Int. J. Nano Dimens., 7 (4): 295-307, Autumn 2016

ORIGINAL ARTICLE

Synthesize and characterization of Aminosilane functionalized MCM-41 for removal of anionic dye: Kinetic and thermodynamic study

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Received 11 March 2016; revised 28 July 2016; accepted 23 August 2016; available online 02 November 2016

Abstract
In this study, removal of Acid blue 62 from aqueous solution by mesoporous silicate MCM-41 modified by Aminopropyltriethoxysilane (APTES) composite was studied. Properties of synthesized composite were analyzed and confirmed by SEM, EDX and FTIR. Results show that Langmuir adsorption isotherm has the best compatibility with the results of experiments. Kinetic analysis using pseudo-first-order model, pseudo-second-order and the intra-particle diffusion model was carried out. Results also confirmed that adsorption process is compatible with the pseudo-second-order kinetic model. Thermodynamic parameters such as Gibbs free energy changes (ΔG^o), Enthalpy changes (ΔH^o) and Entropy changes (ΔS^o) were calculated. Negative value of ΔG^o and positive value of ΔH^o show that adsorption of Acid blue 62 on aminated nanocomposite is a spontaneous process also endothermic.

Key words: *Acid blue 62; Adsorption; Adsorption isotherm; Adsorption kinetic; MCM-41.*

How to cite this article
Torabinejad A, Nasirizadeh N, Yazdanshenas M E, Tayebi H. Synthesize and characterization of Aminosilane functionalized MCM-41 for removal of anionic dye: Kinetic and thermodynamic study. Int. J. Nano Dimens., 2016; 7 (4): 295-307, DOI: 10.7508/ijnd.2016.04.005.

INTRODUCTION

Dyes have been extensively used in textile industries, pulp mills and dyestuff manufacturing, and more than 9 million tons of highly colored dye wastewaters are produced annually [1]. Disposal of these dyes and remediation of associated contaminated sites remain a worldwide concern [2, 3]. Therefore, before discharging wastewaters to aquatic ecosystems, it is necessary to reduce dye concentration in the waste water. Adsorption process is known to be a promising technique, which has great importance due to ease of operation and comparable low cost of application for removing dyes from wastewater [4, 5]. Highly functional porous materials with high surface area are generally used as suitable adsorbents to investigate adsorption efficiency for removing of dyes [4, 6]. Since the discovery of the mesoporous materials familyM41S by the Mobil company in 1992 [7], research efforts have been made extensively in their preparation and applications such as catalysts [8], ion exchangers [9], separators [10], and adsorbents [11- 13], etc. As the best investigated member of the M41S group, the hexagonal MCM-41 has attracted more awareness because of its interesting properties, particularly the high surface area and pore volume, narrow mesoporous size distribution, and high thermal and hydrothermal stability [14]. To improve the adsorption capacity of MCM-41, surface modifications have been used successfully in tailoring the surface chemistry and pore openings of these materials [4, 15]. Surface modification also improves selectivity of the MCM-41 using the specific interactions between the adsorbents and the adsorbates. Amines as the well-known functional groups are used in many studies for surface modification of different types of adsorbent [16, 17]. Many organo-functional groups have been applied to improve the organic molecules adsorption capability of MCM-41 [18]. Transition metals such as nickel has been extensively used to modify the MCM-41 silica framework to make the material as potential catalysts [8, 9]. This

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paper presents an assessment of aminosilane-MCM-41 for the removal of Acid blue 62 from aqueous solution. We decided to evaluate Acid blue 62 removal potential of aminated-MCM-41 under various operating conditions such as pH, initial dye concentration, adsorbent dosage and temperature, The kinetics, thermodynamics and isotherms of dye adsorption onto aminosilane-MCM-41 were also investigated. Various characterization techniques such as SEM, EDX and Fourier transform infrared (FTIR) spectroscopy were applied to characterize the changes of MCM-41 physiochemical properties due to the loading of Aminopropyltriethoxysilane and provide more information about the adsorption characteristics.

EXPERIMENTAL

Synthesis of MCM-41

MCM-41 was synthesized according to method as described by Kamarudin *et al.* [19] briefly, 2.4 g cetyltrimethylammonium bromide (CTAB) as template was dissolved in 120 g deionized water and stirred until homogeneous and clear solution was formed. After that, 8 ml ammonium hydroxide was poured in the solution and stirred for 5 min. Then, 10 ml of tetraethylorthosilicate (TEOS) as a source of silicon was added into the solution. The solution was stirred for 24 h. Then the solution was transferred to a Teflon-lined steel autoclave and heated to 145°C for 2 days. After that, the pH was adjusted typically during 48-72 h to reach a stable value. The final product was filtered , washed with the deionized water and dried in oven at 100 °C for 24 h. Calcination was performed at 600°C for 5 h.

Preparation of amin- functionalized MCM-41

The aminated MCM-41 nano powder was synthesized as follows: 1.00 g of MCM-41 and 10 mL of 3-Aminopropyltrimethoxysilane (APTES) were stirred with 50 mL of normal hexane. It was carried out under the reflux for 6 h. Then, the prepared product were filtered, washed with acetone and deionized water, and finally dried for 24 h under vacuum at 50°C [11].

Characterization

The presence of functional groups on the surface of MCM-41 were demonstrated by Fourier Transform Infrared Spectrometry (FTIR, 8400S,Shimadzu, Japan) in the wave numbers ranging from 400 to 4,000 cm^{-1} using KBr method. Sample surface morphologies were analyzed by a HITACHI S-4160 scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectroscopy (EDAX).

Batch adsorption experiments

Batch experiments were carried out in a 250 mL Erlenmeyer flask containing 50 mL of dye solutions for initial concentrations of 40, 60, 80, 100, 120 mg L^{-1}. Dye solutions were prepared in phosphate buffer of 0.1 M. The experiments were performed under varying pH (3–11) and adsorbent dose (0.04– 0.20 g). A pH of the solution was adjusted using 1.0 M HCl and NaOH. To investigate the effect of temperature, adsorption of Acid blue 62 on MCM-41 and composite in the temperature ranges of 25 up to 45°C, initial dye concentration of 40 up to 120 ppm, 0.1 g of composite and 0.16 g of MCM-41 at equilibrium time was studied. After adsorption, for each concentration and after 15, 30, 45, 60, 90, 120 and180 minutes of contact times, the treated solution was centrifuged by a Kokusan Ensinkico centrifuge apparatus at 5000 rpm for 30 minutes. The concentration of dye solutions was measured using ultraviolet-visible spectrophotometer (6310, JENWAY, UK) prior and after adsorption process. q_e and q_t were obtained through the following relationship [11]:

$$q_t=(C_i- C_t) \times V/M \quad (1)$$

Where q_t (mg/g) is the adsorption capacity at any time t, C_i, and C_t (mg/L) are dye solution concentrations at initial time and any time t, V, and M are volume of dye solution (L) and adsorbent dosage (g), respectively. Batch equilibrium experiments were also done to determine the adsorption of dye onto composites at equilibrium state. The adsorption capacity at equilibrium was calculated using the following equation [11]:

$$q_e=(C_i- Ce)\times V/M \quad (2)$$

Where C_e (mg L^{-1}) is the dye concentration at equilibrium. The removal efficiency was also calculated as follows [11]:

$$\text{Removal efficiency} = (C_i - C_t)/C_i \times 100 \quad (3)$$

RESULTS AND DISCUSSION

Characterization of amine-MCM-41 adsorbent

Fig. 1 shows the SEM images of MCM-41 and aminated MCM-41 nanoparticles. As seen in Fig. 1(a), MCM-41 nanoparticles are spherical and uniform. Fig. 1(b) shows colonies of aminated MCM-41 particles. It can be seen that the particle size increased due to the coverage of MCM-41

surface by aminopropyltriethoxysilane. So, this image shows that aminopopyl is well established on the support.

EDX spectra of MCM-41 and aminated MCM-41 are shown in Fig. 2. The EDX analysis of MCM-41 (Fig. 2(a)) shows the presence of C, O and Si. The EDX spectrum of the aminated MCM-41 composite (Fig. 2 (b)) confirms the presence of N in addition to the other elements. Also, after loading of MCM-41 by aminosilane groups, weight percent of Si increased from 27.5 to 35.4%. So, it can be conclude that after loading of MCM-41, aminopropyltriethoxysilane as a functional group is established on the surface of support.

FTIR spectra in the range of 4000–400 cm^{-1} were used to confirm the presence of aminosilane on the surface of MCM-41. Fig. 3a and b are for MCM-41 and NH_2-MCM-41, respectively. In Fig. 3a, broad band in the range of 3750-2800 cm^{-1} is related to reflection of structure of Si-OH groups with absorbed water molecules and destroyed places, the observed peak at 1095 cm^{-1} is related to vibrations of Si-O-Si, the peaks at 802 cm^{-1} and 462 cm^{-1} are related to symmetric stretch and bending stretch, respectively [11,20]. As can be seen in the Fig.3b for NH_2-MCM-41, a broad band is observed at 1596 cm^{-1} related to bending vibration of N-H groups. Stretch bands of N-H and C-N are also observed in the range of 3750-3000 cm^{-1} and 1350-850 cm^{-1}, respectively. Also, reduction in peak intensity in the range of 3750-3000 cm^{-1} is as a result of loading of MCM-41 by aminosilane groups which confirms nano NH_2-MCM-41 is formed.

Effect of pH

The effect of pH on the removal of Acid blue 62 by MCM-41 and aminated MCM-41 nanocomposite in the range of 3-11 is investigated and shown in Fig. 4. As can be seen, the maximum removal of dye occurred at pH 3 and according to the dye being anionic, this trend is expected. Since the adsorbent surface is positively charged at lower pH values, the strong electrostatic attraction between the positive charges of the adsorbent and the negative charges of dye molecules leads to the maximum adsorption of dye. If the pH increases, the number of negative charges of the sites increase and positive charges decrease, so the electrostatic repulsion of negatively charged polyaniline and molecules of anionic dye leads to lower adsorption of dye [21]. The low adsorption of Acid blue 62 in alkaline environment is due to the competition between OH^- ions and anionic dye molecules to be adsorbed on the sites. Experiments were carried out at 25°C, 0.1 g of absorbents, initial dye concentration of 40 ppm, and contact time of 120 min.

Effect of adsorbent dosage

To investigate the effect of adsorbent dosage, 0.02-0.2 g of MCM-41 and nanocomposite were examined for 120 min with 40 ppm of dye solution. The percentage of dye removal for two adsorbents is shown in Fig.5. As seen, synthesized composite showed the highest efficiency in comparison with MCM-41 and more than 0.1 g of composite dosage, no changes have been observed in the dye removal efficiency. So 0.1 g of composite was used in subsequent experiments.

Due to well-distributed aminosilane-functionalized groups on the surface of MCM-41, the numbers of amine groups per unit area of MCM-41 will increase, leading to increase in adsorption capacity of composite in comparison with MCM-41. The optimum dosage of MCM-41 is 0.16 g. At these dosages, no changes in dye removal were observed.

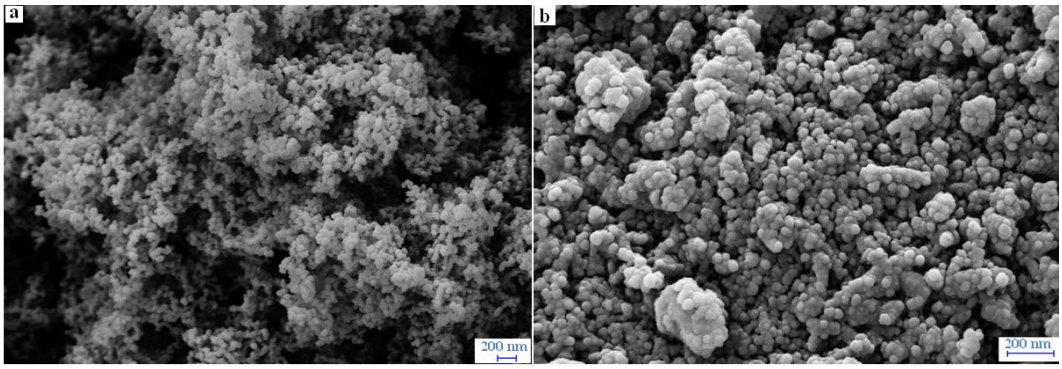

Fig.1: SEM images of MCM-41 (a) and aminated MCM-41 nanocomposite (b).

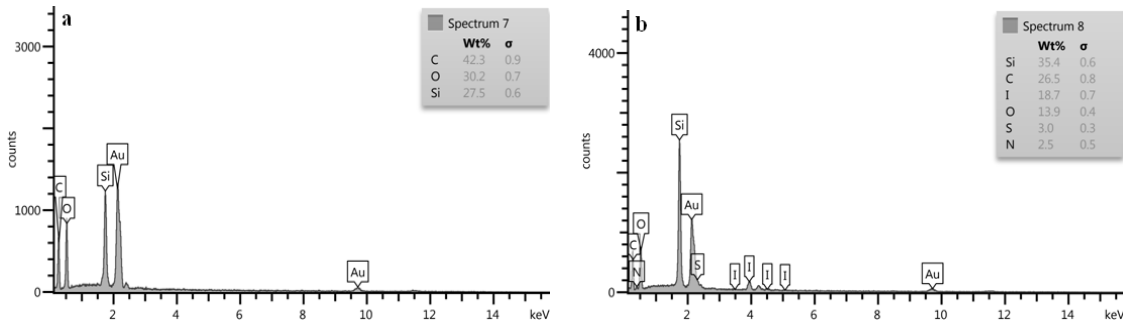

Fig. 2: EDX spectrum of MCM-41 (a) and aminated MCM-41 nanocomposite (b).

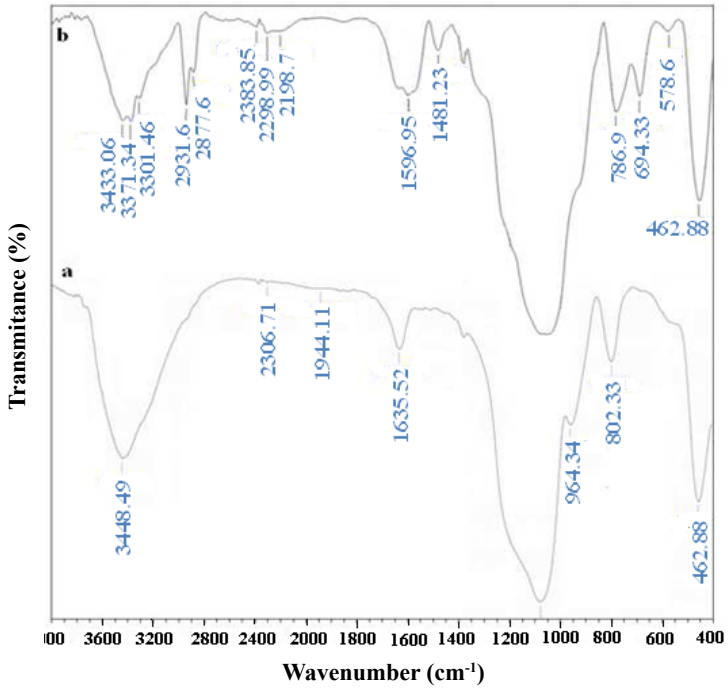

Fig. 3: FTIR spectra of MCM-41 (a) and aminated MCM-41 nanocomposite (b).

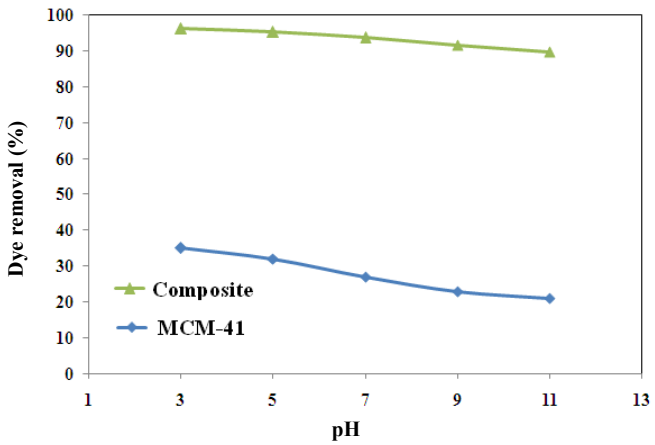

Fig.4: Effect of pH on Acid blue 62 removal (0.1 g of adsorbents, temperature of 25 °C, initial dye concentration of 40 ppm and 120 min contact time).

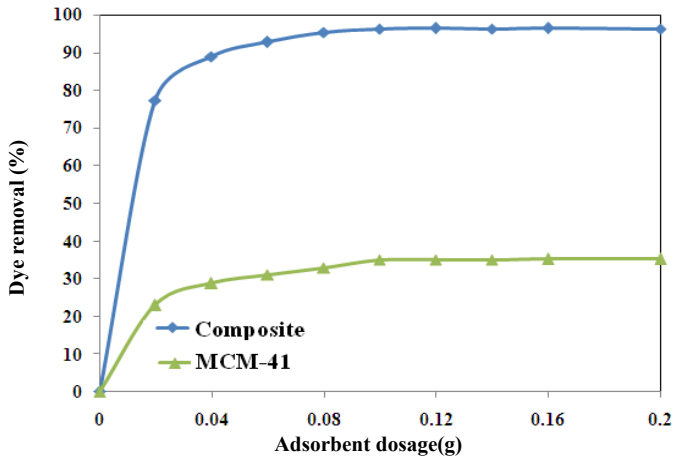

Fig. 5: Effect of adsorbent dosage on percentage of dye removal (initial dye concentration of 40 ppm, contact time of 120 min and pH =3).

Effect of contact time

To study the effect of contact time, experiments were carried out in the range of, 40 up to 120 ppm of dye solutions, contact times of 0–180 min, 0.1 g of composite, and pH of 3. As seen in Fig.6, almost after 120 min, dye adsorption on the surface of composite will reach the equilibrium state. So, 120 min of contact time was considered as an equilibrium time. The aggregation of dye molecules occurs on the surface of composite with an increase in the contact time. So, deeper penetration of dye into the sites having higher energies is impossible. The rest of experiments were considered for 120 min of contact time. The individual, smooth, and continuous adsorption curves show the saturation state and indicate monolayer covering of adsorbent surface by dye molecules [22].

Effect of dye concentration

As can be seen in Fig.7, with the increase in initial dye concentration from 40 up to 120 ppm, dye removal percentage will decrease, while adsorption capacity will increase. Initial dye concentration supplies the required driving force for overcoming mass transfer resistance between liquid and solid phases. Increase in the initial dye concentration also improves the interactions between dye and adsorbent [11, 12].

Effect of temperature

The effect of temperature on the adsorption of Acid blue 62 onto MCM-41 and aminated MCM-41 is shown in Fig.8. As can be seen in Fig.8, with the increase in temperature, efficiency of composite for the removal of dye is increased, while the efficiency of MCM-41 is independent of temperature. It is because of the presence of functional groups on the surface composite. Also, the increase of temperature, causes the increase of surface activity and increase the dye removal efficiency. So, it can be concluded that the adsorption of Acid blue 62 on the surface of composite in the range of 25 up to 45°C is the endothermic process [11, 12].

Thermodynamic studies

Thermodynamic parameters such as $\Delta G^{o,}$ ΔH^{o} and ΔS^{o} could be calculated by following equations [21, 23]:

$$k_c = C_{Ae}/C_e \quad (4)$$

$$\Delta G^{o} = -RT \ln k_c \quad (5)$$

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} \quad (6)$$

$$\log k_c = \Delta S^{o}/2.303R - \Delta H^{o}/2.303RT \quad (7)$$

In these equations, k_c, C_e and C_{Ae} are the equilibrium constant, the equilibrium concentration in solution (mg/L) and adsorbed dye on the adsorbent in the equilibrium state, respectively. ΔG^{o}, ΔH^{o} and ΔS^{o} are the changes in Gibbs free energy, enthalpy and entropy, respectively. The values of ΔHo and ΔSo could be calculated from the slope and intercept of the plot of log kc versus 1/T (equ.7). As shown in Fig.9, ΔGo could be calculated from equation (6). It is clear that adsorption of Acid blue 62on composite sample was enhanced with the increase of temperature from 298 K up to 318 K. So, the adsorption was endothermic. The values of thermodynamic parameters (ΔG^{o}, ΔH^{o}, ΔS^{o})

at different temperatures and different initial concentrations are shown in Table 1. Negative values of ΔG^{o} indicate that the adsorption process is feasible and spontaneous. As Table 1 exhibits, with the increase of temperature, Gibbs free energy becomes more negative and it shows that the increase of temperature promotes the spontaneity of the adsorption process. However, an increase of the initial dye concentration could make lower the Gibbs free energy, which is an indication of the fall in the spontaneous adsorption process. The positive values of the ΔH^{o} indicate that the adsorption is endothermic. Hence, the magnitude of the heat of adsorption (ΔH^{o}) could describe the type of adsorption. The process of adsorption may be physical or chemical. Involved forces in physical adsorption process are weak. So, heat of adsorption usually is not more than 21 kJ/mol.

In chemical adsorption, involved forces are more powerful than physical adsorption and heat of adsorption in chemical adsorption is such as heat of chemical reactions about 21-42 kj/mol [11, 22]. According to the obtained values of ΔH^{o}, the adsorption of Acid blue 62onto aminated MCM-41 nanocomposite is physical adsorption.

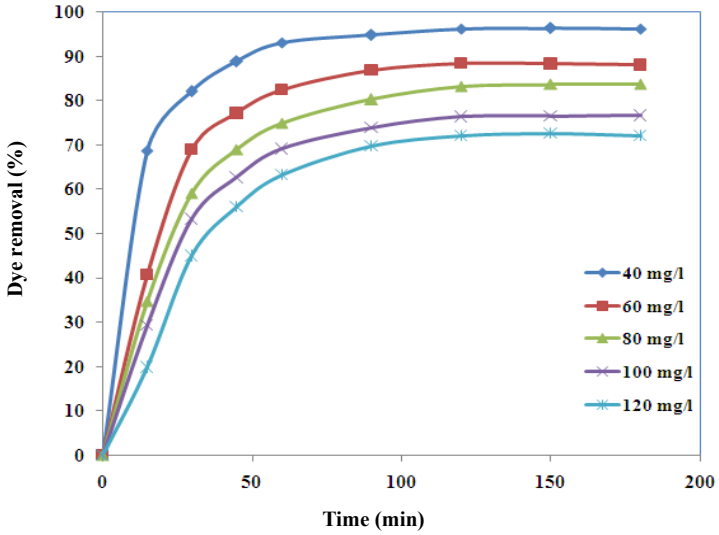

Fig. 6: Effect of contact time on the percentage of dye removal (initial dye concentration of 40 up to 120 ppm, adsorbent dosage of 0.1 g in 50 mL of dye solutions and pH=3).

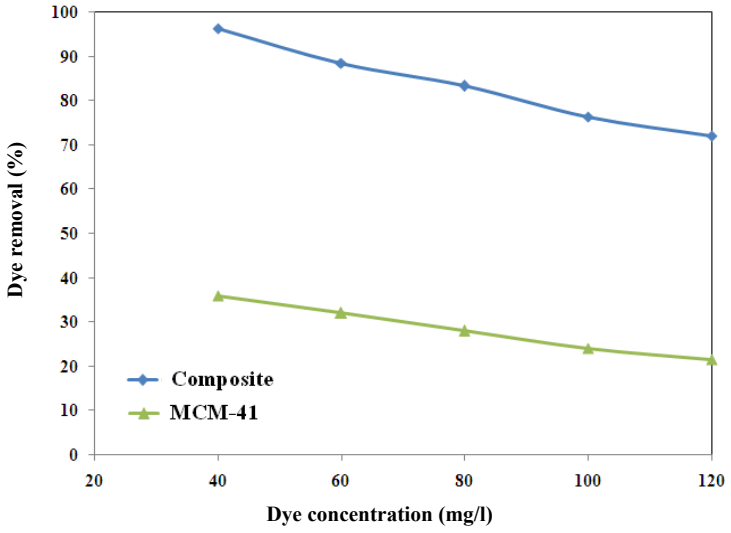

Fig. 7: Effect of initial dye concentration on the percentage of dye removal (Initial dye concentration: 40 up to 120 ppm, 0.1 g of nanocomposite, 0.16 g of MCM-41 and contact time of 120 min).

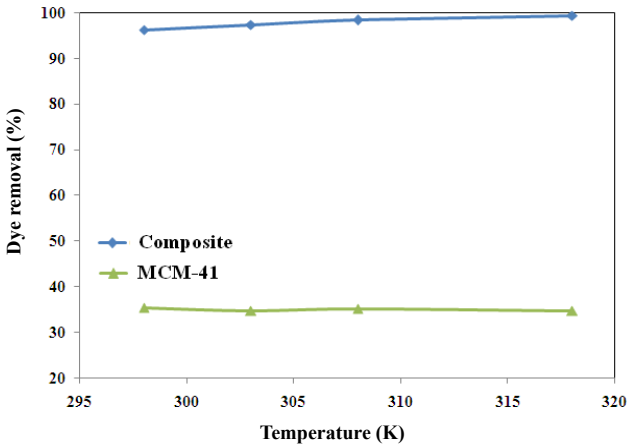

Fig. 8: Effect of temperature on dye removal percentage.

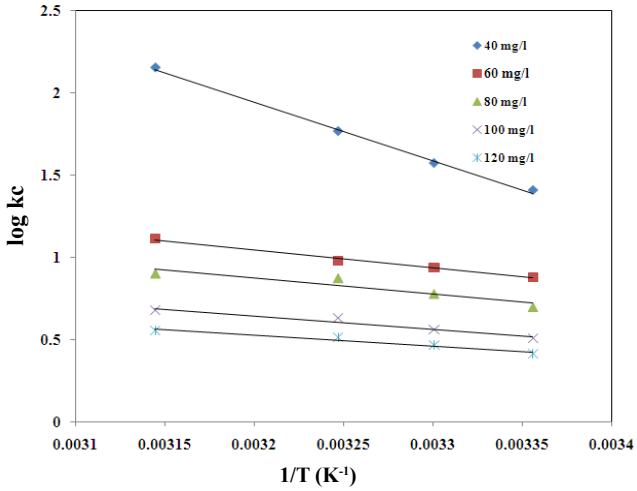

Fig. 9: Effect of temperatures in the range of 25 °C to 45 °C on the thermodynamic parameters (initial dye concentration: 40-120 ppm, composite dosage of 0.1 g, pH=3 and contact time of 120 min).

Table 1: Thermodynamic parameters for adsorption of Acid blue 62 on aminated MCM-41 nanocomposite.

Initial dye concentration (mg/l)	ΔH° (KJ/mol)	ΔS° (J/mol.K)	ΔG°(KJ/mol) 25°	30°C	35°C	45°C
40	68.45	256.065	-7.854	-9.138	-10.418	-12.979
60	20.73	86.353	-5.003	-5.435	-5.867	-6.730
80	18.59	76.186	-4.113	-4.494	-4.875	-5.637
100	15.392	61.577	-2.958	-3.266	-3.573	-4.189
120	12.474	49.974	-2.418	-2.668	-2.918	-3.418

Also, the mean adsorption energy (E) calculated from D-R model was found to be in the range of 0.9-4 kJ/mol (2672.61 J/mol), which are in the energy range of physical adsorption reactions [24]. The values of ΔS° was applied to describe the randomness of Acid blue 62 adsorption process in the adsorbent-solution interface. A positive value of ΔS° exhibits an increase in the irregularities in the interface of solution-adsorbent during the adsorption process, which implies an improvement of the efficiency. The positive values of entropy and enthalpy changes for adsorption of many dyes onto different adsorbents have been reported in many literatures [22, 25].

Equilibrium studies of adsorption

Adsorption isotherms are a major issue and play an important role in determination of maximum adsorption capacity. Adsorption isotherms indicate the effectiveness of the adsorbent during adsorption process and provide possibility of economic assessment of commercial applications of adsorbent for removal of some specific solutes. For this reason, Temkin, Dubinin-Radushkevich, Redlich-Peterson, Freundlich and Langmuir isotherms were applied. Parameters of each isotherm were calculated using linear regression and are presented in Table 2. Compatibility between the experimental data and the results of models could be ranked according to R^2 values as follows:

Langmuir Freundlich Redlich-Peterson Temkin Dubinin-Radushkevich.

For Langmuir isotherm, four kinds of linear regression were used the first kind was better matched with the experimental data and has the highest value of R^2 in comparison with three other linear models. Langmuir model is used to determine the value of adsorption capacity. q_m value signifies to the maximum adsorption capacity of the adsorbent (mg/g). Also, the Langmuir constant (k_L) is a coefficient that correlates the adsorbent to the adsorbate. High amounts of k_L values indicate the binding affinity for dye molecules. Freundlich isotherm model is based on experimental data in the nature and is available for heterogeneous surfaces [26]. Freundlich model exhibits that energy of adsorption decreases exponentially on the active sites of an adsorbent. Constant of Freundlich isotherm, k_f, is used for relative evaluation of the adsorption capacity (L g^{-1}). Constant *n* shows adsorption intensity and *1/n* is the heterogeneity factor of the surface. High values of k_f express readily of adsorption of dye molecules from aqueous solutions and high values of *n* indicate suitable and desirable adsorption. The value of *n* below to unity shows that adsorption is chemical process. If the value of *n* is equal to unity, the adsorption is linear. The values of *n* in the range of 2 to 10 suggest a favorable and physical adsorption. As can be seen in Table 2, *n* value obtained from linear regression is 3.95 that show desired adsorption. The correlation coefficient of Redlich-Peterson isotherm that is combination of Langmuir and Freunlich isotherms is obtained 0.985 that was smaller than that of Langmuir isotherm. So the Langmuir isotherm is also dominant isotherm. Dubinin-Radushkevich isotherm was evaluated and its correlation coefficient was obtained 0.923, is also lower than that of Langmuir isotherm. In order to study multilayer adsorption on the surface of composite, Temkin isotherm was examined. Correlation coefficient of Temkin isotherm was calculated about 0.982 that is lower than the correlation coefficient of Langmuir model, indicates monolayer adsorption was occurred on the surface of composite [27,28]. The dimensionless parameter R_L in the Langmuir isotherm is one of the effective parameters that is expressed by the following equation [29]:

$$R_L=1/(1+ K_lC_o) \quad (8)$$

Where C_o and b are the initial dye concentration and Langmuir constant, respectively. The type of adsorption, which is classified according to the values of R_L, is listed in Table 3. The values of R_L for the Langmuir isotherm are shown in Table 4 which demonstrates the adsorption of Acid blue 62onto the composite was a favorable. As can be seen, for whole linear models of Langmuir isotherm, adsorption of Acid blue 62 on composite is favorable.

Adsorption kinetics

Study of adsorption kinetics is a very important factor in the investigation of adsorption. In order to predict adsorption mechanism and determining of controlling steps such as mass transfer and chemical reaction. Kinetic models were used. To determine the rate of dye adsorption on the surface of composite, kinetic models of intra-particle diffusion, pseudo-first-order and pseudo-second-order were investigated. These models contain whole levels of adsorption such as outer film penetration, adsorption, and particle penetration. So they are sample model (like model). Kinetic pseudo-first-order model for reversible reactions that is between equilibrium solid or liquid is used while in pseudo-second-order model was assumed that speed limiter level may be chemical adsorption. In pseudo-first-order model, speed of adsorbent active sites that is occupied, is proportional with numbers of empty sites while in pseudo-second-order model, controller level of adsorption speed contains capacity forces that were done through sharing or changing electrons between adsorbent and adsorbate.

The pseudo-first order kinetic model

Pseudo first order model was suggested by Lagergren. This model is expressed using the following equation [29]:

$$\ln(q_e-q_t)=\ln(q_e)-k_{ad}t \quad (9)$$

Table 2: The values of parameters for each isotherm model.

Isotherm model	Isotherm equation	Linear form of isotherms	R^2
Langmuir	$q_e = q_m.K_L.C_e/(1+K_LC_e)$	1:$C_e/q_e = K_l/q_m + (1/q_m)\ C_e$ C_e/q_e vs. C_e q_m=100.00 , K_l=4.30	0.999
		2 : $1/qe = K_L/q_mCe + 1/qm$ 1/qe vs.1/Ce q_m=76.92 , K_l= 1.54	0.902
		3 : $q_e = q_m - (K_L)\ qe/Ce$ $q_e$vs. q_e/C_e q_m= 78.62 , K_l=1.70	0.783
		4 : $q_e/C_e = q_m/K_l - q_e/K_l$ q_e/C_evs. qe q_m=32.82 , K_l=1.90	0.559
Freundlich	$q_e=K_fC_e^{1/n}$	ln q_e=ln K_f + 1/n ln C_e Ln q_e vs. ln C_e n= 3.95 , K_f = 33.98	0.992
Redlich-Peterson	$q_e=k_RC_e / (1+\alpha_RC_e^{\beta})$	Ln(K_R*(C_e/q_e)-1) vs. blnC$_e$ + ln a_R K_R= 22 , α_R=0.325 , β=0.907 K_r was calculated by trial and error	0.985
Temkin	q_e=Bln (AC_e)	q_e vs. ln C_e B=13.63 A=12.16	0.982
Dubinin-Radushkevich	$q_e=q_m\exp(-K_{ads.}\epsilon^2)$	lnq_e vs. $(\ln(1+1/C_e))^2$ q_m=116.00 mg/g $K_{ads.}$=7e-8 mg/l $E=1/(\sqrt{2\beta})$= 2672.61 J/mol	0.923

Table 3: Effect of RL values on adsorption quality.

Adsorption quality	R_L
Unfavorable adsorption	$R_L > 1$
Favorable adsorption	$0 < R_L < 1$
Irreversible adsorption	R_L=0
Linear adsorption	R_L=1

Table 4: Values of RL for the adsorption of Acid blue 62 on nanocomposite at 298K and different initial concentrations.

Langmuir isotherm	R_L 40ppm	60ppm	80ppm	100ppm	120ppm
Linear type 1	0.006	0.004	0.003	0.002	0.002
Linear type 2	0.016	0.010	0.008	0.006	0.005
Linear type 3	0.014	0.010	0.007	0.006	0.005
Linear type 4	0.013	0.007	0.007	0.005	0.004

In the Lagergren pseudo first order model, q_e (mg g^{-1}) and rate constant k_{ad} (min^{-1}) were calculated at different concentrations from the plot of $\ln(q_e-q_t)$ versus *t* as shown in Fig.10. The findings are listed in the Table 5. The correlation coefficients of pseudo-first-order model are lower than that of the pseudo-second-order. In addition, the significant difference between experimental and calculated values of equilibrium adsorption capacity (q_e) was observed that shows the experimental data are not compatible with the pseudo-first-order kinetic model.

The pseudo-second order kinetic model

Pseudo-second order kinetic model of Ho has also been investigated which is given by the following equation [29]:

$$t/qt = 1//khqe2 + t/qe \quad (10)$$

From the plot of the values of t/q_t versus *t* and as are shown in Fig. 11, straight lines are obtained where the values of q_e and k_h could be estimated from the slope and intercept values. As demonstrated previously (Table 5), it could be concluded that the pseudo-second order model has the highest correlation coefficient. In all initial concentrations, straight lines with high correlation coefficient (0.995) were obtained. In addition, calculated q_e from pseudo-second-order model was compatible with experimental data. So, it could be concluded that the pseudo-second-order kinetic model expresses the adsorption process and it confirms that the controlling step of adsorption of Acid blue 62 on the composite surface may be chemical adsorption. As can be seen in Table 5, *K* values will decrease with increase of initial dye concentration. In higher concentrations, competition of dye molecules to achieve the active sites is higher and the rate of adsorption will be lower.

Intra-particle diffusion model

This kinetic model is based on the model that was presented by Weber and Morris [30] where the diffusion model is expressed using the following equation:

$$q_t=k_p t^{0.5}+C \quad (11)$$

Where C and k_p are the intercept and intra-particle diffusion rate constant (mg g^{-1} $min^{-0.5}$), respectively. In the eq. (11), k_p is the slope of the line which is obtained from plotting q_t values (mg/g) versus $t^{0.5}$ and the intercept value indicates the boundary layer effects. With an increase in the intercept values, contribution of adsorption on the controlling step of the rate will increase. Table 5 demonstrates the values of k_p obtained from the findings of the present study. It reveals that the diffusion rate increases with the enhancement of initial dye concentration, which is caused due to the high driving force values and the increase of C_o. If graphs from linear regression of q_t values against $t^{0.5}$ pass through the origin, intra-particle diffusion is the only rate-controlling step. However, as demonstrated in Fig.12, the linear graphs do not pass through the origin. Therefore, intra-particle diffusion is not the only rate-controlling step and other kinetic mechanisms may control the adsorption rate, which is proven with other studies of adsorption [31, 32].

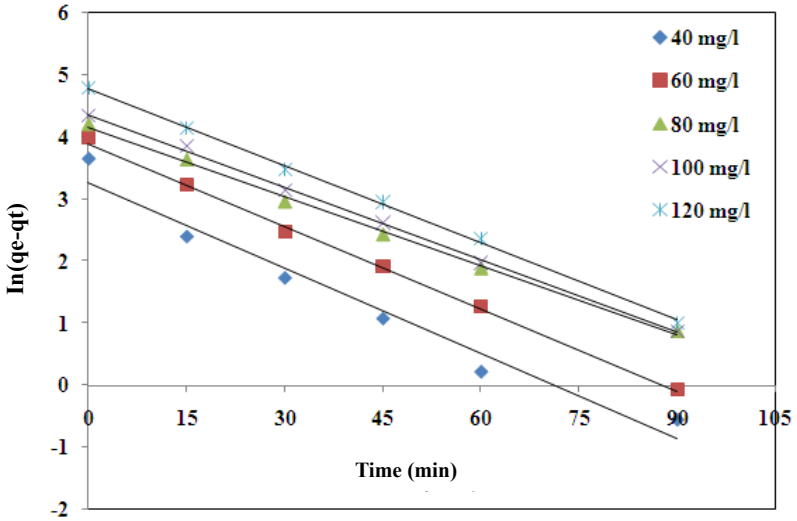

Fig. 10: Pseudo-first order kinetic model for adsorption of Acid blue 62 onto the nanocomposite at 25 °C.

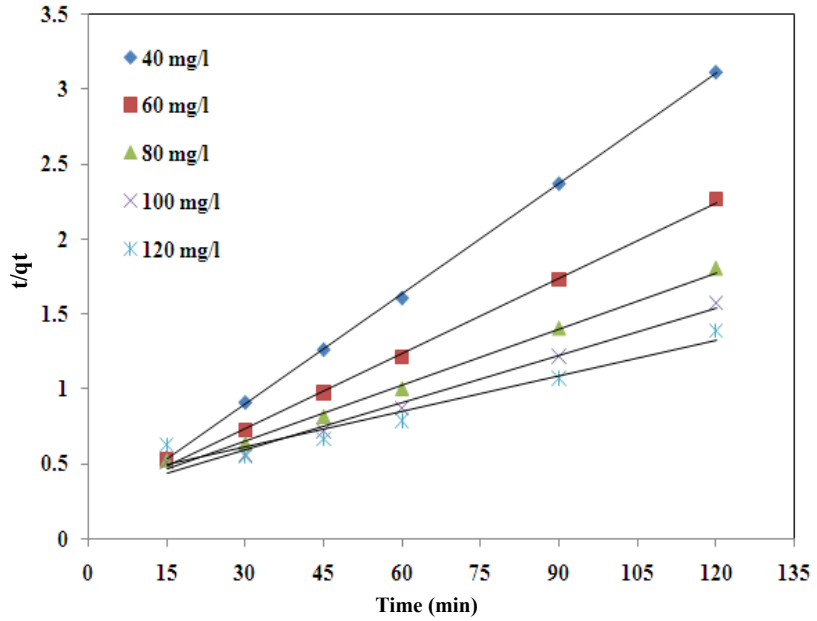

Fig. 11: Pseudo-second order kinetic model for adsorption of Acid blue 62 onto the nanocomposite at 25 °C.

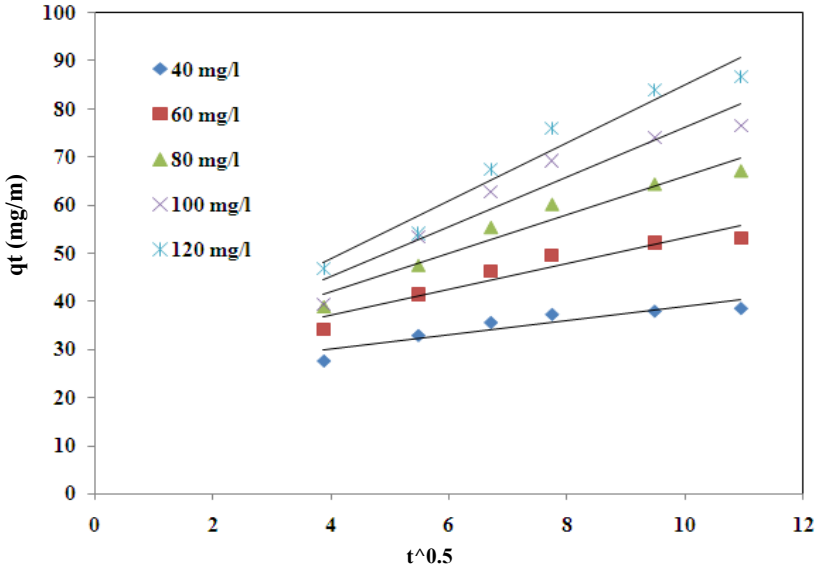

Fig. 12: Intra-particle diffusion model for adsorption of Acid blue 62 onto nanocomposite at 25 °C.

Table 5: Comparison of the constants of pseudo-first order, pseudo-second-order, intra-particle diffusion kinetic models, experimental and calculated values of qe at different initial concentrations of Acid blue 62.

Initial dye concentration (mg/L)	Pseudo-first order			Pseudo-second order				Intraparticle diffusion		
	k_{ad} (min^{-1})	q_e (mg/g)	R^2	k_h (g mg^{-1} min^{-1})	q_e (mg/g)	R^2 (mg/g)	$q_{e,exp.}$	K_p (mg/g.$min^{0.5}$)	C	R^2
40	0.045	26.000	0.964	0.00325	41.666	0.999	38.488	1.471	24.050	0.835
60	0.044	49.107	0.998	0.00106	52.500	0.998	53.024	2.647	26.550	0.909
80	0.037	63.117	0.997	0.00051	63.330	0.995	66.605	4.009	25.840	0.946
100	0.036	77.944	0.998	0.00010	75.000	0.997	76.326	5.176	24.260	0.916
120	0.041	80.554	0.998	0.00013	84.860	0.998	86.488	6.041	24.460	0.952

CONCLUSION

In this study the practical adsorbent with modification of mesoporous silicate MCM-41 by aminopropyltriethoxysilane was synthesized and used for removal of Acid blue 62 from aqueous media. Presence of aminosilane groups on the surface of MCM-41 leads to the improvement of the composite ability for dye removal. It was observed that with the increase of pH, dye removal efficiency was reduced due to ionic effects. With the increase of the composite dosage up to 0.1 g, dye removal efficiency increased because of dye concentration gradient between the solution and the surface of composite, then no significant changes were seen. By studying the changes of the initial dye concentration, it was observed that dye removal decrease with the increase of dye concentration. To investigate the equilibrium of adsorption, the contact time of 180 minutes in 40 ppm dye solution was evaluated. It was observed that after 120 minutes of contact, adsorption efficiency is constant and the equilibrium was achieved. Thermodynamic studies showed that temperature has a significant effect on dye removal. Percentage of dye removal increased with the increase of temperature, this is because of the increase of surface activity. The findings of thermodynamic study showed that the adsorption process is endothermic. Negative values of Gibbs free energy indicated that the adsorption process is spontaneous. Good conformity of experimental data with the isotherm models can be ranked based on R^2 values as following:
Langmuir Freundlich Redlich-Peterson Temkin Dubinin-Radushkevich

Therefore, between all studied isotherms for adsorption of Acid blue 62 on composite, Langmuir model was the predominant model and expressed the monolayer adsorption on the surface of composite. According to kinetic studies, pseudo-second-order kinetic model is compatible with thermodynamic behavior of Acid blue 62 adsorption on the surface of the composite in different dye concentrations.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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