH value.

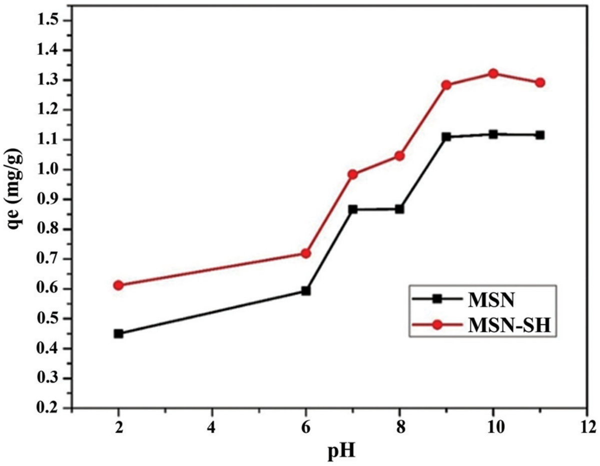


Figure 3 Effect of pH on adsorbed amount of MB at equilibrium for MSN and MSN-SH

2.2 Effect of adsorption time

The equilibrium time is an important factor in an economical adsorption system. Effect of contact time on adsorption of methylene blue by MSN and MSN-SH was investigated by varing contact time from 5 to 120 min. Figure 4 shows the effects of contact time on adsorption efficiency of methylene blue. The adsorption rate was observed increase the adsorption efficiency of MB. The rates of MB removal for both adsorbents were instant initially and became slower with a longer contact time until 9 constants was reached within 30 min. At the early stage of adsorption, the driving force of diffusion is large due to high concentration gradient of MB between the bulk phase and the absorption site on absorbent surface resulting in an initial fast absorption. As longer contact time, adsorption sites are highly occupied from binding with MB thus slowing down the adsorption rate.

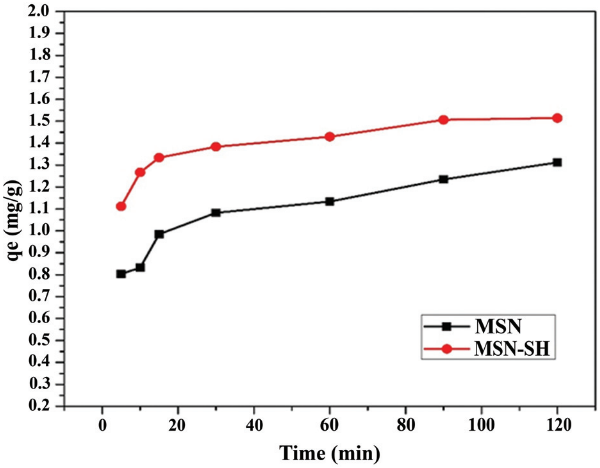


Figure 4 Effect of pH on adsorbed amount of MB at equilibrium for MSN and MSN-SH

2.3 Effect of adsorbent dose

To study the effect of MSN and MSN-SH dose on MB uptake, the amount of adsorbent added was varied. Figure 5 shows the effect of adsorbent dose on the removal efficiency of MB. It was observed that the removal efficiency of MB increased with the increase in adsorbent dose up to 0.05 g then increased slowly with further increase in adsorbent dose up to 0.20 g. Thus, the optimum adsorbent dose was used 0.05 g in the following experiments.

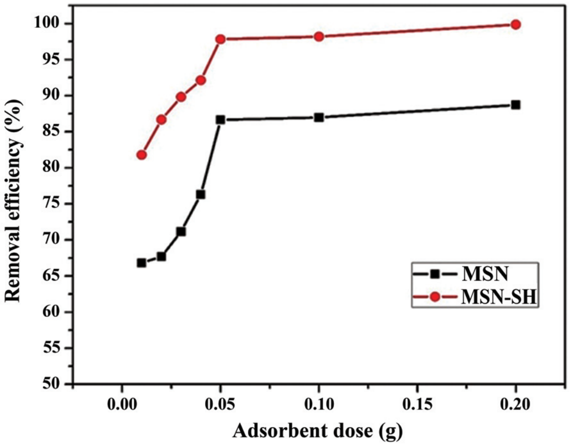


Figure 5 Effect of adsorbent dosage on adsorbed amount of MB at equilibrium for MSN and MSN-SH

2.4 Effect of shaking rate

The increase in adsorption capacity at a higher shaking rate could be explained in terms of the reduction of boundary layer thickness around the adsorbent particles [12]. The effect of shaking rate on MB adsorption is shown in Figure 6. As the shaking rate increased from 0 to 200 rpm, the absorption capacity remained constant.

2.5 Effect of temperature

Temperature had a pronounced effect on the process of adsorption. The adsorption capacity of MB was studied as a function of temperature in the range of 30 to 60 ^{o}C. The results obtained are shown in Figure 7. The adsorption of MB by the MSN and MSN-SH decreased with an increase in the temperature. Thus, the sorption reaction of the system was exothermic [10].

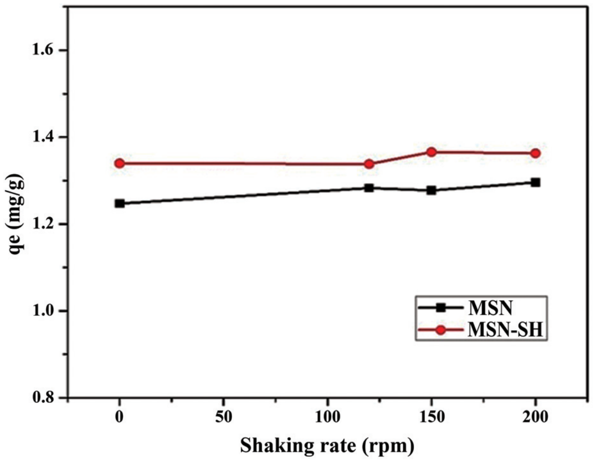


Figure 6 Effect of shaking rate on adsorbed amount of MB at equilibrium for MSN and MSN-SH

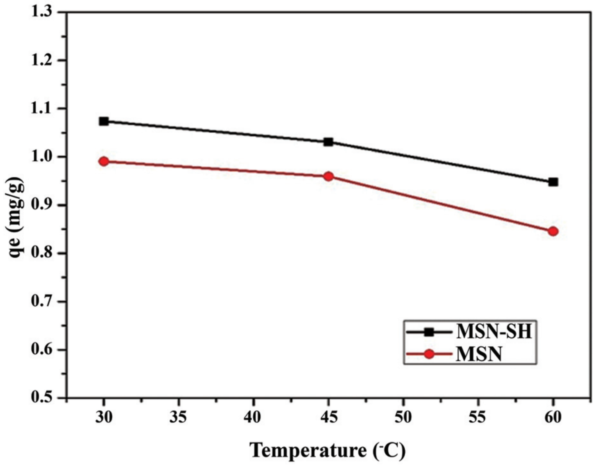


Figure 7 Effect of temperature on adsorbed amount of MB at equilibrium for MSN and MSN-SH

2.6 Effect of initial concentration solution

The rate of adsorption is a function of the initial concentration of the adsorbate, which makes it an important factor to be considered for effective adsorption. Effect of initial MB concentration on adsorption by MSN and MSN-SH was investigated by varying NB concentration from 1 to 40 mgL^{-1}. The results obtained are shown in Figure 8. The adsorption capacity increased with the increase of initial concentration of MB due to the surface of the adsorbent and MB solution increasing.

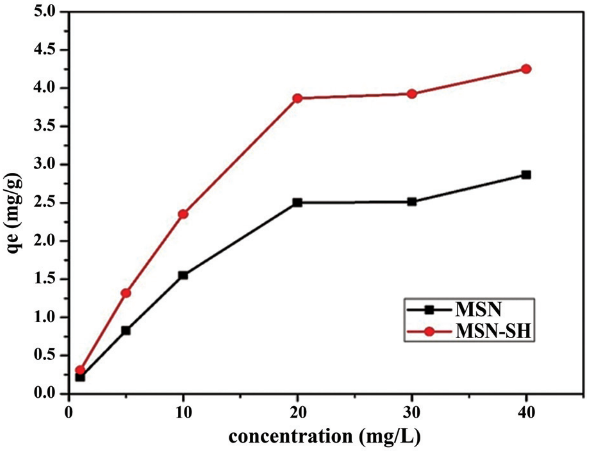
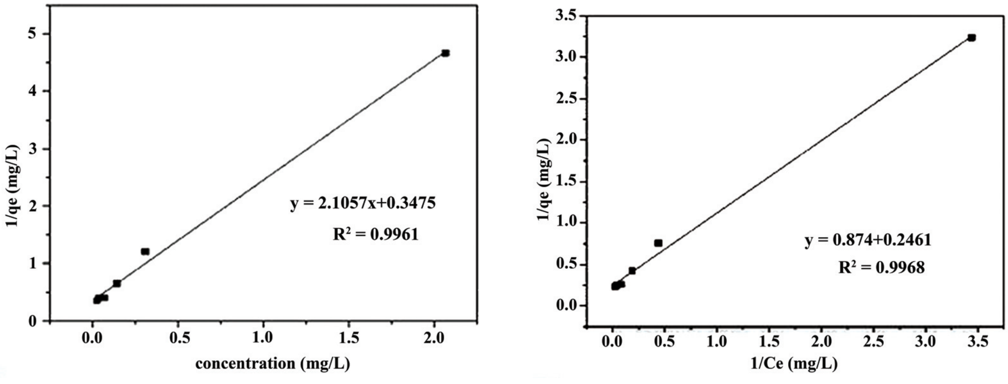


Figure 8 Effect of MB concentration on absorption capacity for MSN and MSN-SH

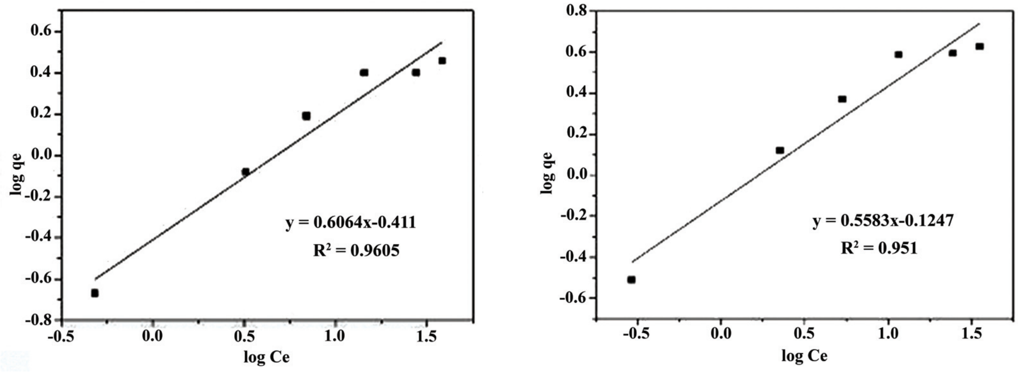
3. Adsorption isotherms

Adsorption isotherm is important for determining the adsorption behavior of the absorbent. Therefore, MB was selected as models to determine the adsorption isotherm model of MSN and MSN-SH. Figure 9 shows the adsorption isotherm for MSN and MSN-SH adsorbent.



(a) Langmuir model of MSN (b) Langmuir model of MSN-SH

Figure 9 Adsorption isotherm model



(c) Freundlich model of MSN (d) Freundlich model of MSN-SH

Figure 9 Adsorption isotherm model (Cont.)

The isotherm curves demonstrate the adsorption as a function of the equilibrium concentration of MB in solution. Both Langmuir and Freundlich adsorption isotherms were used to normalize the adsorption data. The results are summarized in Table 2.

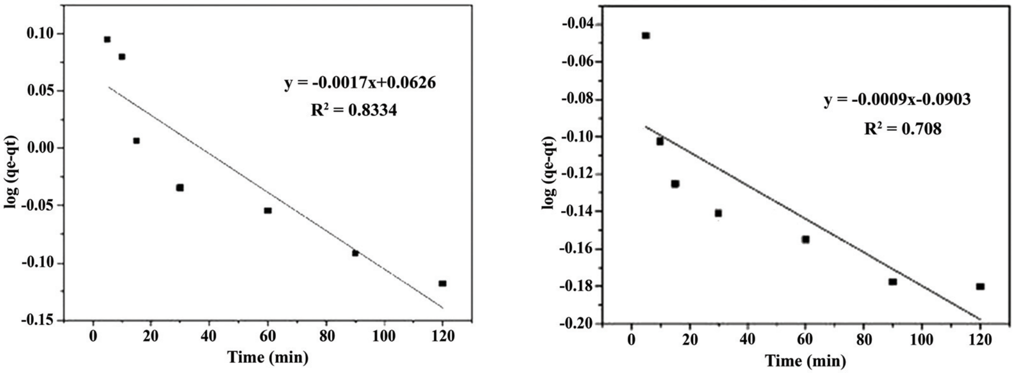
Table 2 Isotherm parameters for various adsorption isotherms for the adsorption of MB onto MSN and MSN-SH

Adsorbent	**Langmuir isotherm model**			**Freundlich isotherm model**		
	q_m (mgg^{-1})	**K_L (Lmg^{-1})**	**R^2**	**1/n**	**K_F ($(mgg^{-1})(Lmg^{-1}))^{1/n}$**	**R^2**
MSN	2.878	0.165	0.9961	0.388	1.65	0.9605
MSN-SH	4.063	0.282	0.9968	0.750	1.79	0.9510

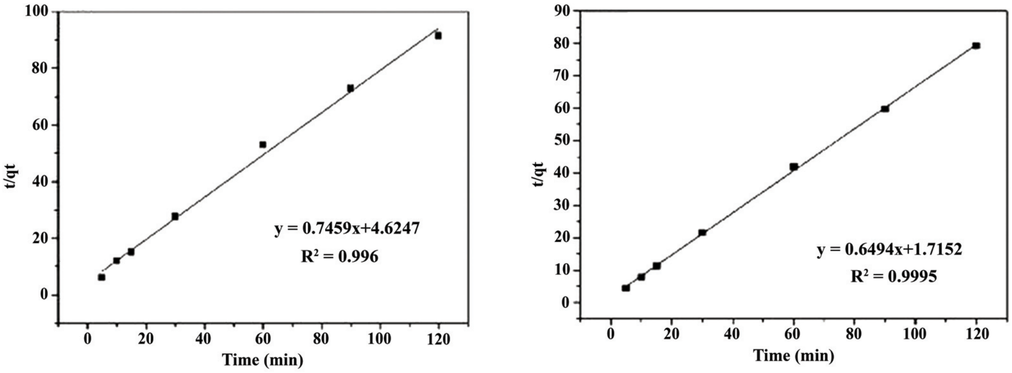
The results show that Langmuir model fitted better than the Freundlich model, demonstrating that the adsorption of MB onto MSN and MSN-SH adsorbent can be considered to be a monolayer adsorption process.

4. Adsorption kinetics

The adsorption mechanism depended on the mass transport as well as the physical or chemical characteristics of the adsorbent. The pseudo second order equation assumes the adsorption of one MB molecule onto one active site on the adsorbent surface, while in the pseudo second order model one MB molecule is adsorbed onto two active site [4]. Figure 10 shows the linear regression curves of the pseudo first order model and pseudo second order model for the adsorption of MB onto MSN and MSN-SH. The results are summarized in Table 3. Results showed that the pseudo second order kinetic model fitted better with adsorption experiment data of the MB adsorption by MSN and MSN-SH than the pseudo first order kinetic model.



(a) MSN (b) MSN-SH



(c) MSN (d) MSN-SH

Figure 10 Kinetic model by pseudo first order model and pseudo second order model

Table 3 Comparison of the pseudo first order model and pseudo second order model for the adsorption of MB onto MSN and MSN-SH

Adsorbent	**pseudo first order model**			**pseudo second order model**		
	K_1 (min^{-1})	**q_e (mgg^{-1})**	**R^2**	**K_2 (min^{-1})**	**q_e (mgg^{-1})**	**R^2**
MSN	-0.00390	1.155	0.8334	0.388	1.341	0.9960
MSN-SH	-0.00207	0.812	0.7080	1.382	1.539	0.9995

Conclusion

Mesoporous silica nanospheres (MSN) and thiol-functionalized MSN (MSN-SH) were synthesized by employing the biphasic system under weak basic condition of l-arginine and using CTAB as a template. Then surface modification was done by thiol functionalization. This approach to synthesize the thiol-functionalized nanostructures is attractive because thiol-functionalized have high dye loading capacity due to the density immobilized thiol groups on the surface of them. The rate of adsorption followed pseudo second order rate equation and Freundlich isotherms were found to be applicable for the adsorption equilibrium data.

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