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Sorptive Removal of Trinitroglycerin (TNG) from Water Using Nanostructured Silica-based Materials

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Trinitroglycerin (TNG), a nitrate ester, is widely used in the pharmaceutical industry for the treatment of angina pectoris (chest pain) and by the military for the manufacturing of dynamite and propellants. Currently, TNG is considered as a key environmental contaminant due to the discharge of wastewater tainted with the chemical from various military and pharmaceutical industries. The present study describes the use of a nanostructured silica material (Mobil Composite Material no. 48 [MCM-48]) prepared by mixing tetraethylorthosilicate (TEOS) and cetyltrimethylammonium bromide (CTAB) to remove TNG from water. The sorption of TNG onto MCM-48 rapidly reached equilibrium within 1 h. Sorption kinetics were best described using a pseudo-second order model, whereas sorption isotherms were best interpreted using the Langmuir model. The latter gave a maximum sorption capacity of 55.2 mg g⁻¹ at 40°C. The enthalpy and entropy of TNG sorption onto MCM-48 were 1.89 kJ mol⁻¹ and 79.0 J mol⁻¹ K⁻¹, indicating the endothermic nature of the TNG sorption onto MCM-48. When MCM-48 was heated at 540°C for 5 h, the resulting calcined material (absence of the surfactant) did not sorb TNG, suggesting that the surfactant component of the nanomaterial was responsible for TNG sorption. Finally, we found that MCM-48 lost approximately 30% of its original sorption capacity after five sorption-desorption cycles. In conclusion, the nanostructured silica based sorbent, with high sorption capacity and remarkable reusability, should constitute the basis for the development of an effective technology for the removal of TNG from contaminated water.

TRINITROGLYCERIN (Table 1) is one of the most widely used explosives and propellants (Akhavan, 1998). It has also been used in the health sector as a coronary vasodilator (Hartley et al., 1992). At concentrations ranging between 30 and 1300 mg kg⁻¹, TNG has been reported to be acutely toxic to mammalian species (Oh et al., 2004). Schwartz (1946) and Bressler (1949) reported that exposure to trace amounts of TNG may cause throbbing headaches associated with fever and nausea. In severe cases, an intense headache may become accompanied by psychic disturbances, mental confusion, and hallucinations (Bressler, 1949). Trinitroglycerin wastewater discharges from pharmaceutical and explosives manufacturing could contaminate groundwater and public drinking-water supplies (Hartley et al., 1992). It is thus critical to remove TNG from contaminated wastewaters. Several methods including sorption (Smith, 1983), chemical reduction with cast iron (Oh et al., 2004), biodegradation (Bhaumik et al., 1997; Christodoulatos et al., 1997; Accashian et al., 2000), and phytoremediation (Riefler and Medina, 2006) have been investigated for the removal of TNG from water. As for sorption, granular activated carbon (GAC) has thus far proven to be the most effective sorbent for TNG removal (Oh et al., 2004). However, GAC sorbent lose up to 50% of its sorption capacity after one sorption cycle (Concurrent Technologies Corporation, 1995).

The present study describes the use of a newly developed nanostructured silica-based material as a sorbent to effectively remove TNG from water. The nanosilica based material was previously synthesized by the hydrolytic condensation of the surfactant CTAB with TEOS. Aggregates of the surfactant molecules bonded with Si-O linkages in nanostructured silica act as the sorptive phase for organic pollutants in water (Aloulou et al., 2004).

During the last decade, nanostructured silica materials received a great deal of attention from the scientific community mainly because of their highly ordered porous structure, well-designed specific surface areas, and high porosity (Saad et al., 2008). Nanostructured silica-based materials have been applied as

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Abbreviations: BET, Brunauer–Emmett–Teller; C-MCM-48, calcined Mobil Composite Material no. 48; CTAB, cetyltrimethylammonium bromide; DNG, dinitroglycerol; EA, elementary analysis; GAC, granular activated carbon; HPLC, high performance liquid chromatograph; MCM-48, Mobil Composite Material no. 48; MNG, mononitroglycerol; TEOS, tetraethylorthosilicate; TNG, trinitroglycerin; UV, ultra violet; XRD, X-ray diffraction.

Table 1. Physicochemical properties of trinitrolycerin (TNG).†

Name	TNG
Molecular formula	C ₃ H ₅ (NO ₃) ₃
Log <i>K</i> _{ow}	1.62
Water solubility at 20°C (mg L ⁻¹)	1800
Vapor pressure at 20°C (mm Hg)	2.6 × 10 ⁻⁴

† All values were taken from Hartley et al. (1992) except for log *K*_{ow} (*K*_{ow}, octanol-water partition coefficient), taken from Tachon et al. (2008).

catalysts (Brunel, 1999), as sorbents (Saad et al., 2007, 2008), and as chemical sensing agents (Moller and Bein, 1998). Recently, nanostructured silica materials were used to remove organic pollutants such as 3-chlorophenol (Denoyel and Sabio, 1998), trichloroacetic acid (Bruzzoniti et al., 2000), 2,6 dinitrophenol (Sayari et al., 2005), toluene, naphthalene, and methyl orange (Zhao et al., 2005) from aqueous industrial wastewaters. To the best of our knowledge, the removal of TNG from water and wastewaters using nanostructured silica materials has not been reported before. The main objective of this work is to assess the potential use of the silica-based nanomaterials for the removal of TNG from polluted water because this important industrial chemical, which is widely used worldwide by the military and the health industry, is presently contaminating vast areas of soil and water.

Materials and Methods

Chemicals

Tetraethyl orthosilicate (TEOS, purity >98%), CTAB (water solubility = 36 g L⁻¹, critical micelle concentration = 0.33 g L⁻¹, purity >99%), and ammonium hydroxide (NH₄OH, 25%) were purchased from Sigma-Aldrich (Oakville, ON). Sodium hydroxide (99%) was obtained from EMD (Mississauga, ON). Trinitrolycerin dissolved in acetone (1000 mg L⁻¹) was provided by General Dynamics (Valleyfield, QC). Trinitrolycerin standard solution in acetonitrile (1000 mg L⁻¹) was purchased from Cerilliant Corporation (Round Rock, TX). All chemicals were used as received without further purification.

Synthesis of MCM-48 and C-MCM-48

The nanostructured silica MCM-48 was synthesized as described by Schumacher et al. (1999). Briefly, CTAB (2.4 g) was dissolved in deionized water (50 mL) followed by the addition of ethanol (50 mL) at room temperature. The resulting solution was treated with NH₄OH to bring pH to 12. Tetraethylorthosilicate (3.3 g) was then added to the above surfactant solution under stirring and the reaction was performed for 2 h at ambient temperature. The white precipitate formed was then filtered off, washed repeatedly with deionized water and isopropanol until pH reached 6 to 7 to get rid of the nonbonded fraction of the surfactant but entrapped within the nanosilica matrix (Zhao et al., 2005). The washed nanomaterial was dried at 50°C overnight before use as sorbent.

The surfactant in MCM-48 was completely removed by thermal decomposition at high temperature as described by Zhao et al. (2005). In a typical experiment the surfactant-containing MCM-48 (1 g) was heated in a furnace at 540°C for 5 h. The resulting calcined sorbent was henceforth denoted as C-MCM-48 (calcined Mobil Composite Material no. 48).

Material Characterization

The nanostructured silica material was first degassed at 120°C for 12 h, followed by determining nitrogen adsorption-desorption isotherms at 77 K using a Quantachrome (Boyton Beach, FL) Autosorb 1 volumetric analyzer. The specific surface area was determined using the linear part of the Brunauer-Emmett-Teller (BET) plot drawn at different relative pressures (P/P_0 , where P = applied pressure and P_0 = system initial pressure) ranging from 0.05 to 0.20. The pore size distributions were calculated from the nitrogen-desorption isotherm using the Barrett-Joyner-Hallenda and the Horvath-Kawazoe methods for the mesoporous (pore size ≥ 2.0 nm) and microporous (pore size < 2.0 nm) materials, respectively (Horvath and Kawazoe, 1983; Barrett et al., 1951). The total pore volume was evaluated from the nitrogen adsorbed amount at a $P/P_0 = 0.99$. Structural properties of the synthesized nanomaterials were examined by powder X-ray diffraction (XRD) using a Rigaku (The Woodlands, TX) D-Max-Ultima III diffractometer with nickel-filtered CuK α radiation at wavelength of 1.5406 Å. Powder diffraction patterns were obtained between 1° and 10° with a speed of 1° min⁻¹. Quantitative determination of the surfactant content was measured by C,H,N- elemental analysis (Fisons Instruments EAS1108, Place Frontenac Pointe Claire, Quebec, Canada).

Sorption-Desorption Studies

Sorption kinetics experiments were conducted by mixing MCM-48 (10 g L⁻¹) with 100 mL of 50 mg L⁻¹ TNG aqueous solutions in serum bottles (200 mL). Trinitrolycerin was first added to the serum bottle from an acetone stock solution (1000 mg L⁻¹), followed by evaporation of the solvent before the addition of MCM-48. Each bottle was stirred using a magnetic stirrer at room temperature. Aliquots of the solution (0.5 mL) were then sampled at various time intervals (2–120 min), filtered through a Millex-HV 0.45- μ m syringe filter (Millipore, Billerica, MA) and analyzed for TNG and its degradation products. The experiments were made in triplicate. The amount of TNG sorbed at time t , Q_t (mg g⁻¹), was calculated using Eq. [1]:

$$Q_t = (C_i - C_t)(V/m) \quad [1]$$

where C_i is the initial TNG concentration (mg L⁻¹), C_t is the TNG concentration in the aqueous phase at time t (mg L⁻¹), V is the solution volume (L), and m is the mass of the sorbent (g). To determine the role of the surfactant in the sorption process, we conducted a control sorption experiment using a calcined nanomaterial (C-MCM-48) and TNG in water under the same conditions described for MCM-48.

In a second experiment, sorption isotherms were conducted to probe the effects of temperature (10–40°C) on the sorption of TNG onto MCM-48 and to determine the maximum sorption capacities. Sorption experiments were performed in 20-mL borosilicate vials each filled with 10 mL of TNG solutions (100–700 mg L⁻¹) and the sorbent MCM-48 (10 g L⁻¹). All tests were performed at a pH range of 7.0 to 7.6 for 1 h. Aliquots of the solutions were withdrawn, filtered through a Millex-HV 0.45- μ m syringe filter, and analyzed for TNG and its degradation products. Experiments were made in triplicate.

The amount of TNG retained in the sorbent phase (mg g^{-1}), Q_c , was calculated using Eq. [2]:

$$Q_c = (C_i - C_c)(V/m) \quad [2]$$

where C_c is the equilibrium TNG concentration (mg L^{-1}) and C_i , V , and m have the same definition as in Eq. [1].

In a third experiment to determine the TNG recovery and sorbent reusability, we determined desorption of TNG from MCM-48 using Pyrex tubes (50 mL) (Fisher Scientific, Ottawa, ON, Canada) filled with MCM-48 (5 g L^{-1}) and 20 mL of aqueous TNG solution (200 mg L^{-1}). The mixture was stirred for 1 h, then centrifuged (3700 g) for 10 min. The clear aqueous phase was decanted. The remaining precipitate was then treated with 20 mL of acetonitrile–water solution (50% v/v) and agitated (500 rpm min^{-1}) for 18 h (water failed to desorb TNG from MCM-48). The washed sorbent was

reloaded once again with 20 mL of aqueous TNG (200 mg L^{-1}), and the sorbent was washed with acetonitrile–water solution (50% v/v) as described above. Four successive TNG sorption–desorption cycles were conducted using the same sorbent batch. The TNG recovery (%) was calculated using Eq. [3]:

$$\text{Recovery (\%)} = \frac{\text{TNG desorbed}}{\text{TNG sorbed on MCM-48}} \times 100 \quad [3]$$

Chemical Analysis

Trinitroglycerin was analyzed using high performance liquid chromatograph (HPLC)/ultraviolet (UV) equipped with a Discovery C18 separation column (25 cm by 4.6 mm by $56 \mu\text{m}$ particle size) (Supelco, Oakville, ON). Methanol–water mixture (50%, v/v) was used as the mobile phase at a flow rate of 1 mL min^{-1} for 15 min. The suspected partially denitrated TNG products 1,3-DNG, 1,2-DNG, 1-MNG, and 2-MNG were analyzed using HPLC/UV equipped with Ion-310 column (15 cm by 6.5 mm by $50 \mu\text{m}$ particles size) (Supelco, Oakville, ON). Sulfuric acid solution ($96 \mu\text{M}$) was used as mobile phase at a flow rate of 0.6 mL min^{-1} for 45 min. The wavelength was set at 205 nm for the UV detector. The injection volume for all HPLC analyses was $50 \mu\text{L}$.

Results and Discussion

Characterization of MCM-48

Results of the nitrogen adsorption–desorption analysis of C-MCM-48 and MCM-48 are presented in Fig. 1 and Table 2. Nitrogen adsorption–desorption isotherm of C-MCM-48 (Fig. 1a) exhibited a not-well-defined type IV isotherm with tendency to change to type I isotherm. This behavior is characteristic of materials with pore sizes on the borderline between mesopore (pore size $\geq 2.0 \text{ nm}$) and micropore (pore size $< 2.0 \text{ nm}$) ranges. Furthermore, the isotherm of MCM-48 (Fig. 1a) did not show capillary condensation step and the isotherm shape is type I, characteristic of microporous materials. As presented in Table 2, The BET surface area decreased from $1484 \text{ m}^2 \text{ g}^{-1}$ for C-MCM-48 to $269 \text{ m}^2 \text{ g}^{-1}$ for MCM-48. The corresponding pore sizes were 2.2 and 1.1 nm (see Fig. 1b), and the pore volumes were 0.89 and $0.16 \text{ cm}^3 \text{ g}^{-1}$ for C-MCM-48 and MCM-48, respectively. The decrease in the textural properties for MCM-48 was attributed to the occupation of the mesopores by the surfactant as previously reported by Kruk and Jaroniec (2000).

Powder XRD patterns are depicted in Fig. 2. Both C-MCM-48 and MCM-48 exhibited typical XRD patterns of cubic $1a3d$ structure with characteristic Bragg peaks around 2.8° and 3.0° attributed to the

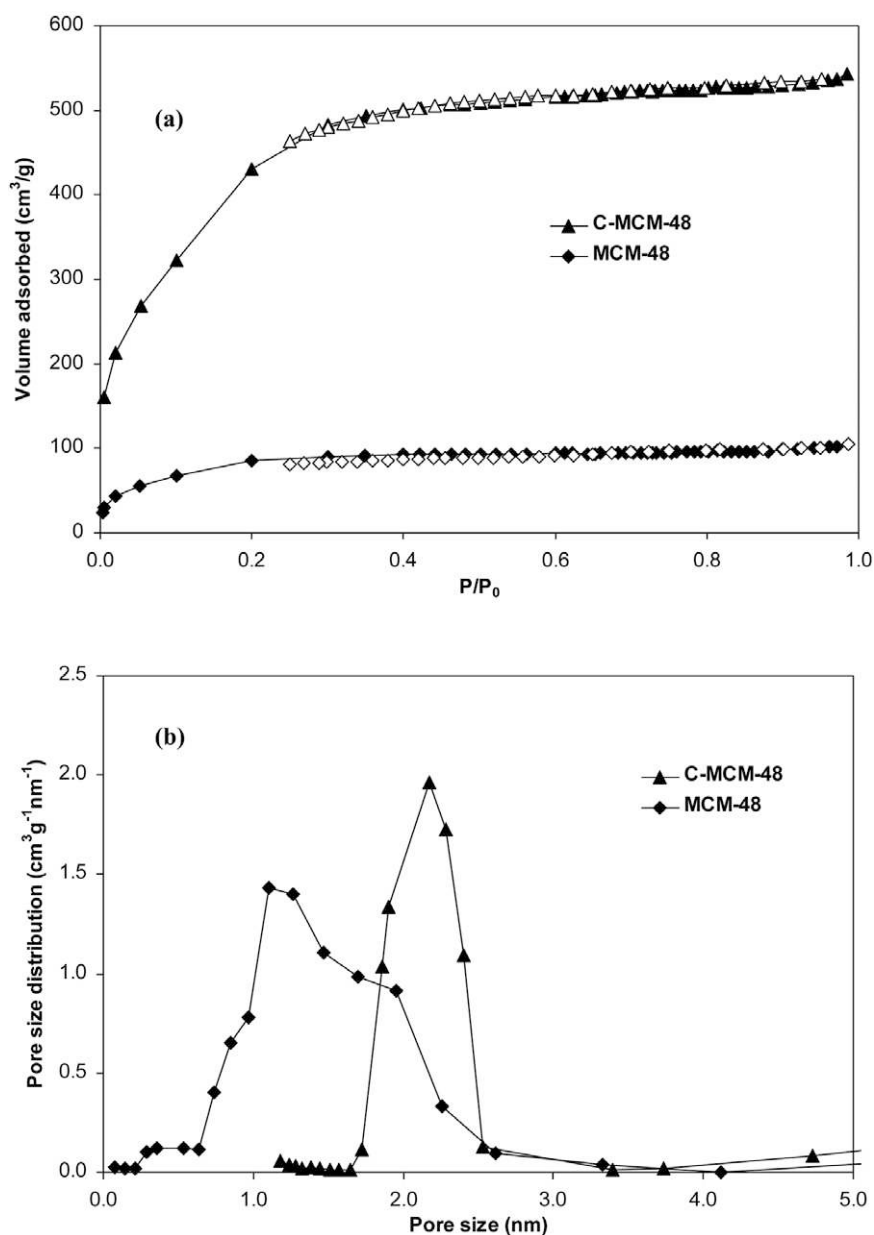


Fig. 1. (a) Nitrogen adsorption–desorption isotherms and (b) pore size distribution of Mobil Composite Material no. 48 (MCM-48) and calcined Mobil Composite Material no. 48 (C-MCM-48).

Table 2. Textural properties of Mobil Composite Material no. 48 (MCM-48) and calcined Mobil Composite Material no. 48 (C-MCM-48).

Sorbent	BET surface area†	Pore diameter	Total pore volume	Surfactant content
	m ² g ⁻¹	nm	cm ³ g ⁻¹	% w/w
C-MCM-48	1484	2.1	0.89	0.46
MCM-48	269	1.1	0.16	44.08

† BET, Brunauer–Emmett–Teller.

(211) and (220) diffraction lines, respectively (Hamoudi et al., 2007).

The surfactant content (% w/w) estimated by C,H,N-elemental analysis were 44.1 and <0.5% for MCM-48 and C-MCM-48, respectively. The theoretical values of the surfactant content based on the MCM-48 molar composition are 40% (w/w) and 0.0% (w/w) for MCM-48 and C-MCM-48, respectively (Schumacher et al., 1999). The little overestimation of the surfactant content could be attributed to humidity and/or solvents impurities present inside the porous structure of the synthesized materials.

Sorption Kinetics

Since the textural properties (surface area, porosity, and pore diameter) of the calcined material C-MCM-48 were superior to those of MCM-48 (Table 2), we found that when we allowed C-MCM-48 (10 g L⁻¹) to directly contact an aqueous solution of TNG (50 mg L⁻¹) at room temperature, only 2.5 ± 0.7% of TNG was removed. These experimental findings suggested that the surfactant incorporated inside the porous structure of MCM-48 was responsible for TNG removal. We also found that when an aqueous solution of TNG (50 mg L⁻¹) was contacted with the surfactant CTAB alone (10 g L⁻¹) above its critical micellar concentration value (0.33 g L⁻¹), only 4.5 ± 2.1% of TNG was removed. However, when the CTAB-containing MCM-48 material (10 g L⁻¹) was contacted with aqueous solution of TNG (50 mg L⁻¹), more than 91.5 ± 0.2% was removed. This variation in the sorption capacity of CTAB micelles alone and the CTAB-containing MCM-48 could be attributed to molecular structural variations between

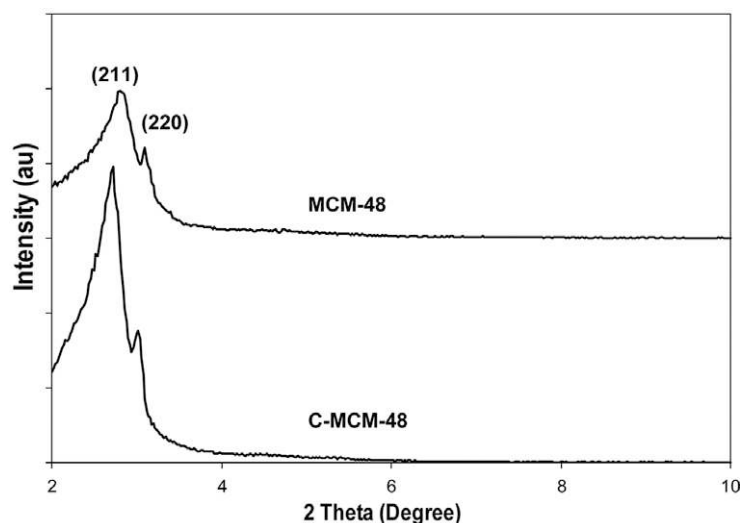


Fig. 2. X-ray diffraction patterns for Mobil Composite Material no. 48 (MCM-48) and calcined Mobil Composite Material no. 48 (C-MCM-48).

CTAB micelles and CTAB-containing MCM-48. Compared to CTAB micelles the CTAB-containing MCM-48 has porous structure with high specific surface area and remarkable interconnectivity. These characteristics should act to increase the contact surface area between TNG and the sorbent and hence improve the MCM-48 sorption capacity. Also the weak affinity between TNG and CTAB micelles could be attributed to a weak interaction between a hydrophobic CTAB and amphoteric TNG molecules.

Subsequently, the effect of time on the sorption of TNG (50 mg L⁻¹) onto MCM-48 (10 g L⁻¹) was investigated. As shown in Fig. 3, sorption of TNG was a biphasic process, a rapid sorption phase in the first 2 min (70% of TNG) followed by a slower one that reached equilibrium after 1 h. The kinetic data of TNG sorption onto MCM-48 have been analyzed on the basis of pseudo-second-order equation (Ho and McKay, 1999):

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_c^2} + \frac{1}{Q_c} t \quad [4]$$

where k_2 is the pseudo-second-order rate constant (g min⁻¹ mg⁻¹), Q_c (mg g⁻¹) is the sorption capacity at equilibrium, and Q_t (mg g⁻¹) is the sorption capacity at time t (min). On plotting the value of t/Q_t versus t (Fig. 4), a straight line with a linear regression coefficient (r^2) of 0.9987 was obtained. These experimental findings indicate that the sorption rate may be controlled by the concentration of TNG and the amount of the active sites on the MCM-48 surface. At the initial sorption phase, the active sites were not occupied and the sorption rate was fast. When these sites become more occupied, the rate decreased until the final sorption equilibrium was attained (Yu et al., 2009). The value of k_2 calculated from the intercept $1/k_2 Q_c^2$ was 0.165 g min⁻¹ mg⁻¹.

Sorption Isotherms and Sorption Thermodynamics

Figure 5 shows the sorption isotherms of TNG onto MCM-48 at different temperatures. For all temperatures studied (10, 20, and 40°C), the sorption of TNG increased until equilibrium is obtained. We found that an increase in temperature is accompanied by an increase in the equilibrium uptake of TNG, indicating the endothermic character of the sorption process. Indeed, when the silica surface is covered by the cationic surfactant, CTAB in the present case, the hydrophobic organic chain of the surfactant would act as a solvent leading to the removal of TNG from the aqueous solution by a process often termed adsolubilization (Denoyel and Sabio, 1998). In adsolubilization, when temperature is increased, so is the solute–surfactant interaction (Nayyar et al., 1994; Saphanuchart et al., 2008) leading to higher removal of TNG at a high temperature. This is in agreement with the findings of Boubberka et al. (2005) and Wang and Wang (2008), who used surfactant-modified clays for the removal of dyes from contaminated water and noted an increase in sorption with temperature. In contrast, Shu et al. (2009) reported that sorption of chlorobenzenes on a surfactant-modified kaolinite or bentonite was impaired with increasing temperature. Whereas Zhu and Zhu (2008) found that the effect of temperature on the sorption of naphthalene onto

surfactant-modified clays depends on the surfactant content; a low surfactant content (7%, w/w) leads to exothermic sorption, while high surfactant content (30%, w/w) leads to endothermic sorption. Apparently, the effect of temperature on sorption varies from one case to another, and in our case the process was endothermic and sorption increases with temperature.

In all studied cases, we did not observe any significant degradation of TNG, judging from the absence of any of the potential degradation products of TNG such as 1,3 DNG, 1,2-DNG, 1-MNG, and 2-MNG (detection limit 0.1 mg L⁻¹).

Langmuir and Freundlich sorption isotherms were used to determine the best fit to the sorption data. Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogeneous sorbent surface containing a finite number of sorption sites, whereas the Freundlich isotherm describes sorption in which the sorbent has a heterogeneous surface (Myers, 1999). Both Langmuir and Freundlich isotherms are expressed as shown in Eq. [5] and [6], respectively:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \quad [5]$$

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad [6]$$

where Q_m is the maximum amount retained on the sorbent phase at equilibrium (mg g⁻¹), K_L is the sorption equilibrium constant (L mg⁻¹), C_e is the equilibrium concentration of substrate in the solution (mg L⁻¹), K_F is the Freundlich constant representing the sorption capacity (mg^{1-1/n} g⁻¹ L^{1/n}), and n is the Freundlich exponent depicting the sorption intensity. Table 3 summarizes both Langmuir and Freundlich parameters at different temperatures, and Fig. 5 summarizes predicted isotherms. From calculated r^2 values (Table 3) and isotherms shown in Fig. 5, it appears that sorption of TNG on MCM-48 is best explained by Langmuir model, that is, sorption is typically a monomolecular layer process. Maximum sorption capacities Q_m of 25.7, 40.4, and 55.2 mg g⁻¹ were obtained at 10, 25, and 40°C, respectively. Thus, TNG removal by the nanostructured MCM-48 significantly outperformed other investigated materials. For instance, Lebeda et al. (2001) sorbed 1.1 mg TNG per gram of synthetic activated carbon, and Tomaszewski et al. (2003) sorbed 0.18 mg of TNG per gram of commercial activated carbon. Table 3 also summarizes the two thermodynamic parameters enthalpy (ΔH^0) and entropy (ΔS^0) of the sorption of TNG onto MCM-48. These parameters were obtained by plotting $\log K_L$ as a function of $1/T$, where K_L is the Langmuir sorption equilibrium constant (L mg⁻¹) and T is the sorption temperature (K). Both ΔH^0 and ΔS^0 were estimated as 1.89 kJ mol⁻¹ and 79.03 J mol⁻¹ K⁻¹, respectively. The positive value of ΔH^0 confirmed the endothermic nature of TNG sorption onto MCM-48, whereas the low magnitude of ΔH^0 (1.89 kJ mol⁻¹) confirmed the physical nature (mainly Van der Waals forces) of the sorption process

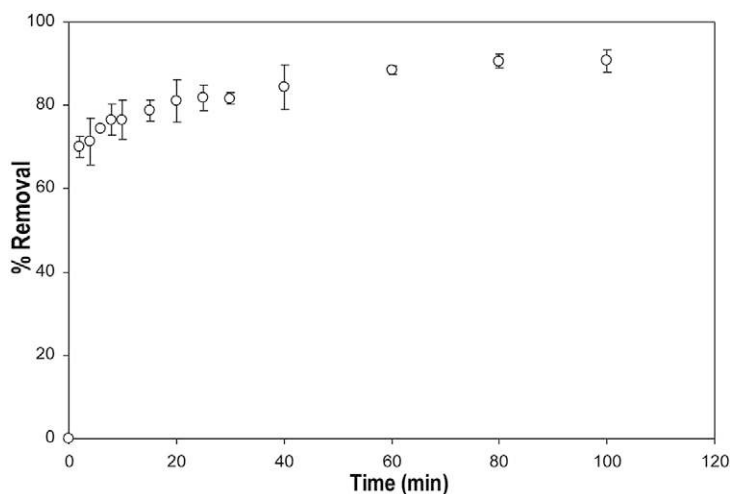


Fig. 3. Sorption kinetic profile of trinitroglycerin (TNG) onto Mobil Composite Material no. 48 (MCM-48). Operating conditions: initial TNG concentration 50 mg L⁻¹, sorbent amount 10 g L⁻¹, and ambient temperature.

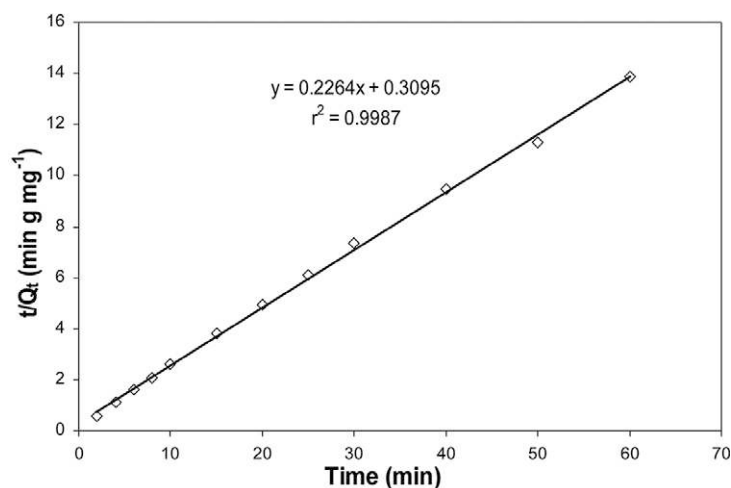


Fig. 4. Pseudo-second-order equation for trinitroglycerin (TNG) sorption onto Mobil Composite Material no. 48 (MCM-48). Q_t , amount of TNG sorbed at time t .

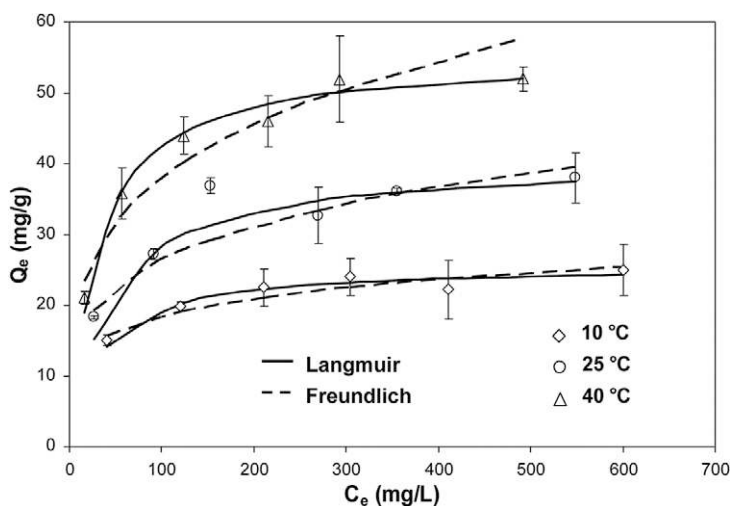


Fig. 5. Experimental and theoretical sorption isotherms of trinitroglycerin (TNG) onto Mobil Composite Material no. 48 (MCM-48). Sorbent amount, 10 g L⁻¹. Solid lines represent the Langmuir model; dotted lines represent Freundlich model. Error bars represent the standard deviations of three replicates. Fitting parameters are given in Table 3. Q_e , amount of TNG retained in the sorbent phase; C_e , equilibrium TNG concentration.

Table 3. Langmuir and Freundlich constants and thermodynamic parameters for trinitrolycerin (TNG) sorption onto Mobil Composite Material no. 48 (MCM-48).

Temp. (K)	Freundlich fitting†			Langmuir fitting†				
	K_F	$1/n$	r^2	K_L	Q_m	r^2	ΔH°	ΔS°
	$\text{mg}^{1-1/n} \text{kg}^{-1} \text{L}^{1/n}$			L mg^{-1}	mg g^{-1}		kJ mol^{-1}	$\text{J mol}^{-1} \text{K}^{-1}$
283	8.15	0.18	0.894	0.030	25.74	0.993	1.89	79.03
298	8.77	0.24	0.966	0.022	40.40	0.996		
313	11.25	0.30	0.935	0.033	55.24	0.977		

† K_F , Freundlich constant representing the sorption capacity; n , Freundlich exponent depicting the sorption intensity; K_L , sorption equilibrium constant; Q_m , maximum amount of TNG retained on the sorbent phase at equilibrium; ΔH° , thermodynamic parameter enthalpy of the sorption of TNG onto MCM-48; ΔS° , thermodynamic parameter entropy of the sorption of TNG onto MCM-48.

(Sharma et al., 2009). The positive value of ΔS° is an indication of increased randomness on the sorbent–sorbate interface during the sorption of TNG.

Desorption of TNG and Reusability of MCM-48

When deionized water was used to desorb TNG from MCM-48 only <1% of TNG was recovered, but when a mixture of acetonitrile and water (50% v/v) was used, >95% of TNG was recovered (Fig. 6). These experimental findings, which exclude

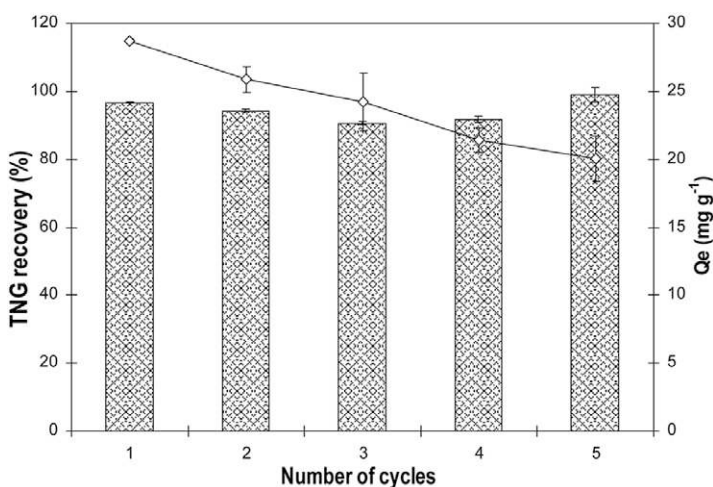


Fig. 6. Percentage recovery of trinitrolycerin (TNG) and amount removed (mg g^{-1} sorbent) during five sorption–desorption cycles. Initial concentration, 200 mg L^{-1} . Sorbent amount, 5 g L^{-1} . Q_e , amount of TNG retained in the sorbent phase.

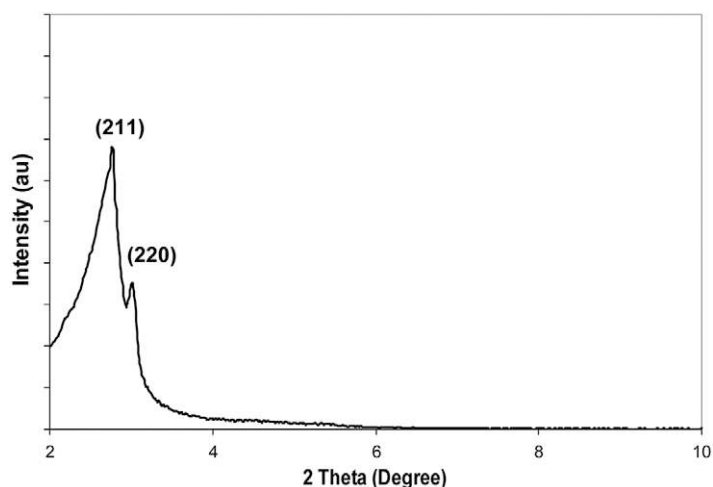


Fig. 7. X-ray diffraction pattern of Mobil Composite Material no. 48 (MCM-48) after five regenerating cycles.

the presence of strong chemisorption between TNG and MCM-48, supported our earlier suggestion of the occurrence of adsolubilization between the organic part of the surfactant and TNG. The incomplete recovery of TNG after each sorption–desorption cycle is best explained by the inner trapping of a fraction of TNG inside the micropores of MCM-48.

To gain insight into the reusability of the MCM-48 nanostructured silica material, we treated MCM-48 (10 g L^{-1}) repeatedly with 20 mL of TNG aqueous solutions (200 mg L^{-1}) for five consecutive sorption–desorption cycles. We found that TNG sorbed onto MCM-48 in the first and fifth cycles were 29.6 ± 0.8 and $20.3 \pm 0.2 \text{ mg g}^{-1}$, respectively (Fig. 6), indicating a loss of only 31.4% in MCM-48 sorption ability in five successive uses (only 6% was lost after the first cycle). It is known that acetonitrile could break down fused silica tubing for liquid chromatography coupled mass spectroscopy after a certain number of uses. Therefore, it is plausible that acetonitrile may dissolve MCM-48, causing the release of CTAB, thus leading to a decrease in the sorption capacity of MCM-48. However, after five sorption–desorption cycles using a solution of acetonitrile–water (50% v/v), negligible silica dissolution could be observed. The loss in sorption capacity could thus be mainly attributed to the displacement of the surfactant following acetonitrile use to desorb TNG. Elemental analysis of the washed material after five regenerating cycles showed a loss of ~7% of the surfactant content (37.1%, w/w), which is in line with TNG sorption data. Furthermore, XRD analysis of the washed material (Fig. 7) showed that MCM-48 preserved its ordered cubic structure since the position of characteristic Bragg peaks around 2.8 and 3.0° remain intact. Despite this loss in MCM-48 sorption capacity, its performance as sorbent outperformed other materials used for the removal of TNG from aqueous solutions. For instance, GAC lost 15 to 50% of its original sorption capacity after each regenerating cycle (Concurrent Technologies Corporation, 1995) compared with ~6% for MCM-48.

Conclusions

Nanostructured silica MCM-48 proved to be an effective high-capacity sorbent for the removal of TNG from aqueous solutions. The present study shows that the uptake expressed as amount of TNG retained per gram of nanostructured MCM-48 exceeded those previously reported in the literature. A maximum TNG sorption capacity of 55.2 mg g^{-1} was obtained at 40°C . The removal of TNG from water

was enhanced by an increase of temperature, indicating the endothermic nature of the sorption of TNG onto MCM-48.

Reusability studies showed that MCM-48 lost only 31.5% of its original sorption capacity during five sorption-desorption cycles. The present nanosilica-based material with large sorption capacity and high reusability may serve as basis for the development of a promising remediation technology for the removal of TNG from contaminated water. Finally, to avoid the release of the surfactant from the nanomaterial, future studies should focus on the development of a more stable nanostructured silica material containing an irreversibly bound surfactant.

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