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Nanoporous calcined MCM-41 silica for adsorption and removal of Victoria blue dye from different natural water samples

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ABSTRACT

In this work, nanoporous MCM-41 silicate was used for the Victoria blue adsorption and removal from the aqueous solutions. The properties of the synthesized MCM-41 were determined by X-ray diffraction analysis, transmission electron microscopy, and TGA analysis. The method is based on the adsorption of Victoria blue after passing on MCM-41 in a column. The adsorption with respect to contact time, pH, flow rate of sample, and initial concentration of analyte was investigated to provide more information about the adsorption characteristics of MCM-41. After adsorption of the dye, the concentrations of residual dye were determined by UV–Vis spectrophotometer. Adsorption process is well described by Langmuir and Temkin isotherms in comparison with Frundlich isotherm. Results suggested that the adsorption of Victoria blue on calcined MCM-41 was a spontaneous and endothermic process. The experimental data fitted very well with the pseudo-second-order kinetic model for Victoria blue onto calcined MCM-41. Adsorption capacity was found to be 192.3 mg g^{-1}. The method was applied to the adsorption and removal of Victoria blue in different environmental water samples.

Keywords: Nanoporous MCM-41; Adsorption; Victoria blue dye; Kinetic; Equilibrium; Removal

1. Introduction

In recent years, various silica-based particles with different porosities (meso, micro, and macro) and scales (nano to micron) have been synthesized and applied for different applications [1]. Among their currently recognized potential applications is their use as adsorbents in the separation of large molecules, as catalyst supports and as hosts for a variety of opto-electronic materials. Among these sorbents, nanoporous silicas such as MCM-41, MCM-48, and SBA-15 have attracted great attention because of their good mechanical and thermal stability, and their lower susceptibility to swelling and shrinking [2]. MCM-41 is a synthetic, mesoporous silicate material, which currently has limited use as an industrial catalyst [3]. Mesoporous MCM-41 has superior advantages over zeolites due to its relatively large and tunable pore size (14–100 Å), high surface area, and long range of

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ordered pore structure [4]. MCM-41 materials with hexagonal arrangement of parallel mesopores are attractive as host molecules for various guests and have been investigated for adsorptive removal of various inorganics [5–9] and organics such as aniline [10], p-chlorophenol, phenols [11,12], dyes [13–15], and pharmaceutical compound [16,17] in aqueous solutions.

This material is considered to have good potential for adsorption/separation applications due to its regular hexagonal structure, uniform pore distribution, large surface area, and large pore volume [18]. While there are some examples of the use of MCM materials in separation method, these are limited and further work needs to be done to develop the applications of MCM-41.

The dye chosen for such study was the non-biodegradable Victoria blue (Fig. 1), a basic blue with the molecular weight 514.14 and molecular formula $C_{33}H_{40}ClN_3$. This dye is a triarylmethane dye and extensively used for dyeing wool, silk, and cotton. It is also used for staining in microscopic work. Victoria blue dye is known to cause strong coloration and toxicity in the wastewater and can produce irritation to eyes and respiratory system. It may even promote tumor growth in some species of fish [19].

In this study, our objective is to examine the potential of MCM-41 for uptake of Victoria blue, from river water, broth culture medium samples in an acidic medium through spectrophotometric measurements. To the best of our knowledge, this is the first report for adsorption and removal of Victoria blue.

The adsorption processes with respect to pH and contact time were measured to provide more information about the adsorption characteristics of MCM-41. The equilibrium data were fitted into Langmuir and Freundlich equations to determine the correlation between the isotherm models and experimental data. The kinetic and equilibrium parameters were calculated to determine the adsorption mechanisms.

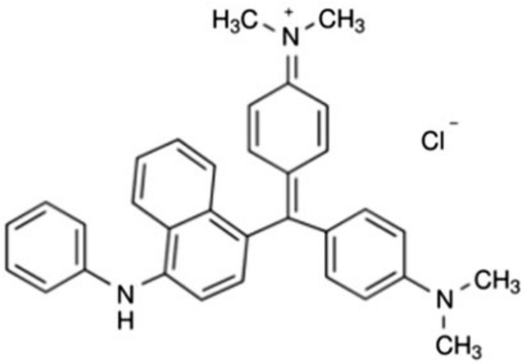

Fig. 1. Chemical structure of Victoria blue.

2. Experimental

2.1. Chemicals and reagents

Analytical reagent-grade chemicals and double-distilled water were used throughout the study. Victoria blue, phosphoric acid (98%), acetic acid, acetone, and hydrochloric acid (37%) were purchased from Merck (Darmstadt, Germany). Cetyltrimethylammonium bromide (CTAB) and fumed silica (99.8% metal free) were purchased from Merck. A stock solution of Victoria blue (200 $\mu g\ mL^{-1}$) was prepared by dissolving and diluting 0.020 g of dye powder to 100 mL with double-distilled water. Standard and working solution of Victoria blue were prepared by dilution of stock solution. pH adjustments were performed with 0.01–1.0 M HCl (Merck) and NaOH (Merck) solutions. An acetate buffer pH 5 was prepared by addition of 0.1 M NaOH to 0.1 M acetate acid and using a pH meter to adjust the pH at 5.0.

2.2. Apparatus

The spectrophotometric measurements were carried out with a Cintra 101 spectrophotometer (GBC SCIENTIFIC EQUIPMENT, Australia). pH adjustments were carried out by a Metrohm (Herisau, Switzerland) digital pH meter Model 632 with a combined glass electrode which was used to measure pH values. A Teb Azma vacuum pump (Tehran, Iran) was used for pumping the solution, and a Metrohm model E649 (Switzerland) stirrer was used. The IR spectra were taken on a KBr tablet using a BOMEM MB-Series 1998 FT-IR spectrometer. The thermogravimetric curve of the MCM-41 was recorded on a BAHR, SPA 503 at heating rate of 10°C min^{-1}. The thermal behavior was studied by heating 1–3 mg of samples in aluminum-crimped pans under nitrogen gas flow, over the temperature range of 25–650°C. X-ray diffraction (XRD; Bruker D8ADVACE) with Ni-filtered Cu Kα radiation (1.5406 Å) was investigated. Data were recorded with a speed of 2° min^{-1} and a step of 0.05°. Hitachi S5200 in transmission mode at 30 kV, 30 1A current was used for TEM images.

2.3. Synthesis of MCM-41

MCM-41 was synthesized as reported previously [20]. For this purpose, 0.6 g of sodium hydroxide in

10 g deionized water was added to a solution of cetyltrimethyl ammonium bromide (7.89 g in water). After stirring for 3 h, a solution of fumed silica (1.8 g in 20 mL water) was added to the surfactant solution. The prepared gel was then kept for 24 h at room temperature. The molar composition of the final gel was 30 SiO_2, 5.2 CTAB, 7.5 NaO_2, and 2,500 H_2O. Finally, the gel mixture was placed in a Teflon-lined stainless steel autoclave and kept at 100˚C for 72 h. The solid product washed with deionized water and then dried at 100˚C for 3 h and calcinated at 500˚C for 6 h.

2.4. Preparation of a mini-column for adsorption and removal of Victoria blue

A glass tube (10 cm length and 7 mm i.d.) with a very fine bore was packed with 0.01 g of the MCM-41 adsorbent and used for adsorption and removal of Victoria blue. About 100 mL solutions containing different concentrations of Victoria blue dye and 2 mL of acetate buffer (pH 5) were passed through the mini-column at a flow rate of 6 mL min^{-1}. Then, the residual concentration of Victoria blue was determined using a UV–Vis spectrophotometer at a wavelength of 616 nm. The percentage removal of Victoria (%) was calculated according to the following equation:

$$R(\%) = \frac{(C_0 - C_t) \times 100}{C_0} \tag{1}$$

where C_0 and C_t are the initial and residual concentrations in mg L^{-1}. A blank solution was also run under the same analytical conditions without adding any Victoria blue.

2.5. Water sample preparations

River water samples were collected from Karoon River, Ahvaz, Iran; the drinking water samples were collected from tap water in Ahvaz city and mineral and hot water springs in Sarein, Ardabil, Iran. Analysis of water samples for determination of analyte content was performed as follows: the water samples were filtered through a Whatman No. 40 filter paper. Before analysis, 200 mL of sample was poured in a beaker and 2 mL concentrated HNO_3 was added. The samples, while stirring were heated for 15 min. The content of beaker was filtered and diluted to 250 mL with distilled water. After adjusting the pH of final solution to 5, the procedure given in the above section was performed.

3. Results and discussion

3.1. Characterization of adsorbent

The XRD pattern (Fig. 2) shows the diffraction peaks at (100, 110, and 200) indicating uniform pore channels in a regular hexagonal array [20,21]. This pattern showed a sharp XRD peak around $2\theta = 2^\circ$ and few weak peaks in $2\theta = 3–5^\circ$, which indicated well-hexagonal structure of MCM-41. The well-ordered hexagonal arrays of nanoporous are also confirmed by the TEM image as in Fig. 3 with high uniformity and the pore size evaluated at 24 nm [21]. To have an insight into the thermal degradation behaviors of the prepared hybrid adsorbents, TGA thermal analysis was carried out. The results of the TG analysis showed that the sample exhibits a one-stage degradation pattern over the range of 100–1,000˚C. This weight loss might be due to the loss of the adsorbed water as well as the dehydration of the surface –OH groups. However, it is thought that the thermal stability of nanoporous MCM-41 is quiet high.

3.2. Effect of pH

Fig. 4 illustrates the effect of pH on the adsorption of Victoria blue by using MCM-41 at ambient temperature by varying the initial pH of 5 mg L^{-1} solution for fixed adsorbent mass of 0.01 g. It shows that the adsorption capacity of Victoria blue onto MCM-41 increases significantly up to pH 4 and then is constant up to 7 and decreases at pHs higher than 7. This result indicates that the pH lower than 4 and higher

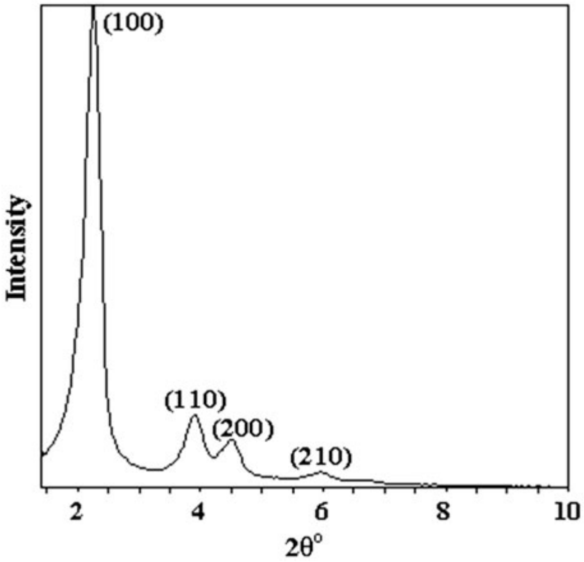

Fig. 2. XRD pattern of MCM-41.

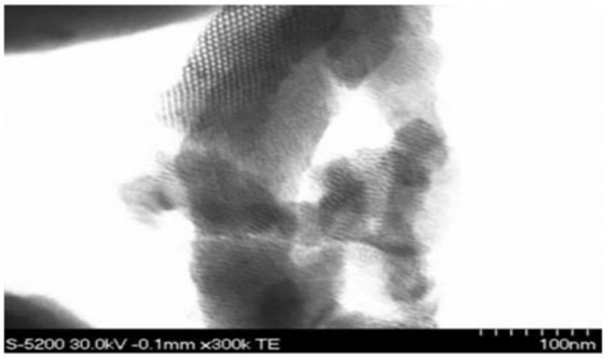

Fig. 3. TEM of MCM-41.

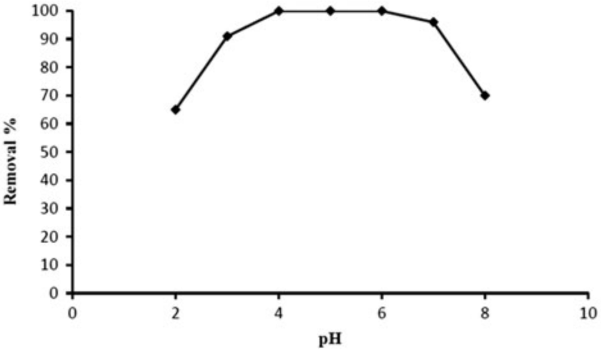

Fig. 4. Effect of pH on the adsorption of Victoria blue; 0.01 g of MCM-41 as adsorbent.

than 7 will not favor adsorption of this dye on MCM-41. Higher adsorption of the dye at this range of pH might be due to increased protonation by neutralization of the negative charge at the surface of adsorbent. This indicated that the adsorption capacity of MCM-41 was pH dependent. Therefore, the pH 5 was selected as the optimum value for the sorption of Victoria blue, and 3 mL of phosphate buffer solution with pH 5 was used to maintain this pH value. The zero point of charge of the surface of nanoporous silica MCM-41 was measured [22]. Suspensions of 0.5 g in 100 mL of adsorbent was prepared and put into contact with 0.10 mol L^{-1} of NaCl solutions adjusted at different pH values (pH 3–9 adjusted by NaOH or HCl). The aqueous suspensions were agitated for 24 h until the equilibrium pH was achieved. The pH value at the point of zero charge (pH_{pzc}) was determined by plotting the difference of final and initial pHs (ΔpH) vs. the initial pH. As is shown in Fig. 5, the pH_{PZC} of the nanoporous MCM-41 was about 4. Above the pH of zero point charge, the adsorbent surface is negatively charged; therefore, adsorption of Victoria blue onto the adsorbent takes place. At alkaline pH, the adsorption decreases and the adsorption capacity becomes small; it can be related to the existing forms of the Victoria blue species because surface nanoporous MCM-41 is negatively charged and the dye is negative too at this pH range. So, the dye cannot interact with adsorbent. Thus, pH 5 was selected for future studies.

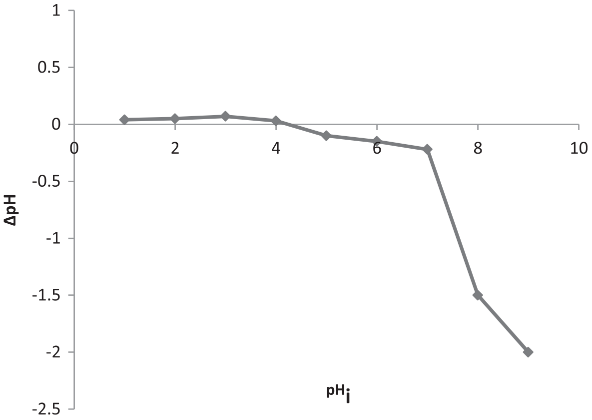

Fig. 5. Point of zero charge.

3.3. Effect of amount of adsorbent

The adsorbent dosage is particularly important factor because it determines the extent of dye removal. In the adsorption step, an appropriate amount of solid phase should be used in order to obtain quantitative retention of dye on adsorbent. With increasing solid content, the active sites and surface functional groups at MCM-41 increase and thereby can provide more adsorption sites for the binding of Victoria blue. On the other hand, an excess amount of the adsorbent also prevents the quantitative elution of the retained dye by a small volume of eluent. The effect of the amount MCM-41 on the adsorption of Victoria blue at pH 3 was examined in the range of 0.0025–0.02 g. The results display that up to 0.015 g of MCM-41 efficiency of extraction increased and further addition has no significant effect on recovery. The percent adsorption of Victoria blue using different amount of the adsorbent (Fig. 6) showed that the appropriate amount of the solid adsorbent could be 0.01 g.

3.4. Effect of sample flow rate

In order to study the effect of sample flow rate, 100 mL portions of sample solution were passed through the column at different flow rates in the ranges of 2–20 mL min^{-1}. The results showed that the recovery values for analyte was quantitative in flow

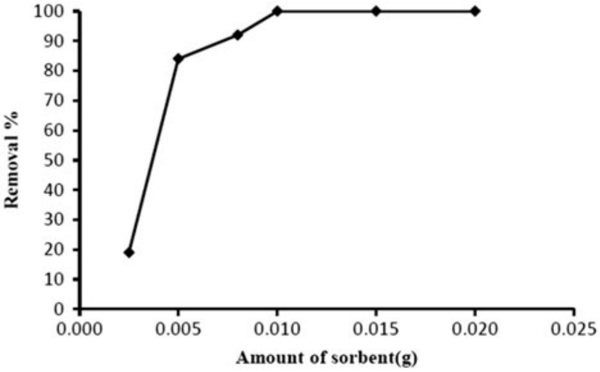

Fig. 6. Effect of amount of MCM-41 on the removal of 5 μg mL^{-1} Victoria blue, pH 5, $T = 25$°C; 0.01 g of MCM-41.

rate between 2 and 6 mL min^{-1} (>98% with the coefficient of variation less than 3%) so a flow rate of 6 mL min^{-1} was chosen for further studies. Furthermore, the chosen flow rate provides complete adsorption of Victoria blue with the additional benefit of a decrease in analysis time.

3.5. Adsorption studies

The mass transfer from the solution to the adsorption sites within the adsorbent particles is constrained by mass-transfer resistances that determine the time to reach the state of equilibrium. The time progress of the adsorption process is referred to as adsorption kinetics [23]. The adsorption studies for the evaluation of MCM-41 adsorbent for the adsorption of Victoria blue from the aqueous solutions were carried out using the batch contact adsorption method.

For these experiments, the amount of Victoria blue dye adsorbed onto MCM-41 was measured as a function of time and concentration. A known mass of adsorbent (0.01 g) was immersed into a 100 mL Erlenmeyer flask along with different concentrations of Victoria blue dye at pH 5. The flasks were shaken for specified durations at room temperature. Then, the concentrations of dye in the supernatant were determined by spectrophotometric measurements. The effect of contact time on adsorption of different concentrations of Victoria blue dye in the range 3–240 min was studied (Fig. 7). As illustrated, the apparent adsorption equilibrium was usually established within 60 min. No significant change in the percentage removal of Victoria blue was observed after 2 h. Adsorption equilibrium can be achieved within 120 min, after which the adsorption of Victoria blue on the surface of the nanoporous MCM-41 adsorbent was negligible.

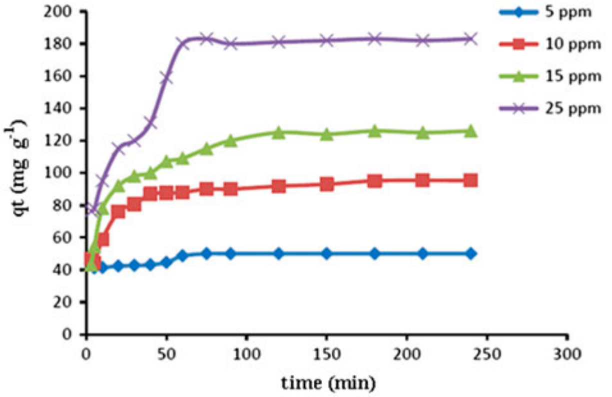

Fig. 7. Adsorption of Victoria blue on MCM-41 as a function of contact time, pH 5, $T = 25$°C; 0.01 g of MCM-41.

The amount of Victoria blue adsorbed at time t, q_t (mg g^{-1}), was calculated by Karim et al. [24]:

$$q_t = \frac{(C_i - C_t)V}{W} \tag{2}$$

where C_i and C_t are the initial and equilibrium concentrations in mg L^{-1}, W is the dry mass of adsorbent in grams, and V is the volume of solution in L.

q_e (mg g^{-1}) which is the amount of adsorbed target dyes (mg) per g of adsorbent at equilibrium time was calculated by using the equation [25]:

$$q_e = \frac{(C_i - C_e)V}{W} \tag{3}$$

where C_e is the concentration of dye in solution at equilibrium time.

3.6. Kinetic studies

In order to present the kinetic equation representing adsorption of Victoria blue dye on nanoporous MCM-41, pseudo-first-order, pseudo-second-order and intraparticle equations were used to test the experimental data. These kinetic models are used to examine the controlling mechanism of the adsorption process, such as adsorption surface, chemical reaction, and/or diffusion mechanisms. The parameters of the kinetic models can be obtained by suitable linearisation procedures. The pseudo-first-order kinetic model found by Lagergren and Svenska is widely used to predict adsorption kinetic and was defined as [26]:

$$\ln(q_1 - q_t) = \ln q_1 - K_1 t \tag{4}$$

where q_1 and q_t (mg g^{-1}) are the amounts of adsorbate adsorbed at equilibrium and at any time, t (min), respectively and k_1 (min^{-1}) is the adsorption rate constant. The slopes and intercepts of plots of ln (q_1−q_t) vs. t were used to determine the first-order rate constant k_1 and equilibrium adsorption density q_1. Table 1 lists the computed results obtained from the first-order kinetic model. The correlation coefficients for the first-order kinetic model obtained at all the studied concentrations were low. It was also observed in the present work that q_1 values computed from the Lagergren plots deviated considerably from the experimental q_e values. This indicates that pseudo-first-order equation might not be sufficient to describe the mechanism of Victoria blue adsorption on the adsorbent.

The kinetics data were also fitted by pseudo-second-order model [27] expressed by the following equation:

$$t/q_t = \left(1/k_2 q_2^2\right) + (1/q_2)t \tag{5}$$

where q_t and q_2 are the amount of dye adsorbed (mg L^{-1}) on nanoporous MCM-41 at time t (min) and equilibrium time, respectively; k_2 (g mg^{-1} min^{-1}) is the corresponding adsorption rate constant. The plot of t/q_t vs. t (Fig. 8) yields very good straight lines for different initial Victoria blue concentrations. A comparison of the results with the correlation coefficients is shown in Table 1. The correlation coefficients for the second-order kinetic equation all were higher than 0.996 for all concentrations. The calculated q_2 values also agree very well with the experimental data. The results show that the adsorption of Victoria blue on the adsorbent follows a pseudo-second-order kinetic model. The pseudo-second-order kinetic analysis reveals that the values of the initial adsorption rates, increases with increase in the initial dye concentration. (Fig. 9). The lower the concentration of Victoria blue in the solution, the lower the probability of collisions between these species is and hence the faster dye could be bonded to the active sites on the surface of the adsorbent. The applicability of pseudo-second-order kinetics increases as the system approaches equilibrium. Mathematical expressions have been proposed in order to describe the dependence of the pseudo-second-order constant on parameters such as the initial sorbate concentration, the progress of the sorption process and the solid/solution ratio. In addition to the pseudo-second-order, pseudo-first-order rate equations, and the intraparticle diffusion model is commonly used technique for identifying the steps involved during adsorption, described by external mass transfer (boundary-layer diffusion) and intraparticle diffusion. The intraparticle diffusion model is expressed as in the following equation [28]:

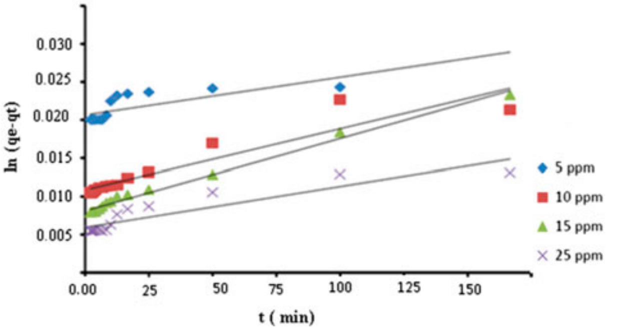

Fig. 8. Pseudo-first-order adsorption kinetics of Victoria blue onto MCM-41.

Table 1
Kinetic parameters for adsorption of Victoria blue on nanoporous MCM-41 adsorbent

C_0 (mg L^{-1})	$q_{2\ \text{calculated}}$ (mg g^{-1})	$q_{1\ \text{experimental}}$ (mg g^{-1})	K_1 (min^{-1})	R^2
Pseudo-first-order model				
5	50	14.2	0.00024	0.533
10	100	24.3	0.0004	0.871
15	150	33.7	0.00047	0.989
25	200	43.5	0.00026	0.825
Pseudo-second-order model				
	$q_{2\ \text{calculated}}$ (mg g^{-1})	$q_{2\ \text{experimental}}$ (mg g^{-1})	K_2 (g mg^{-1} min)	R^2
5	50	52.43	0.005	0.9993
10	100	100	0.001	0.9998
15	150	142.0	0.0007	0.9983
25	200	200	0.0005	0.9965

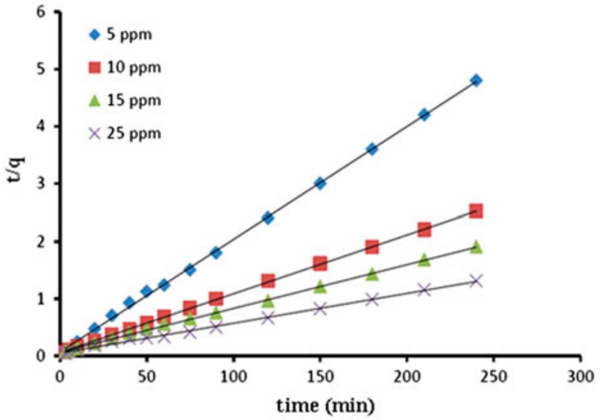

Fig. 9. Pseudo-second-order adsorption kinetics of Victoria blue onto MCM-41.

$$q_t = k_d\left(t^{1/2}\right) \tag{6}$$

where k_d is the diffusion coefficient. Fig. 10 presents the typical plots for the adsorption of dye on MCM-41 using diffusion model. As shown in Fig. 11, the two-phase plot suggests that the adsorption process proceeds by surface adsorption and intraparticle diffusion, namely, the initial curved portion of the plot indicates a boundary-layer effect while the second linear portion is due to intraparticle or pore diffusion. In this work, it was found that the pore diffusion played an important role in the adsorption of Victoria blue dye on the adsorbent and results indicating that the adsorption processes is pseudo-second-order equation which is in agreement with the fact that the reaction rate depends on the dye concentration and also the active sites on the adsorbent surface. The applicability of the pseudo-second-order equation could be explained on the ground of the model assuming that the overall sorption rate is limited by the rate of sorbate diffusion in the pores of sorbent.

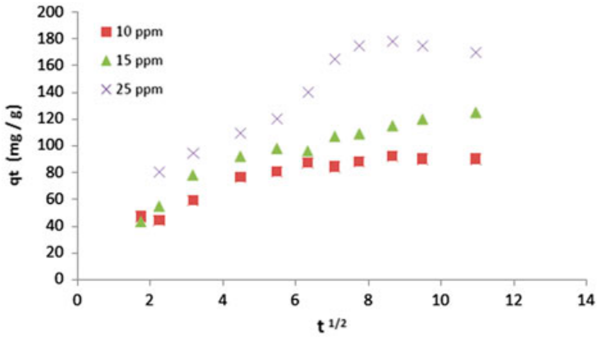

Fig. 10. Intraparticle diffusion adsorption kinetics of Victoria blue onto MCM-41.

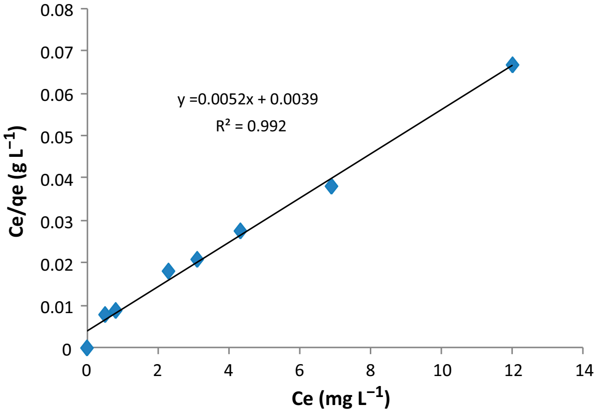

Fig. 11. Langmuir isotherm for adsorption of Victoria blue dye onto MCM-41.

3.7. Adsorption isotherms and adsorption capacity

It is known that equilibrium analysis not only allowed for the estimation of adsorption capacities, adsorption isotherm study is important in the treatment of samples as it provides valuable information on the pathways of adsorption reactions. There are many adsorption isotherms in the literature for analyzing experimental adsorption equilibrium data such as Langmuir, Freundlich, Dubinin–Radushkevich, Sips, Temkin, Redlich–Peterson [29–32]. In order to better design an adsorption system for determination of Victoria blue, Langmuir, Freundlich, and Temkin models have been tested in the present study.

The Langmuir isotherm model is based on the assumptions of a structurally homogeneous adsorbent. The bonding sites on the adsorbent have the same affinity for adsorption of a single molecular layer. The bonding to the adsorption sites can be either chemical or physical but must be strong enough to prevent displacement of the adsorbed molecules. Linear form of Langmuir isotherms is represented in following equation [33–35]:

$$C_e/q_e = 1/q_{\max}K_L + C_e/q_{\max} \tag{7}$$

where q_e is the equilibrium concentration of target on the adsorbent (mg g^{-1}), $q_{\max}$ is the monolayer adsorption capacity of the adsorbent (mg g^{-1}), K_L is the Langmuir adsorption constant. The plot of C_e/q_e vs. C_e gives a straight line and the values of $q_{\max}$ and K_L

can be calculated from the slope and intercept of the plot, respectively.

Another important parameter, R_L, known as the separation factor, could be calculated using the binding constant K_L obtained from the Langmuir isotherm as follows [36]:

$$R_L = \frac{1}{1 + K_L C_0} \tag{8}$$

From the magnitude of the R_L, the adsorption process can be defined as: $R_L > 1 \rightarrow$ unfavorable, $R_L = 1 \rightarrow$ linear adsorption, $0 < R_L < 1 \rightarrow$ favorable, $R_L = 0 \rightarrow$ irreversible.

The Freundlich model does not predict surface saturation. It considers the existence of a multilayered structure. Freundlich isotherm is described by the following equation [37]:

$$\log q_e = \log K_F + 1/n \log C_e \tag{9}$$

where K_F (mg g^{-1}) and n are the Freundlich adsorption isotherm constants. K_F and n indicate the extent of adsorption and the degree of nonlinearity of adsorption. A high value of n shows good adsorption over the entire studied concentration range, while small n indicates the good adsorption properties at high concentrations. A higher value of K_F indicates a higher capacity for adsorption than a lower value [38].

The isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage [39]. The Temkin isotherm has been generally applied in the following form [40]:

$$q_e = B \ln A + B \ln C_e \tag{10}$$

$B = RT/b_T$, b_T is the Temkin constant related to heat of sorption (J/mol) and A is the Temkin isotherm constant (L/g), R is the gas constant (8.314 J/mol K), and T is the absolute temperature (K).

The isotherm constants and R^2 values for each model are given in Table 2. The results indicate that the Langmuir isotherm is more adequate than the other isotherms and fits better with data experiments. The calculated R_L values found in this study for 5–25 mg L^{-1} concentrations of Victoria blue dye in the pH value 5 are in the range of 0.023–0.127, which implies that the dye adsorption onto nanoporous is a favorable adsorption process. The maximum adsorption capacity (q_{max}) for the adsorption of Victoria blue dye on nanoporous MCM-41 calculated from the Langmuir isotherm was evaluated to be 192.3 mg g^{-1} for Victoria blue. The n and k adsorption level was determined from Freundlich adsorption isotherm. In case of $n = 1$ indicates linear adsorption and equal adsorption energies for all sites. Values of n between 2 and 10 indicate good adsorption. However, $n < 1$ shows that the marginal adsorption energy decreases with increasing surface concentration. The n and K_F values were 2.83 and 92.15 (L mg^{-1}) indicating that this dye could be easily adsorbed on the hybrid adsorbent. The correlation coefficient for Temkin isotherm is higher than the Freundlich value, The Temkin adsorption potential, K_T, of MCM-41 for Victoria blue dye is 43.5 indicating a high potential of this nanoporous adsorbent for target dye.

3.8. Adsorption thermodynamics

The Thermodynamic parameters, Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) of sorption were calculated using the following equations [41]:

$$\Delta G^\circ = RT \ln K_d \tag{11}$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{12}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature (K). The thermodynamic parameters, were estimated to evaluate the feasibility and exothermic nature of the adsorption process.

Table 3 summarizes these thermodynamic parameters for the adsorption of Victoria blue dye on MCM-41 at different temperatures. The positive value of $\Delta S°$, suggests increased randomness at the solid/solution interface during the sorption dye onto nonporous MCM-41. The negative value of $\Delta H°$ indicates the exothermic nature of the adsorption process. It is noted that the Gibbs free energy value is negative, which indicate the feasibility and spontaneous adsorption of Victoria blue onto MCM-41. The degree of spontaneity of the reaction increases with increase in temperature.

3.9. Reusability and stability of the adsorbent

Regeneration property is one of the important parameter in solid-phase extraction methods. The stability and potential regeneration of the column were investigated to find reusability and stability of

Table 2
Isotherm parameters and correlation coefficients calculated by various adsorption models for adsorption onto 0.01 g of nanoporous MCM-41 adsorbent in 100 mL, pH 5, and room temperature

Model	Linear equation	Parameters	Value of parameters
Langmuir	$C_e/q_e = 1/[q_m K_L] + C_e/q_m$	q_m (mg g^{-1})	192.3
		K_L (L mg^{-1})	1.37
		R^2	0.992
Freundlich	$\log q_e = \log K_F + 1/n \log C_e$	n	2.83
		K_F (L mg^{-1})	92.15
		R^2	0.968
Temkin	$q_e = B \ln K_T + B \ln C_e$	b_T	43.5
		K_T (L mg^{-1})	9.13
		R^2	0.995

Table 3
Thermodynamic parameters for the adsorption of Victoria blue dye adsorption on nanoporous MCM-41 adsorbent

Temperature (℃)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
15			
20	−638	−512.6	0.428
30			
60			

the synthesized sorbent, the solid sorbent was reused at optimum experimental conditions for the simultaneous separation and preconcentration of dye from aqueous samples. The sorbent can be used again to adsorb the interested analyte after regeneration. In order to reuse this nanoporous adsorbent after each extraction, a short regeneration step was performed by washing with 4 mL of methanol–acetic acid (95:5, v/v). The results showed that the sorbent could be used 5 times and maintained their adsorption capacity at an almost constant value. The stability of the sorbent was checked for several months and it was found that it is stable for at least nine months.

3.10. Application and analysis of real samples

In order to assess the applicability of the method it was applied to the separation, removal of Victoria blue dye from different complex matrices. Therefore, river water, spring water, and tap water were selected as models for evaluating method ruggedness. The removal of spiked samples is satisfactorily reasonable and was confirmed using addition method, which indicates the capability of the system in the removal of Victoria blue dye. A good agreement was obtained between the added and measured analyte amounts. The removal values calculated for the added standards were always higher than 95%, thus confirming the accuracy of the procedure and its independence from the matrix effects. The percent of recoveries in spiked samples are given in Table 4.

Table 4
Determination of Victoria blue dye in water samples

Sample	Added (μg mL^{-1})	Recovery (%)
Karoon river water	5	100
	10	100
	15	97
Sarein river water	5	100
	10	100
	15	96
Tap water	5	100
	10	100
	15	95

4. Conclusion

MCM-41 represents one of the most convenient materials for fast and sensitive removal of Victoria blue dye. The proposed method could be effectively used for the solid phase extraction of Victoria blue. The adsorption capacity of nanoporous MCM-41 for adsorption of this dye was 192.3 mg g^{-1}. The percentage removal of Victoria blue dye in spiked samples with a relative standard deviation of less than 2% reflects the validity and accuracy of the method when applied to real samples. The adsorption kinetics was found to be fast and followed pseudo-second-order rate law. Adsorption equilibrium was studied with Langmuir, Freundlich and Tempkin isotherm models. The adsorption process followed Langmuir isotherm.

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References

[1] M. Aw, S. Simovic, Y. Yu, J. Addai-Mensah, D. Losic, Porous silica microshells from diatoms as biocarrier for drug delivery applications, Powder Technol. 223 (2012) 52–58.

[2] K. Kailasam, K. Muller, Physico-chemical characterization of MCM-41 silica spheres made by the pseudomorphic route and grafted with octadecyl chains, J. Chromatogr. A 1191 (2008) 125–135.

[3] J. Grams, I. Sobczak, Application of ToF-SIMS to the study of surfactant removal from AuNbMCM-41 and AuMCM-41 materials, Int. J. Mass Spectrom. 289 (2010) 138–143.

[4] J. Wloch, M. Rozwadowski, M. Lezanska, K. Erdmann, Analysis of the pore structure of the MCM-41 materials, Appl. Surf. Sci. 191 (2002) 368–374.

[5] Q. Qin, J. Ma, K. Liu, Adsorption of nitrobenzene from aqueous solution by MCM-41, J. Colloid Interface Sci. 315 (2007) 80–86.

[6] K.A. Northcott, K. Miyakaw, S. Oshim, Y. Komatsu, J.M. Perera, G.W. Stevens, The adsorption of divalent metal cations on mesoporous silicate MCM-41, Chem. Eng. J. 157 (2010) 25–28.

[7] P. Figueira, C.B. Lopes, A.L. Daniel-da-Silva, E. Pereira, A.C. Duarte, T. Trindade, Removal of mercury (II) by dithiocarbamate surface functionalized magnetite particles: Application to synthetic and natural spiked waters, Water Res. 45 (2011) 5773–5784.

[8] F. Raji, M. Pakizeh, Kinetic and thermodynamic studies of Hg(II) adsorption onto MCM-41 modified by $ZnCl_2$, Appl. Surf. Sci. 301 (2014) 568–575.

[9] J. Cao, Y. Wu, Y. Jin, P. Yilihan, W. Huanga, Response surface methodology approach for optimization of the removal of chromium(VI) by NH2-MCM-41, J. Taiwan Inst. Chem. Eng. 45 (2014) 860–868.

[10] X. Yang, Q. Guan, W. Li, Effect of template in MCM-41 on the adsorption of aniline from aqueous solution, J. Environ. Manage. 92 (2011) 2939–2943.

[11] C. Cooper, R. Burch, Mesoporous materials for water treatment processes, Water Res. 33 (1999) 3689–3694.

[12] M.C. Burleigh, M.A. Markowitz, M.S. Spector, B.P. Gaber, Porous poly silsesquioxanes for the adsorption of phenols, Environ. Sci. Technol. 36 (2002) 2515–2518.

[13] L. Chuen Juang, C. Wang, C. Kung Lee, Adsorption of basic dyes onto MCM-41, Chemosphere 64 (2006) 1920–1928.

[14] C.K. Lee, S.S. Liu, L.C. Juang, C.C. Wang, K.S. Lin, M. Du Lyu, Application of MCM-41 for dyes removal from wastewater, J. Hazard. Mater. 147 (2007) 997–1005.

[15] B. Han, F. Zhang, Zh. Feng, Sh. Liu, Sh. Deng, Y. Wang, Y. Wang, A designed Mn_2O_3/MCM-41 nanoporous composite for methylene blue and rhodamine B removal with high efficiency, Ceram. Int. 40 (2014) 8093–8101.

[16] T. Xuan Bui, H. Choi, Adsorptive removal of selected pharmaceuticals by mesoporous silica SBA-15, J. Hazard. Mater. 168 (2009) 602–608.

[17] M. Liu, L. Hou, Sh. Yu, B. Xi, Y. Zhao, X. Xia, MCM-41 impregnated with a zeolite precursor: Synthesis, characterization and tetracycline antibiotics removal from aqueous solution, Chem. Eng. J. 223 (2013) 678–687.

[18] S. Oshima, Adsorption behavior of cadmium (II) and lead (II) on mesoporous silicate MCM-41, Sep. Sci. Technol. 41 (2006) 1635–1643.

[19] A. Kant, M. Datta, Adsorption characteristics of Victoria blue on low cost natural sand and its removal from aqueous media, Eur. Chem. Bull. 3 (2014) 752–759.

[20] F. Farzaneh, J. Taghavi, R. Malakooti, M. Ghandi, Immobilized vitamin B_{12} within nanoreactors of MCM-41 as selective catalyst for oxidation of organic substrates, J. Mol. Catal. A 244 (2006) 252–257.

[21] P.A. Mangrulkar, S.P. Kamble, J. Meshram, S.S. Rayalu, Adsorption of phenol and *o*-chlorophenol by mesoporous MCM-41, J. Hazard. Mater. 160 (2008) 414–421.

[22] M. Kosmulski, The pH-dependent surface charging and the points of zero charge, J. Colloid Interface Sci. 253 (2002) 77–87.

[23] E. Worch, Adsorption Technology in Water Treatment: Fundamentals, Processes, and Modeling 2012, Walter de Gruyter. Copyright Co, KG, Berlin/Boston, 2012.

[24] A.H. Karim, A.A. Jalil, S. Triwahyono, S.M. Sidik, N.H.N. Kamarudin, R. Jusoh, N.W.C. Jusoh, B.H. Hameed, Amino modified mesostructured silica nanoparticles for efficient adsorption of methylene blue, J. Colloid Interface Sci. 386 (2012) 307–314.

[25] M.T. Sikder, S. Tanaka, T. Saito, M. Kurasaki, Application of zerovalent iron impregnated chitosan-caboxymethyl-β-cyclodextrin composite beads as arsenic sorbent, J. Environ. Chem. Eng. 2 (2014) 370–376.

[26] S.A. Idris, K.M. Alotaibi, T.A. Peshkur, P. Anderson, M. Morris, L.T. Gibson, Adsorption kinetic study: Effect of adsorbent pore size distribution on the rate of Cr(VI) uptake, Microporous Mesoporous Mater. 165 (2013) 99–105.

[27] M. Mureseanu, N. Cioatera, I. Trandafir, I. Georgescu, F. Fajula, A. Galarneau, Selective Cu^{2+} adsorption and recovery from contaminated water using mesoporous hybrid silica bio-adsorbents, Microporous Mesoporous Mater. 146 (2011) 141–150.

[28] G. Li, Z. Zhaob, J. Liu, G. Jiang, Effective heavy metal removal from aqueous systems by thiol functionalized magnetic mesoporous silica, J. Hazard. Mater. 192 (2011) 277–283.

[29] İ. Tosun, Ammonium removal from aqueous solutions by clinoptilolite: Determination of isotherm and thermodynamic parameters and comparison of kinetics by the double exponential model and conventional kinetic models, Int. J. Environ. Res. Public Health 9 (2012) 970–984.

[30] M.A. Kamboh, I.B. Solangi, S.T.H. Sherazi, Sh. Memon, A highly efficient calix [4] arene based resin for the removal of azo dyes, Desalination 268 (2011) 83–89.
[31] T.A. Davis, B. Volesky, A. Mucci, A review of the biochemistry of heavy metal biosorption by brown algae, Water Res. 37 (2003) 4311–4330.
[32] H. Zheng, D. Liu, Y. Zheng, S. Liang, Z. Liu, Sorption isotherm and kinetic modeling of aniline on Cr-bentonite, J. Hazard. Mater. 167 (2009) 141–147.
[33] K. Parida, K.G. Mishra, S.K. Dash, Adsorption of toxic metal ion Cr(VI) from aqueous state by TiO_2-MCM-41: Equilibrium and kinetic studies, J. Hazard. Mater. 241–242 (2012) 395–403.
[34] F. Gimbert, N. Morin-Crini, F. Renault, P.M. Badot, G. Crini, Adsorption isotherm models for dye removal by cationized starch-based material in a single component system: Error analysis, J. Hazard. Mater. 157 (2008) 34–46.
[35] L. Khezami, R. Capart, Removal of chromium (VI) from aqueous solution by kinetic and equilibrium studies, J. Hazard. Mater. 123 (2005) 223–231.
[36] Y.H. Jo, S.H. Do, S.H. Kong, Feasibility test for waste-reclaimed material to remove Cu^{2+} and Zn^{2+} Kinetics and applications to treat a real plating wastewater, J. Environ. Chem. Eng. 2 (2014) 619–625.
[37] Y.A. Ouaissaa, M. Chabani, A. Amrane, A. Bensmaili, Removal of tetracycline by electrocoagulation: Kinetic and isotherm modeling through adsorption, J. Environ. Chem. Eng. 2 (2014) 177–184.
[38] X.P. Xinjiang, D. Zhang, Removal of malachite green from water by Firmiana simplex wood fiber, Electron. J. Biotechnol. 12 (2009) 1–10.
[39] K.Y. Foo, B.H. Hameed, Insights into the modeling of adsorption isotherm systems, Chem. Eng. J. 156 (2010) 2–10.
[40] A.O. Dada, A.P. Olalekan, A.M. Olatunya, O. Dada, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn^{2+} onto phosphoric acid modified rice husk, IOSR, J. Appl. Chem. 3 (2012) 38–45.
[41] E.L. Foletto, G.C. Collazzo, M.A. Mazutti, S.L. Jahn, Adsorption of textile dye on zinc oxide: Equilibrium, kinetic and thermodynamics studies, Sep. Sci. Technol. 46 (2011) 2510–2516.