

COMPARISON OF THE EFFICIENCY OF MESOPOROUS SILICAS AS ABSORBENTS FOR REMOVING NAPHTHALENE FROM CONTAMINATED WATER

ALI BALATI¹, AFSANEH SHAHBAZI^{1,*}, MOSTAFA M. AMINI², SEYED HOSSEIN HASHEMI¹, and KHOSRO JADIDI²

¹ Environmental Sciences Research Institute, Shahid Beheshti University, G.C., Tehran 1983963113, Iran

² Department of Chemistry, Shahid Beheshti University, G.C., Tehran 1983963113, Iran

* Corresponding author: a_shahbazi@sbu.ac.ir

ABSTRACT

Mesoporous silicas MCM-48 and SBA-15 were synthesized and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Fourier transform infrared (FTIR) spectroscopy. Adsorption capacity of two mesoporous silica for removing naphthalene from waste water was determined. The results indicate that under similar conditions, SBA-15 had a better adsorption capacity than MCM-48. In this context, SBA-15 was modified using 3-aminopropyltrimethoxysilane and the effect of contact time, adsorbent dose, solution pH and concentration of naphthalene was investigated in batch adsorption systems. Solution pH appeared to be a key factor affecting the adsorption of naphthalene by NH₂-SBA-15. The adsorption experiments revealed that a higher percentage of up to 79.3% of naphthalene was adsorbed in highly acidic media (pH of 2). The equilibrium data were analyzed using Langmuir and Freundlich isotherms and nonlinear regression analysis. This revealed that based on the correlation coefficient ($R^2 = 0.979$) the Langmuir model provided the best fit to the results. The adsorption kinetic was determined using the pseudo-first order, pseudo-second order and Elovich kinetic models. Of the kinetics models tested, the pseudo-first-order equation provided the best fit to the results ($R^2 = 0.991$) of the absorption of naphthalene by the adsorbent.

Keywords: mesoporous silica, naphthalene, adsorption, isotherm, kinetic

Introduction

Polycyclic aromatic hydrocarbon (PAHs) compounds are included on the priority pollutant lists of the European Union (EU) and United States Environmental Protection Agency (USEPA) because of their mutagenic, carcinogenic, and endocrine-disrupting properties (Vidal et al. 2011). They are ubiquitous environmental contaminants, which accumulate in coastal estuarine and marine sediments as well as aquatic organisms. Because it is difficult to degrade PAHs biologically they accumulate in the air, water bodies, soil and food. It is important, therefore, to develop an effective way of removing PAHs from the environment. The methods proposed include biodegradation (Ebihara and Bishop 2002), absorption (Chang et al. 2004) and high-energy electron beam irradiation (Cooper et al. 2002). However, most of these processes are difficult to handle and not always effective or economical. Of these methods, the addition of adsorbents to water/waste water is an efficient and economical way of removing PAHs from aqueous solutions (Vidal et al. 2011). Hence, it is important for managing environmental pollution to develop high capacity adsorbents for removing persistent organic pollutants from aqueous solutions (Lee et al. 2004). Mesostructured inorganic silicas such as M41S, HMS, MSU and SBA are good adsorbents because of their large surface area and pore volume, and uniform pore size (Sanz et al. 2012). MCM-48 with an interwoven and branched pore structure seems to be a good candidate for adsorbing PAHs from aqueous

solutions (Lee et al. 2004). Of the Among mesoporous silicas, SBA-15 has one of the largest pore sizes, ranging between 4.6 and 30 nm, with interconnected pore channels that make the ideal general purpose adsorbent (Shahbazi et al. 2012). There are very few studies on the adsorption of PAHs by SBA-15 and MCM-48, especially the adsorption of various PAHs by functionalized SBA-15. It would, therefore, be of considerable interest to develop functionalized mesoporous silicas for adsorbing PAHs (Anbia and Amirmahmoodi 2011). Organic/inorganic hybrids, synthesized by chemically grafting amines onto mesoporous silicas, which have high adsorption energy or potential charge association, have been successfully used as adsorbents (Wang et al. 2006). The presence of free pairs of electrons on the amine group of amine-functionalized mesoporous silicas should increase their sorptive properties for organic compounds in aqueous solutions. NH₂-SBA-15 is better at adsorbing halophenols than SBA-15 (Anbia and Amirmahmoodi 2011). Tao et al. (2010) report that adsorption of humic acid by SBA-15 is substantially less than that adsorbed by aminopropyl-functionalized SBA-15. The adsorption capacity and rate of adsorption of Cr(IV) by aminopropyl-, imidazole- and triazole-functionalized SBA-15 are excellent (Li et al. 2008). Compared to many PAHs, naphthalene, the simplest PAH, is a frequently recorded pollutant (Chang et al. 2004) and its efficient removal from waste water would greatly benefit the environment.

The aim of this study was to compare the adsorption of naphthalene from water by mesoporous MCM-48 and

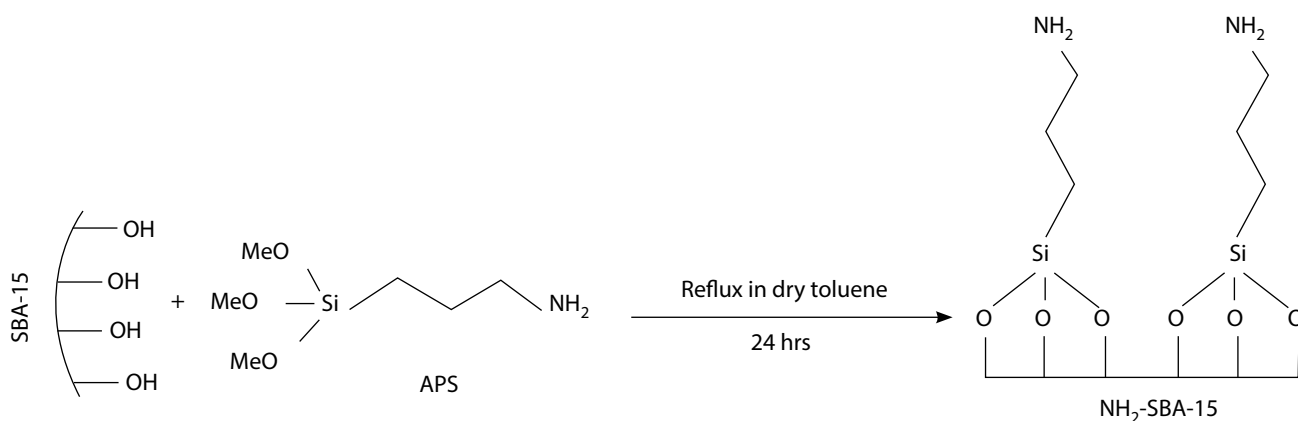


Fig. 1 Schematic illustration of the functionalization of SBA-15.

SBA-15, and find a more efficient mesoporous silica for removing this pollutant. In particular, this work reports the results of a study on the properties of amine-functionalized SBA-15 silica as naphthalene adsorbent. For this, the effects of various operating parameters such as adsorbent dose, pH, and concentration of adsorbate and contact time were studied, and the adsorption features isothermally and kinetically modelled.

Material and Methods

Chemicals and Reagents

Tetraethyl orthosilicate (TEOS, 98%), 3-aminopropyltrimethoxysilane (APS, 98%), cetyltrimethylammonium bromide (C₁₆H₃₃(CH₃)₃NBr; CTAB), sodium hydroxide, dry toluene (99.9%), methanol and naphthalene (Mw = 128.17 g mol⁻¹, water solubility = 31.0 g l⁻¹) were purchased from Merck. Pluronic P123 (Mw = 5800 g mol⁻¹; EO₂₀-PO₇₀-EO₂₀) and HCl (37%) from Aldrich. Aqueous solutions were prepared using double distilled water.

Synthesis of MCM-48 Mesoporous Silica

MCM-48 was synthesized using the conventional hydrothermal method as described by Schumacher et al. (1999). N-Hexadecyltrimethylammonium bromide was dissolved in deionized water, sodium hydroxide, and TEOS added to the mixture. The molar composition of the gel was 1.0 M TEOS: 0.65 M CTAB: 0.62 M H₂O. The solution was stirred for about 1 h, transferred into a polypropylene reactor and then heated and kept at 110 °C for 3 days. The product was filtered, washed with water and calcined at 550 °C for 6 h.

Synthesis and Modification of SBA-15 Mesoporous Silica

The SBA-15 material was synthesized as previously reported (Zhao et al. 1998). In a typical synthesis, 4.0 g of P123 was dispersed in 120 g of water and 8.64 g of 2.0 M HCl solution at 40 °C was added while stirring, after which 8.54 g of tetraethyl orthosilicate was added to

obtain a homogenous solution. The resultant gel mixture was continuously stirred at 40 °C for 24 h and then placed in a Teflon-lined autoclave kept at 100 °C for 2 days. After cooling, the solid product was filtered off and template removed by calcination in air at 500 °C for 4 h. For modification, SBA-15 mesoporous silica (1.0 g) was suspended in 30 ml of dry toluene, then in an atmosphere of dry nitrogen 4 ml of APS was added and the mixture refluxed for 10 h. The solid product was recovered by filtration, washed with dichloromethane and ethanol and dried. It was then Soxhlet extracted with a mixture of ethanol and dichloromethane (1 : 1) in order to remove the residue of the silylating reagent. The material was dried at 70 °C under a vacuum overnight (Lombardo et al. 2012; Shahbazi et al. 2012). The way in which the SBA-15 was functionalized is schematically illustrated in Fig. 1.

Characterization of Materials

The X-ray diffraction (XRD) of samples were recorded on a Philips 1830 powder X-ray diffractometer using Cu-K α radiation over a range of 0.8° to 6.6°, with a 2 θ step size of 0.01° and a step time of 1 s. Fourier transform infrared (FTIR) spectra of materials were recorded within a 500 to 4000 cm⁻¹ region on a BOMEM/MB Spectrometer in a KBr matrix. The morphology of the mesoporous materials was examined using a LEO 1455VP, Cambridge, U.K electron scanning microscope (SEM). TEM images were taken on a JEM-200CX instrument at an acceleration voltage of 200 kV. Single point BET analysis was carried out using a nitrogen adsorption technique and a Micromeritics ASAP 2010 analyzer.

Batch Equilibrium Isotherm and Kinetic Experiments

A series of naphthalene solutions (20% v/v methanol) of different concentrations were prepared by diluting a stock solution of 500 mg l⁻¹. The influence of experimental parameters, such as adsorbent dose (0.5–3.5 g l⁻¹), pH of solution (2.0–10.0, step size: 1), initial concentration (1–18 mg l⁻¹) and contact time (0.25–72 hours) were studied using batch processing. The pH of the naphthalene solution was adjusted by adding negligible volumes

(0–15 μl) of 0.1 M HCl or 0.1 M NaOH. After reaching equilibrium the adsorbents were separated from the solution by centrifugation at 7000 rpm for 10 min. The concentration of naphthalene in the solution was measured using a UV-vis spectrophotometer (UV-Vis 2100 shimadzu) at $\lambda_{\text{max}} = 275.5$ nm. The adsorption capacity of the adsorbent and its efficiency in removing naphthalene was calculated using equation (1) and (2), respectively:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

$$R = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

where q_e is the concentration of the adsorbed solute (mg g^{-1}); C_0 and C_e are the initial and equilibrium concentrations of the solute in solution (mg l^{-1}); V is the volume of the solution (l) and W (g) is the mass of the adsorbent.

Adsorption isotherm for determining the relationship between the amount of naphthalene adsorbed by NH_2 -SBA-15 and the concentration in the aqueous phase was recorded at pH 5 using solutions of predetermined concentrations of naphthalene and a known amount of NH_2 -SBA-15 adsorbent. Adsorption data for naphthalene were fitted using the Langmuir and Freundlich isotherm equations. The Langmuir isotherm model assumes a surface with homogeneous binding sites, equivalent sorption energies and no interaction between the substances adsorbed (Lombardo et al. 2012). The mathematical equation defining this model is:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (3)$$

The efficiency with which the naphthalene was adsorbed was checked using the dimensionless separation parameter R_L in the following equation:

$$R_L = \frac{1}{1 + b C_0} \quad (4)$$

where q_m and b represent the maximum adsorption capacity (mg g^{-1}) and the energy constant (l mg^{-1}) related to the heat of adsorption, respectively. C_0 and C_e are the initial and equilibrium concentrations of the solute in solution (mg l^{-1}). The value of R_L indicates if the Langmuir isotherm is irreversible ($R_L = 0$), favourable ($0 < R_L < 1$) or unfavourable ($R_L > 1$) (Huang et al. 2011a). Freundlich model takes the form of an exponential equation and therefore, assumes that the concentration of adsorbate on the adsorbent surface increases with increase in the concentration of adsorbate. This model predicts an

infinite amount of adsorption (Qin et al. 2012), which is defined by the following equation:

$$q_e = K_f C_e^{1/n} \quad (5)$$

where K_f ($\text{mg}^{(n-1)/n} \text{g}^{-1} \text{l}^{-1}$) and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

The effect of contact time on naphthalene removal was determined by adding 0.6 g of adsorbent (NH_2 -SBA-15) to 200 ml of a solution containing naphthalene at a concentration of 6 mg l^{-1} contained in 500 ml glass Erlenmeyer flasks and stirred continuously at 25°C and pH 5. The samples were collected at different time intervals.

In order to determine the sorption rate, the experimental data were analyzed using three kinetic models, namely, the pseudo-first-order (Eq. 6), pseudo-second-order (Eq. 7), and Elovich models (Eq. 8) (Benguella and Benaissa 2002):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

$$q_t = \frac{1}{\beta} \ln \alpha \beta + \frac{1}{\beta} \ln t \quad (8)$$

where q_e and q_t are the amount of naphthalene adsorbed by the adsorbent in mg g^{-1} at equilibrium and time t , respectively, k_1 is the constant of first-order adsorption in min^{-1} and k_2 is the rate constant of second-order adsorption in $\text{g mg}^{-1} \text{min}^{-1}$, α is the initial adsorption rate in $\text{mg g}^{-1} \text{min}^{-1}$, and β is related to the extent to which the surface is covered and the activation energy involved in chemisorption in g mg^{-1} .

Results and Discussion

Adsorbent Characterization

The XRD patterns of prepared samples are shown in Fig. 2. The patterns for MCM-48 show (2 1 1) and (2 2 0) diffraction peaks, which indicate an $Ia3d$ space group and that MCM-48 has a three-dimensional cubic mesoporous structure (Schumacher et al. 1999). The XRD patterns of SBA-15 and NH_2 -SBA-15 have a single strong peak (1 0 0) followed by two additional peaks (1 1 0, 2 0 0), which indicate they have a hexagonal lattice structure (Zhao et al. 1998). However, the sizes of the (1 1 0, 2 0 0) peaks recorded for NH_2 -SBA-15 are significantly smaller due to the incorporation of organic groups inside the channels of SBA-15 (Shahbazi et al. 2011). This pattern confirms the presence of a 2D hexagonal structure to the pores and suggests that the modification process did

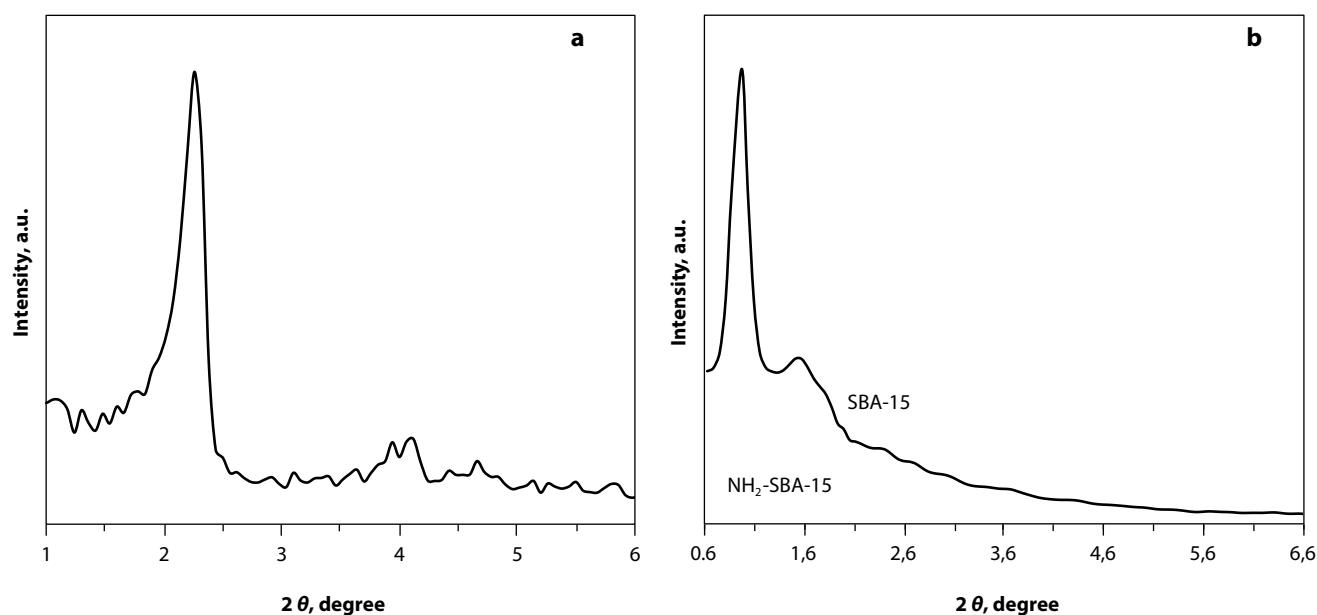


Fig. 2 The X-ray diffraction pattern of a) MCM-48; b) SBA-15 and NH_2 -SBA-15.

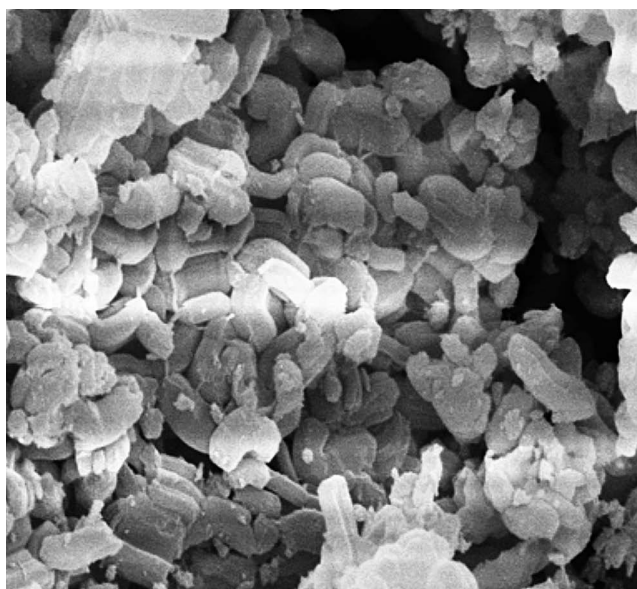


Fig. 3 SEM micrograph of SBA-15.

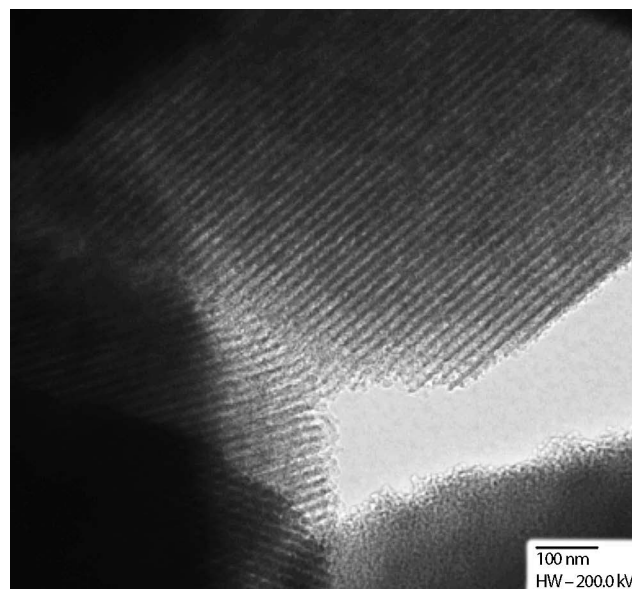


Fig. 4 TEM micrograph of SBA-15.

not affect the integrity of the framework of the ordered mesoporous SBA-15.

The SEM image of SBA-15 (Fig. 3) reveals that this mesoporous silica consists of well-defined wheat-like macro-structures aggregated in rope-like domains of a relatively uniform size. This result is in good agreement with the SBA-15 morphology presented in earlier reports (Shahbazi et al. 2012). Single point BET analysis indicated a surface area of $1238 \text{ m}^2 \text{ g}^{-1}$, $690 \text{ m}^2 \text{ g}^{-1}$ and $560 \text{ m}^2 \text{ g}^{-1}$ for MCM-48, SBA-15 and NH_2 -SBA-15, respectively.

TEM image of SBA-15 (Fig. 4) indicates well-ordered hexagonal arrays of mesopores (1D channels) and further confirms that SBA-15 has a 2D $p6mm$ hexagonal struc-

ture. Channel direction of the 2D-hexagonal structures was parallel to the thickness direction of the nanostructured hexagonal platelet morphologies (Zhao et al. 1998).

The IR spectrum of MCM-48 is shown in Fig. 5a. The peaks at 1078 cm^{-1} and 797 cm^{-1} are associated with Si-O-Si vibrations (Schumacher et al. 1999). Figure 5b shows the IR spectrum of SBA-15 before and after modification. As can be seen, there are several new bands in the amino-functionalized SBA-15. Peaks at 2859 and 2937 are due to C-H stretching vibration and that at 1579 cm^{-1} to N-H (primary amine) bending vibration of the amine group on the surface of the silica (Anbia et al. 2011).

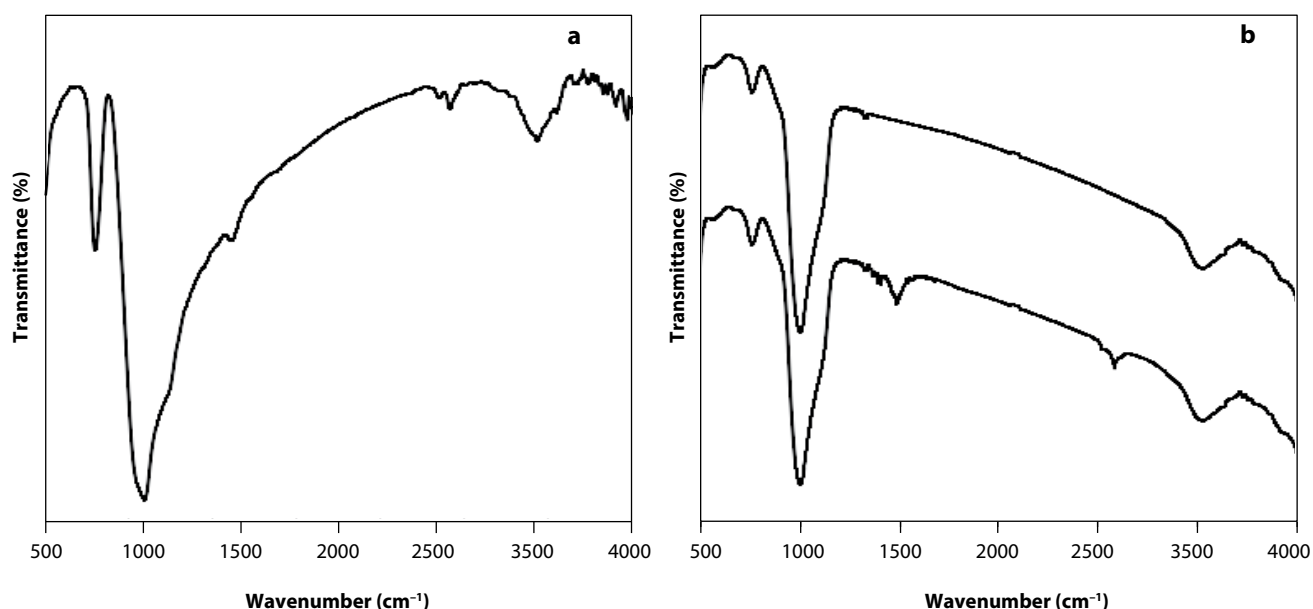


Fig. 5 The FT-IR spectra of a) MCM-48; b) SBA-15 and NH_2 -SBA-15.

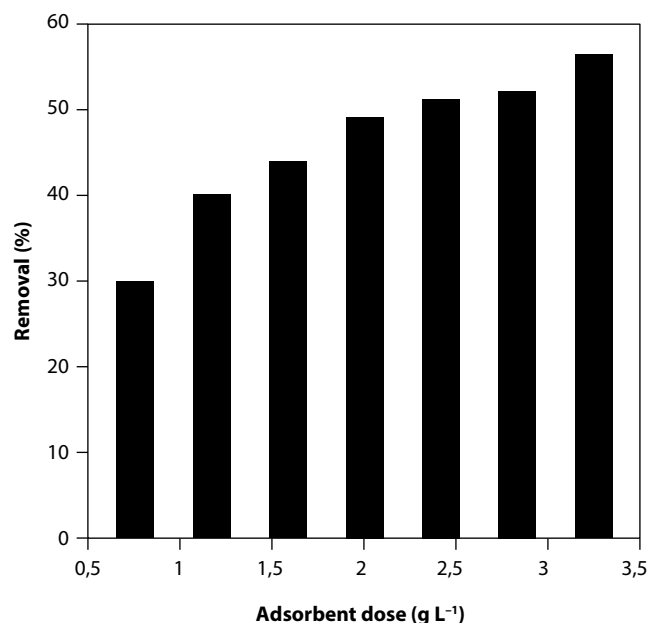


Fig. 6 Effect of the dose of the adsorbent on the percentage of naphthalene removed by NH_2 -SBA-15. (Conditions: 20 ml of 7 mg l^{-1} of naphthalene solution, agitation time 24 h, temperature of 25°C).

Effect of the Tpe of Adsorbent on Naphthalene Removal

The adsorption efficiencies of MCM-48 and SBA-15 were compared under the same sorption conditions. According to the results, the capacity for adsorbing naphthalene was 1.76 times higher for SBA-15 than MCM-48 (0.67 mg g^{-1} vs. 0.38 mg g^{-1}). This could be due both the micro- and mesoporosity structure and larger pore diameter of SBA-15, which improve the diffusion and mass transfer rates of adsorption processes (Huang et al. 2011b). Therefore, SBA-15 was selected for functionaliza-

tion using APS and the follow up experiments on its use as an adsorbent.

Effect of the Adsorbent Dosage

Experiments were done to establish an appropriate adsorbent dose for naphthalene removal from aqueous solutions (Fig. 6). The percentage of naphthalene removed increased from 29.9 to 53.6 with increase in the dosage of NH_2 -SBA-15 from 0.5 to 3.5 g l^{-1} due to the increase in contact surface of adsorbent and greater availability of the adsorbent (Shahbazi et al. 2012). Because of the negligible increase in percentage removal with increase in adsorbent dosage between 3 to 3.5 g l^{-1} a dose of 3 g l^{-1} of NH_2 -SBA-15 ($R = 52.2\%$) was chosen as the optimum adsorbent dosage for use in further experiments.

Effect of pH

The efficiency with which naphthalene is removed by NH_2 -SBA-15 at various pHs is presented in Fig. 7. The pH of solution may affect the surface charge of the adsorbent by the protonation of the functional groups, free surface hydroxyl groups and the degree of ionization and hydrolysis of the species present in solution (Dimos et al. 2009). The highest percentage adsorption of naphthalene by NH_2 -SBA-15 was recorded at $\text{pH} = 2.0$ (79.3%). With increase in pH from 2 to 8 the percentage adsorption of naphthalene decreased from 79.3% to 50.8%. However, the percentage of naphthalene removed increased from 58.1% to 62.3% with increase in pH from 9.0 to 10.0. It is highly likely that interactions occurred between the positively charged amine functional groups of the NH_2 -SBA-15 adsorbent in acidic media (Li et al. 2013) and the delocalized electron system of the aromatic ring of naphthalene (Horak et al. 2004).

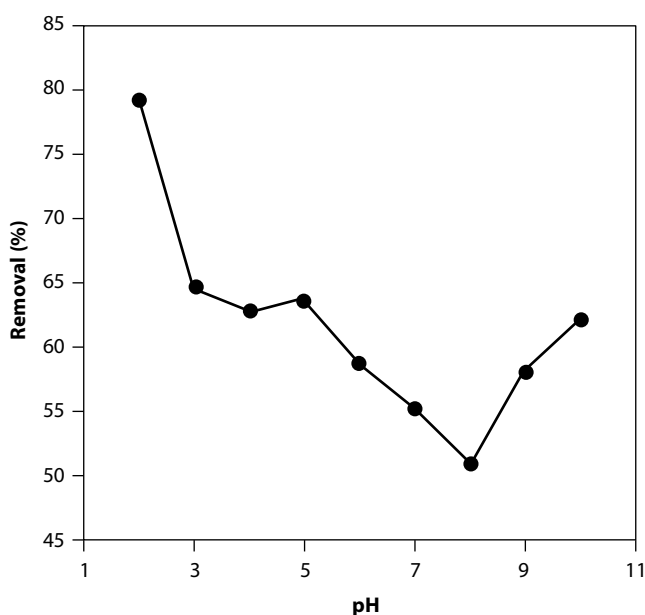


Fig. 7 Effect of pH of the solution on the percentage of naphthalene removed by $\text{NH}_2\text{-SBA-15}$. (Conditions: 0.06 g of adsorbent, 20 ml of 7 mg l^{-1} of naphthalene solution, agitation time 24 h and temperature 25°C).

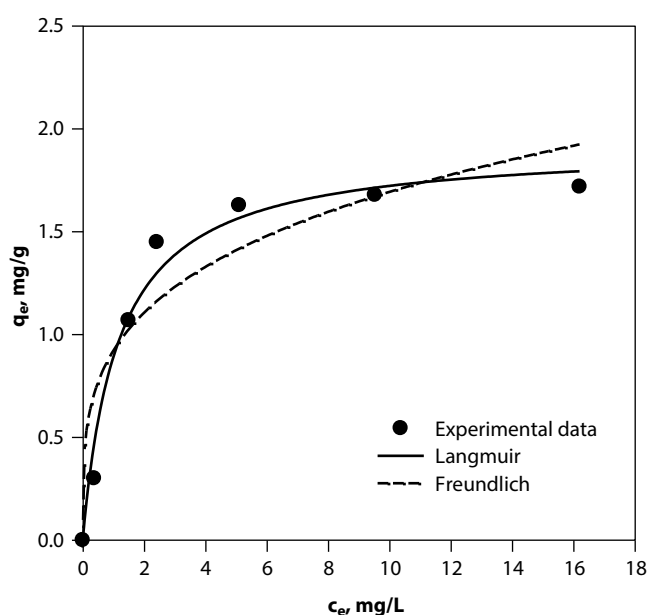


Fig. 8 Isotherms for the adsorption of naphthalene by $\text{NH}_2\text{-SBA-15}$. (Conditions: 0.06 g of adsorbent, agitation time 24 h, pH5, temperature 25°C and 20 ml of different concentrations of naphthalene solution).

Adsorption Isotherms

In order to show the sorption behaviour and estimate the adsorption capacity, adsorption isotherms were studied. The fits of the nonlinear Langmuir and Freundlich adsorption isotherms to the experimental results for the absorption of naphthalene are shown in Fig. 8. The b , q_m , n , K_f values and the nonlinear regression correlation coefficients (R^2) for Langmuir and Freundlich isotherms are given in Table 1. Both isotherms indicate a sharp initial slope indicating that the adsorbent operates at high efficiency at a low concentration and becomes saturated at high adsorbate concentrations. The constant of the adsorption capacity of the adsorbent *i.e.* K_f in the Freundlich isotherm is $0.922 \text{ (mg}^{(n-1)/n} \text{ g}^{-1} \text{ l}^{-1})$. The other Freundlich constant, n , is a measure of both the relative magnitude and diversity of energies associated with the adsorption of naphthalene onto $\text{NH}_2\text{-SBA-15}$ and that the numerical values of $1/n$ are $< \text{unity}$, indicate that the naphthalene was efficiently adsorbed by $\text{NH}_2\text{-SBA-15}$.

The high values of correlation coefficients indicate that the data conform well to the Langmuir model. The value of $q_m = 1.92 \text{ mg g}^{-1}$ predicted from the Langmuir curve for naphthalene is similar to the 1.72 mg g^{-1} recorded.

Similar results are reported for the adsorption of PAHs by different adsorbents (Anbia and Moradi 2009). Therefore, the adsorption process is likely to consist of the formation of a monolayer cover of naphthalene on the surface of the adsorbent. The efficiency of the $\text{NH}_2\text{-SBA-15}$ adsorbent in adsorbing naphthalene can be defined in terms of the separation factor (R_L), the values of which are presented in Table 2. As the values are $0 < R_L < 1$ the efficiency of adsorption of naphthalene of this adsorbent is high.

Adsorption Kinetics

An understanding of adsorption kinetics is a basic requirement for designing adsorption systems. Equilibrium kinetic data for a specific adsorbate/adsorbent system can be obtained from an experimental study of the adsorption of a system after different periods of time (Gök et al. 2008). The amount of naphthalene adsorbed by $\text{NH}_2\text{-SBA-15}$ was determined as a function of the exposure time. Figure 9 shows the time dependence of the amount of molecule solute adsorbed using this adsorbent.

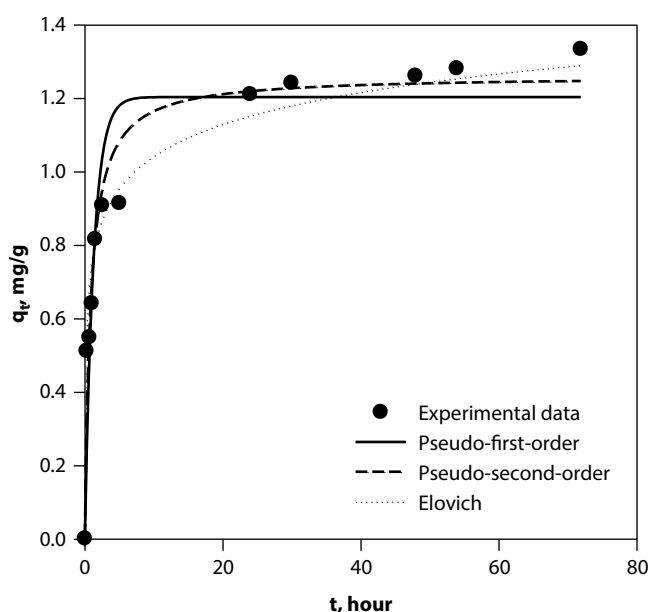
The parameters of the kinetic models and the regression correlation coefficients (R^2) are listed in Table 2.

Table 1. Isotherm parameters for adsorption of naphthalene onto $\text{NH}_2\text{-SBA-15}$

$q_{m,exp}$ (mg g^{-1})	Isotherm models						
	Langmuir				Freundlich		
	$q_{m,cal}$ (mg g^{-1})	b (l mg^{-1})	R_L	R^2	K_f ($\text{mg}^{(n-1)/n} \text{ g}^{-1} \text{ l}^{-1}$)	n	R^2
1.72	1.92	0.864	0.060	0.979	0.922	3.77	0.880

Table 2 Kinetic Parameters for adsorption of naphthalene onto NH₂-SBA-15

Kinetic model	Parameter	Value
Pseudo-first-order	q_e (mg g ⁻¹)	1.71
	k_1 (min ⁻¹)	0.678
	R^2	0.991
Pseudo-second-order	q_e (mg g ⁻¹)	1.92
	k_2 (g mg ⁻¹ min ⁻¹)	0.449
	R^2	0.959
Elovich	α (mg g ⁻¹ min ⁻¹)	6.22
	β (g mg ⁻¹)	0.001
	R^2	0.979

**Fig. 9** Kinetics of the adsorption of naphthalene by NH₂-SBA-15. (Conditions: 0.3 g of adsorbent, 100 ml of 6 mg l⁻¹ of naphthalene, agitation time 24 h, pH5, temperature 25 °C).

The removal efficiency increased sharply during the first 5 hours and then remains constant after 24 hours. Similar results are reported by Vidal et al. (2011) for the adsorption of PAHs onto periodic mesoporous organosilica (PMO). After 72 h the maximum percentage removed was about 72%. The Elovich model assumes that the rate of adsorption changes over time depending upon the percentage of the surface of the adsorbent covered. This kinetic model is valid for systems in which the adsorbing surface is heterogeneous (Pérez-Marín et al. 2007). The Elovich rate equation is commonly used to describe the sorption behaviour in which the equilibrium rate is rapidly reached and slowly decreases in the later periods of the sorption process (Chang et al. 2004). The value of Elovich α constant recorded is 6.22. This indicates the rate of sorption and the 0.001 for β the surface coverage.

Elovich constants reveal that the rate of adsorption of naphthalene was rapid in the initial stages and the surface available for adsorption of the sorbate decreased with time. Comparing the values of R^2 for the pseudo-first-order, pseudo-second-order and Elovich equations indicate that the pseudo-first-order was better than the two others and could be used to predict the adsorption kinetics of naphthalene by the NH₂-SBA-15 adsorbent. Furthermore, the results indicate that the experimentally determined adsorption capacity (1.33 mg g⁻¹) is similar to that predicted (1.71 mg g⁻¹) by the pseudo-first order model.

Conclusions

In this study, the efficiencies of two mesoporous silicas, MCM-48 and SBA-15, in removing naphthalene from waste water were compared. After determining that SBA-15 was better at removing naphthalene, this mesoporous silica was functionalized with amine groups. The optimum conditions for the removal of naphthalene using NH₂-SBA-15 adsorbent is a pH of 5.0 and dose of 3 g l⁻¹, which resulted in a removal efficiency of 79.3%. Of the equilibrium isotherm models investigated, the Langmuir model provided a good fit to the experimental data with high R^2 (0.979) and q_m (1.92 mg g⁻¹) values. The kinetic experiments showed that the adsorption of naphthalene by the NH₂-SBA-15 adsorbent was rapid and maximum adsorption capacities were achieved in approximately 24 h. The results of the kinetic studies indicate that the best fitting kinetic model was the pseudo-first order ($R^2 = 0.991$), followed by the Elovich ($R^2 = 0.979$) and the pseudo-second order equations ($R^2 = 0.959$).

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