

SBA-16 MESOPOROUS NANOSILICA: SYNTHESIS, CHARACTERIZATION AND SORPTION PROPERTIES

Violeta-Carolina Niculescu*, Marius Constantinescu, Felicia Bucura, Daniela Ion-Ebrasu, Amalia Soare

National Research and Development Institute for Cryogenics and Isotopic Technologies – ICSI Rm. Valcea, 4 Uzinei Street, P.O. Box Râureni 7, 240050, Rm. Valcea, Romania

Abstract:

Dyes are intensively used in industries such as textiles, plastics, cosmetics, etc., and they are considered major wastes. Due to their chemical structures, dyes are resistant on exposure to sun or water, therefore being difficult to be removed once released into the aquatic environment, having serious environmental impact. Among these dyes, rhodamine is a fluorescent dye. The mesoporous SBA-16 nanosilica has been synthesized by sol-gel process. The rhodamine 110 adsorption process on SBA-16 was explained by Langmuir and Henry isotherm models. The excellent adsorption and fluorescence properties reduction indicated that the mesoporous silica can be efficiently applied in the wastewater treatment.

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1. INTRODUCTION

Nanoporous materials have gain high interest among scientists due to their potential application in adsorption, gas separation, heterogeneous catalysis or opto-electronics as well as new challenges in bio-medical area (Niculescu et al., 2018; Zabukovec Logar and Kaucic, 2006). Typically, the specific surface area of a nanoporous material is higher than the one of a non-porous material (Detsi et al., 2011). Other important properties of the porous nanomaterials that recommend their intensive application are the distribution of pore sizes, the chemistry of the walls and the crystallinity, which can be tailored to the requirement of the application (Jeevanandam et al., 2018). In order to be to be commercially, a nanomaterial should have low cost and have high stability to regeneration, such materials being the ones based on silicate.

Organic dyes are intensively used as textile dyes or in the food, plastics and cosmetics industries, resulting significant amounts of so-called “coloured wastewater” (Chen et al., 2018). Up to now, about 10,000 of various commercial dyes and pigments were developed

*Corresponding author: Violeta Niculescu, E-mail: violeta.niculescu@icsi.ro, ORCID: 0000-0002-0439-3265

and more than 7×10^5 tones are annually produced (Ibtissam et al., 2012). Many of these dyes possess toxic or carcinogenic effects, their molecules and metabolites being difficult to biodegrade and causing major damages on aquatic organisms or humans. Various methods have been studied for dyes removal from wastewater, such as coagulation, electrochemical, chemical oxidation, membrane separation or adsorption (Melendez-Ortiz et al., 2019). Up to now, the adsorption method is considered as the most suitable in terms of efficiency for dyes removal from the wastewater (Zhul-quarnain et al., 2018).

Among these dyes, rhodamine 110 is a fluorescent dye, used in diagnostic assay manufacturing and various other industries, being considered pollutant chemical in water. The mesoporous nanosilica can be considered as an effective adsorbent for rhodamine, due to its unique structure and characteristics, such as high surface area and pore volume or narrow distribution of pore size (Kohn et al., 2014).

Among the nanoporous silica materials, SBA-16 is a novel material with large (5-15 nm) cage-like mesopores having a three dimensional cubic body-centred Im3m symmetry (Sakamoto et al., 2000; Zhao et al., 1998). Similar to SBA-15, SBA-16 is obtained under acidic conditions using a non-ionic Pluronic surfactant, resulting an intrawall porosity (Hoang et al., 2005). Due to the longer PO chains in Pluronic F127, SBA-16 has thicker pore walls than SBA-15, obtained from Pluronic P123. The structure of SBA-16 has been reported as a triply periodic minimal surface of I-WP (body centred, wrapped package) (Sakamoto et al., 2000) (Figure 1), each mesopore being connected to eight neighbouring mesopores.

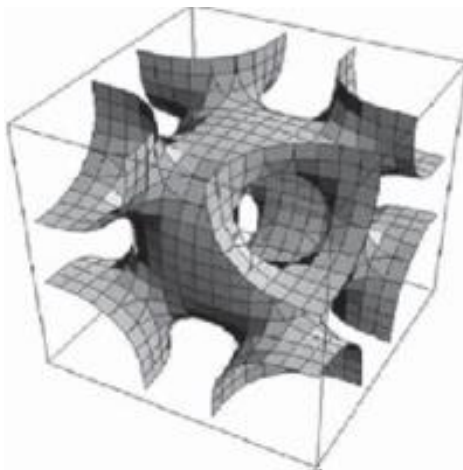


Figure 1. Representation of the SBA-16 material and the corresponding mesophase

SBA-16 material has attracted interest in adsorption, separation or catalysis due to its more accessible pores than those of other porous materials with hexagonal structure (Wang et al., 2004). As a consequence, SBA-16 may display improved adsorption or catalytic activity than SBA-15, due to its potential for mass transport (Trong On et al., 2001).

When comparing SBA-16 nanosilica material with other adsorption materials, it was observed that SBA-16 a shorter adsorption time was required, its adsorption capacity for the cationic dyes varying in the range of 1.5 mg/g to 35 mg/g, depending also on the dye type and concentration in the wastewater (Qin et al., 2018).

Various morphologies of SBA-16 have not been intensively studied. Overall, mesoporous materials with different morphologies can be obtained by changing the raw materials, the stirring or reaction temperature (Kosuge et al., 2004; Kubo and Kosuge, 2007). In this respect, the raw materials can be changed by using the co-surfactant and

inorganic salt as the additives (Almeida et al., 2012). The inorganic salt KCl is used to improve the structural order degree (Fan et al., 2003). Also, the hydrolysis rate of the silicon source can be modified by adjusting the pH value of the synthesis mixture, the hydrothermal treatment temperature or the stirring rate before the hydrothermal treatment (Johansson et al., 2010). When the KCl is introduced in the mixture, the assembly rate is expected to be rapid, which is not indicated in order to form the single SBA-16 crystal or regular particle shapes. Therefore, no stirring must be applied after adding the silicon source, in order to decrease the assembly rate.

Taking into account all the above-mentioned aspects, the aim of this study was the synthesis of SBA-16 with large surface area by a simple sol-gel method, as well as the exploration of its adsorption properties for dyes removal.

2. MATERIALS AND METHODS

SBA-16 was synthesized using a template agent - Pluronic F127 (Sigma Aldrich, Darmstadt, Germany). In a typical synthesis, 3.0 g of Pluronic P127 was dissolved in 144 mL ultrapure water and 13.9 mL 38% HCl solution, under stirring at 25°C. After half an hour, 11 mL butanol Sigma Aldrich, Darmstadt, Germany) was added as co-surfactant, in order to achieve a 1: 3 mass ratio (F127: butanol). Subsequently, 15.3 mL of tetraethyl orthosilicate (TEOS - Sigma Aldrich, Darmstadt, Germany) was added to the solution, under continuous stirring at 45°C for 24 hours, according to the method reported by Gobin (Gobin, 2006). After hydrothermal treatment at 100°C for 24 hours in a Teflon autoclave, the solid was collected by filtration and air dried at 80°C under vacuum. The surfactant was removed by calcination at 550°C for 6 hours.

Fourier transform infrared spectroscopy (FTIR) was performed using Cary 630 ATR-FTIR spectrometer (Agilent Technologies, Inc., Santa Clara, CA, U.S.). The Emission Scanning Electron Microscope with Variable Pressure Field - FESEM VP (Carl Zeiss - Oberkochen, Germany) was used to determine the silica morphology and also to perform the EDX analysis. Autosorb-iQ-C from Quantachrome Instruments (Boynton Beach, FL, U.S.) was used to obtain Brunauer-Emmett-Teller (BET) surfaces and average pore diameters from the nitrogen adsorption-desorption isotherms, at 77 K. The elemental analysis was performed with a Flash EA 2000 equipment (Thermo Scientific, UK). In order to perform the thermogravimetric analysis a 449 F5 Jupiter TGA-DSC system (NETZSCH-Geratebau GmbH, Selb, Germany) was used, in domain of 25°C - 800°C, with a heating rate of 10°C/min under nitrogen flow.

The adsorption experiments were achieved in a 25 mL container: 53 mg mesoporous silica were introduced in 15 mL rhodamine 110 chloride (Sigma Aldrich, Darmstadt, Germany), 25 mg/L solution in ultrapure water, and the mixture was stirred for homogenisation. UV-Vis and fluorescence spectrophotometry (Duetta Fluorescence and Absorbance Spectrometer - Horiba, Ltd., Kyoto, Japan) was performed in order to determine the adsorption capacity of the mesoporous silica. For the kinetic study, the sample was analysed at various time intervals of 15, 30, 45, 60, 90, and 150 mins, while the other parameters were kept constant. In order to determine the equilibrium concentration, 53 mg of the raw adsorbent was introduced into different sample vials each containing 15 mL of varying concentrations of 5 mg/L, 10 mg/L, 15 mg/L, 20 mg/L and 25 mg/L of the dye solution. The mixture was stirred and allowed to stand for 60 minutes (the time necessary time for maximum adsorption), after which it was centrifuged and then analysed using the UV-Vis and fluorescence spectrophotometer.

The adsorption amount and adsorption rate (percentage removal) of the dye on SBA-16 were calculated with the equations:

$$q_t = (C_0 - C_t) \times V \quad (1)$$

$$\text{Sorption (\%)} = \left[\frac{(C_0 - C_t)}{C_0} \right] \times 100\% \quad (2)$$

where C_0 and C_t (mg/L) are the concentrations of the dye solution before and after sorption at t (time) and q_t is the amount of cationic dye (mg) adsorbed on the SBA-16, V (L) is the volume of the used dye solution.

Langmuir and Henry models were used to explain the experimental equilibrium results, the model being assumed for ideal monolayer adsorption (Asimopolos and Asimopolos, 2017; Zhul-quarnain et al., 2018). The Langmuir adsorption isotherm is based on the premise that there are fixed numbers of active sites on the adsorbent surface. Once an adsorbate molecule enters a site, no further adsorption can take place there and no interaction between adsorbed species can occur. The general linear equation is expressed as:

$$q_e = \frac{K_L C_e A_m}{1 + K_L C_e} \quad (3)$$

where C_e is the equilibrium concentration of the dye in the aqueous solution (mg/L), q_e is the equilibrium amount of the cationic dye adsorption by mesoporous silica (mg/g), q_m is the theoretical dye maximum adsorption capacity (mg/g), and K_L is the Langmuir isotherms constant (L/mg).

3. RESULTS AND DISCUSSION

The typical FT-IR spectra for SBA-16 (Figure 2) presents the absorption bands characteristic for nanosilica, such as the wide band attributed to the asymmetric Si-O-Si stretching vibration at 1050 cm^{-1} (Niculescu et al., 2011).

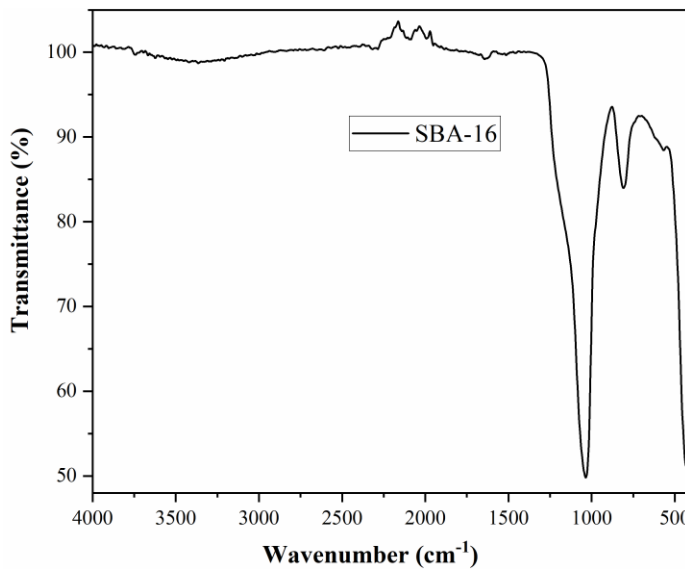


Figure 2. FTIR spectra of SBA-16

Furthermore, a weak band at 800 cm^{-1} can be observed, which is attributed to the symmetrical stretching vibration for Si-O bonds.

The BET results are in agreement with the data in the literature for such materials (Figure 3) (Ferreira Andrade et al., 2012).

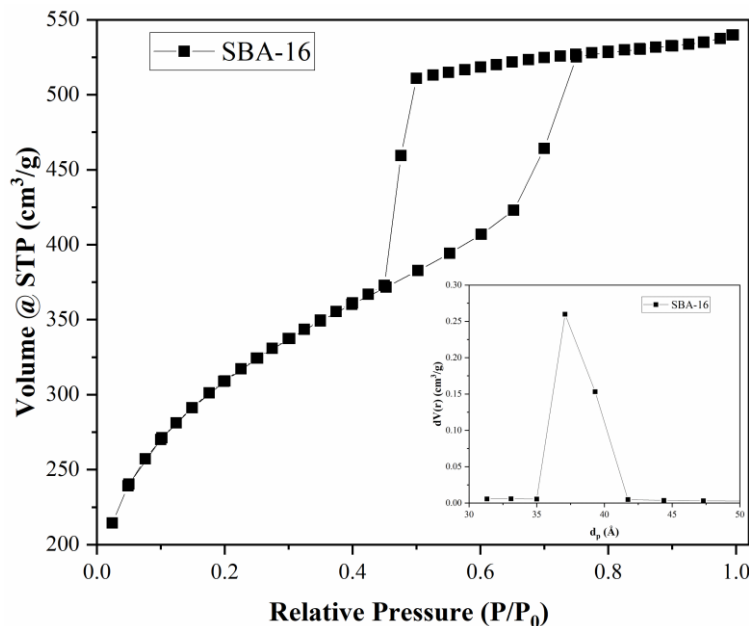


Figure 3. Adsorption-desorption isotherm and pores diameter for SBA-16

One of the fundamental characterization parameters of the nanomaterials is the identification of the pore-network structure based on physical adsorption-desorption analysis. The main morphological parameters (specific surface area and pores size distribution) were determined and correlated to the hydrothermal processing conditions (Dias and Ciminelli, 2000).

Isotherms are type IV, according to the IUPAC definition, associated with the presence of mesopores (Sing et al., 1985). The initial segment of the adsorption isotherm ($P/P_0 < 0.45$) is attributed to the monolayer and multilayer occurrence and it is similar to that given by a nonporous material. The second segment, at higher P/P_0 , exhibits an upward deviation correlated to the continuous filling of mesopores by capillary condensation. The SBA-16 contain no macropores, since the isotherm reached a plateau at high P/P_0 . On reducing P/P_0 , desorption takes place, resulting a hysteresis loop, its form being be related to the shape of the pores (Allen, 1981). SBA-16 contains asymmetric and triangular adsorption and desorption branches, attributed to systems with pore network connectivity and a blocking effect with a H_2 hysteresis loop. As a results, the specific surface was $911 \text{ m}^2/\text{g}$ (figure 3). The next phase was the determination of the pore size distribution. In this respect, the BJH (Barrett, Joyner, and Halenda) procedure was used to calculate the mesopores distributions (from the desorption curve) in the capillary condensation segment. The technique is based on the assumption that the pores are filled with liquid nitrogen at P/P_0 close to unity. The decrease of P/P_0 stimulates the emptying of the next larger size pores and lowers the thickness of the adsorbed layer left behind (Allen, 1981). The BJH method calculated a mean pore diameter around 3.7 nm (Figure 3).

Figure 4 shows the SEM images of the SBA-16 mesoporous silica.

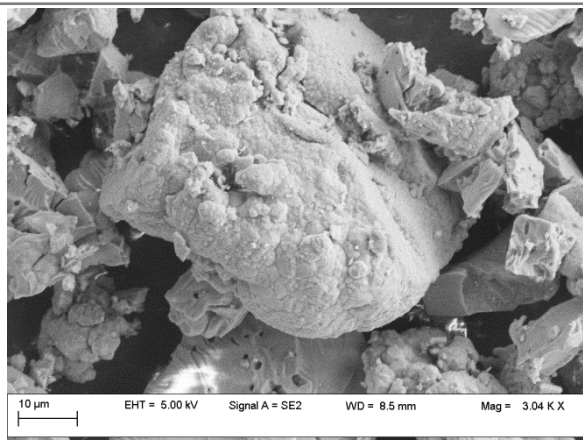


Figure 4. SEM image for SBA-16

The size and shape of the particles indicate a good morphology of the crystals, without other phases, typical for this type of materials. As can be seen in figure 4, the crystals were almost spherical.

Elemental analysis and EDX revealed a content of 53% by weight Si for SBA-16, (Table 1), but also the presence of some residue of carbon element, remained probably from the organic surfactant.

Table 1. Elemental analysis and EDX

Sample	C (%)	H (%)	O (%)	Si (%)
SBA-16	0.29	0.41	46.26	53.04

The SBA-16 degradation curve resulted from the thermogravimetric analysis is represented in Figure 5.

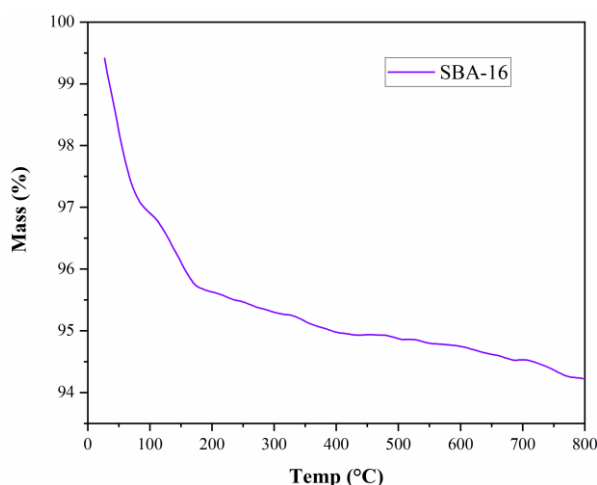


Figure 5. TG analysis of SBA-16

Weight loss of about 3% below 120°C most likely corresponds to the elimination of the absorbed water. Above 150°C and up to 800°C, there is an insignificant weight loss of only 2.7%. As a result, SBA-16 showed excellent thermal stability (Ferreira Andrade et al., 2012).

The fluorescence component analysis is complete if a 3-D excitation and emission matrix (EEM) is executed. The EEM captures much more information than the classical adsorption and fluorescence measurements and it can be used with chemometrics software for very precise, and complex, component analysis.

Figure 6 presents the typical EEM spectra of the rhodamine at the beginning of the experiment.

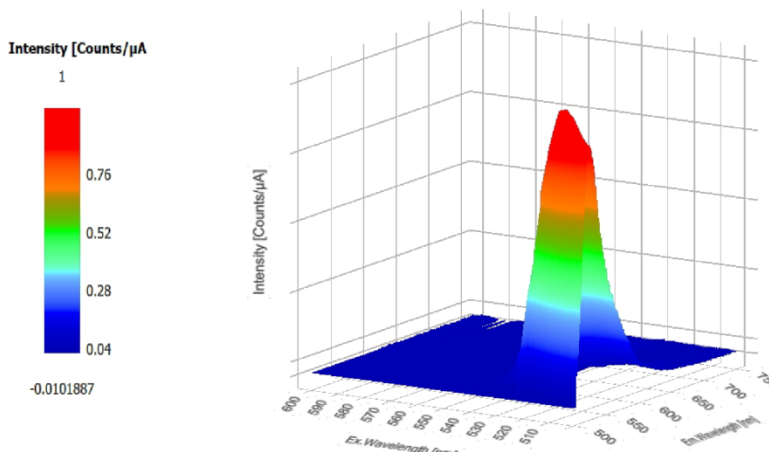


Figure 6. An excitation emission matrix (EEM) of the rhodamine shown as waterfall plot

In order to evaluate the sorption properties of the mesoporous silica, the excitation spectra was extracted from the fluorescence spectra.

Contact time is an important parameter influencing the adsorption efficiency. The contact time was studied in the range of 0 to 150 min, the other experimental conditions being held fixed. Figure 7 presents the effect of the contact time on the adsorption ratio of rhodamine.

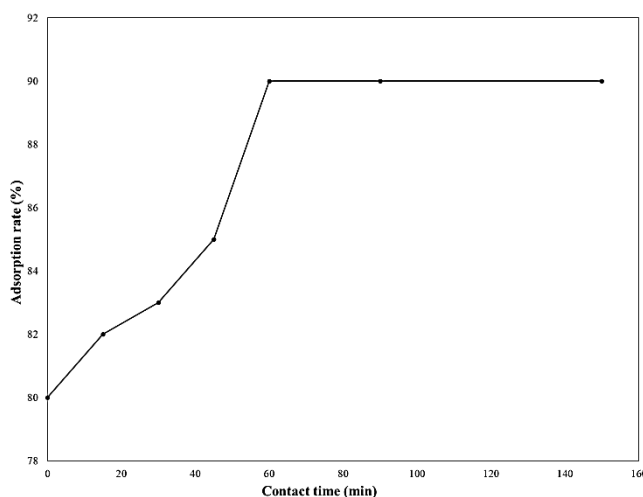


Figure 7. The effect of the contact time on the adsorption capacity

It can be observed that the adsorption reached an equilibrium after 60 min. Therefore, 60 min was selected as the optimized contact time for rhodamine. The maximum adsorption capacity of the SBA-16 (considered the equilibrium adsorption capacity obtained after 60 min) was 6.37 mg/g (mg rhodamine/g silica).

Table 2 presents adsorption isotherms equation according to Langmuir and Henry models.

Table 2. Isotherm models

Isotherm model	Equation	x	y	Slope	Intercept
LANGMUIR I	$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e$	C_e	C_e/q_e	$1/q_m$	$1/q_m K_L$
LANGMUIR II	$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m}$	$1/C_e$	$1/q_e$	$1/q_m K_L$	$1/q_m$
LANGMUIR III	$q_e = q_m + \frac{q_e}{K_L C_e}$	q_e/C_e	q_e	$1/K_L$	q_m
LANGMUIR IV	$\frac{C_e}{q_e} = q_m K_L + q_e K_L$	q_e	q_e/C_e	K_L	$q_m K_L$
HENRY	$q_e = K_L C_e$	C_e	q_e	K_L	0

where C_e is the equilibrium concentration of rhodamine in the solution (mg/L), q_e is the equilibrium amount of the dye adsorption on SBA-16 (mg/g), q_m is the theoretical rhodamine maximum adsorption capacity (mg/g), and K_L is the Langmuir isotherm constant (L/mg). Figure 8 shows the plots for all the Langmuir isotherms, and values of the isotherm parameters are listed in Table 3.

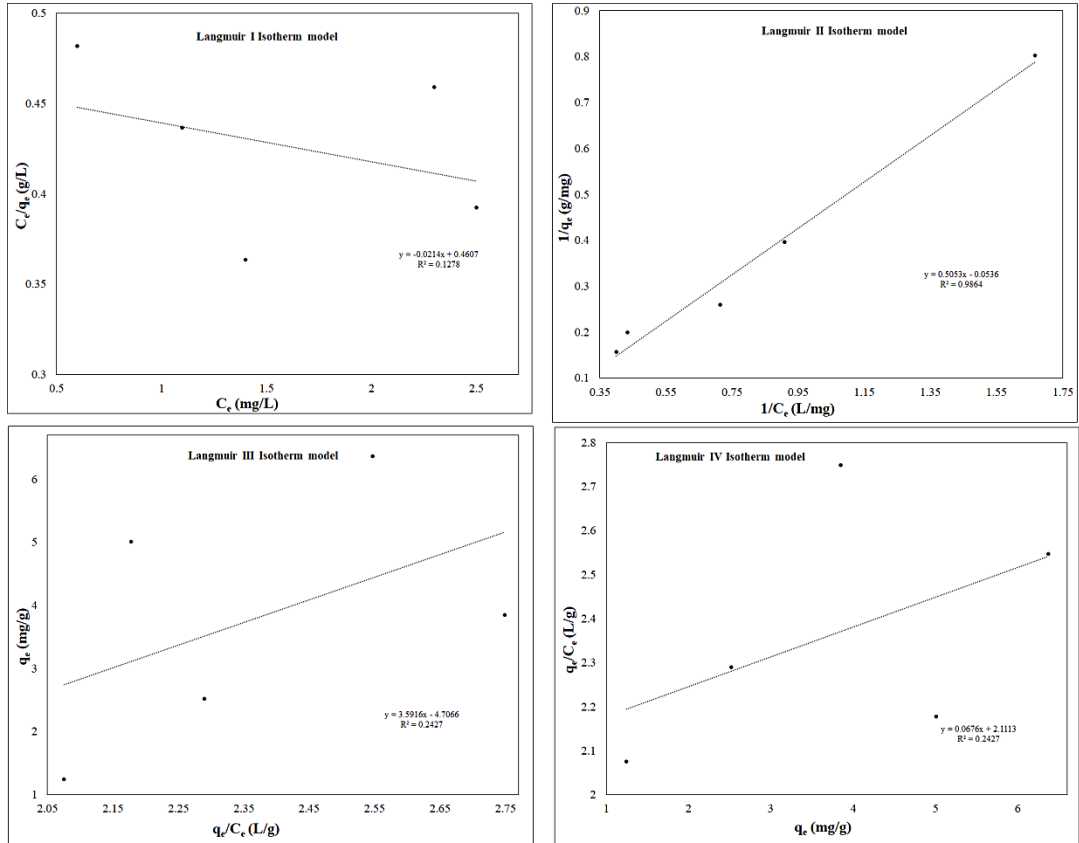


Figure 8. Langmuir Isotherms plot for rhodamine dye adsorption using SBA-16

Table 3. Langmuir Isotherm parameters

Langmuir Isotherm Model	Equation of graph	R ² -value	Slope	Intercept	q _m (mg/g)	K _L (L/mg)
LANGMUIR I	y = 0.0214x + 0.4607	0.1278	0.02114	0.4607	47.3037	0.0459
LANGMUIR II	y = 0.5053x - 0.0536	0.9864	0.5053	-0.0536	-18.6567	-0.1061
LANGMUIR III	y = 3.5926x - 4.7066	0.2427	3.5926	-4.7066	-4.7066	0.2783
LANGMUIR IV	y = 0.0676x + 2.1113	0.2427	0.0676	2.1113	31.2322	0.0676

R²-correlation coefficient; q_m - theoretical rhodamine maximum adsorption capacity (mg/g); K_L - Langmuir isotherm constant (L/mg)

According to table 3, the separation factor of the Langmuir models varied between - 0.15 to 0.3. Comparing the Langmuir coefficients of determination (R²) between the four Langmuir isothermss, Langmuir II model revealed the highest value (0.9864), meaning that this is the best fitting model for the experiment.

Figure 9 represents the plot for the Henry isotherm, and values of the isotherm parameters are listed in Table 4.

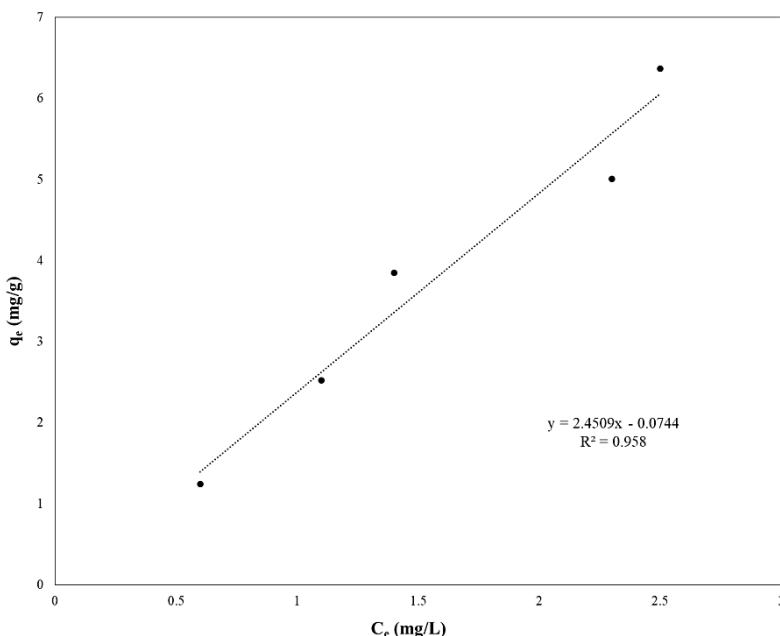


Figure 9. Henry Isotherm plot for rhodamine dye adsorption using SBA-16

Table 4. Henry Isotherm parameters

Isotherm Model	Equation of graph	R ² -value	Slope	K _H (L/mg)
HENRY	y = 2.4509x - 0.0744	0.958	2.4509	2.4059

R²-correlation coefficient; K_H – Henry isotherm constant (L/mg)

Comparing the R² values of Langmuir and Henry isotherm models, it can be observed that had the highest R² value (0.958) was obtained for the Henry model, which makes it the best fitted isotherm describing the adsorption data.

According to the adsorption isotherms, it can be concluded that the adsorption of rhodamine is related to the chemical action between the dye and the mesoporous silica. Considering the chemical structure of the SBA-16 surface, hydrogen bonds could arise

between the hydroxyl groups from the mesoporous silica surface as proton donors and the nitrogen atoms ($R-NH_2$) from the rhodamine molecules as proton acceptors. On the other hand, the adsorption mechanism can be illustrated by the electrostatic interactions between the positively charged rhodamine dye and the negatively charged surface of the SBA-16 mesoporous silica.

Compared with other silica materials used as adsorbents (usually requiring more than two hours to achieve the maximum adsorption capacity) (Qin et al., 2018), the SBA-16 nanosilica as an adsorbent for removing dyes (such as rhodamine) reached the maximum capacity in only one hour with satisfactory adsorption capacity.

In order to demonstrate the stability of the SBA-16 stability, reusability study was achieved. Recycling and reuse are important features that must be addressed for adsorbents in practice. After adsorption of rhodamine, the SBA-16-rhodamine was immersed in ethanol with ultrasonic extraction for 15 min and repeated several times. Then, the material was dried for further using. Figure 10 shows that SBA-16 desorption rate for rhodamine removal remained above 85% after four consecutive adsorption/desorption cycles.

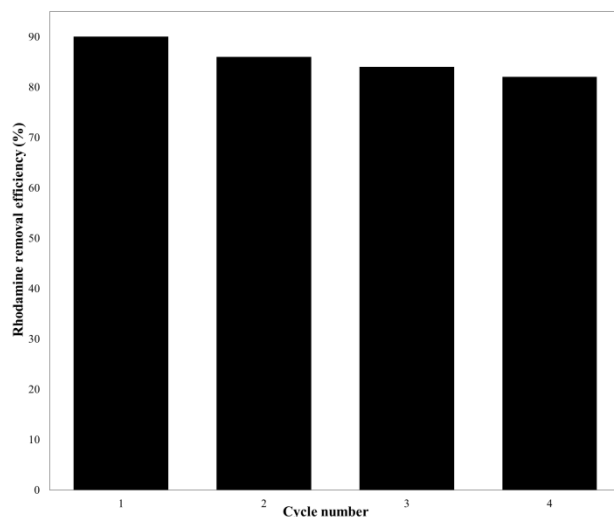


Figure 10. Reusability of SBA-16 for rhodamine removal

It can be concluded that the SBA-16 nanosilica has good reusability for removing various dyes from wastewater. By recycling this material, the costs for dyes removal can also be decreased.

4. CONCLUSION

Environmental concern is still being tackled, scientists being in constant research for the pollutants reduction. The presence of the organic dyes in waters determines high risks for human health. Therefore, their removal may be considered an important research activity. This study showed that mesoporous SBA-16- type silica can be used as a suitable adsorbent for the rhodamine dye removal from water. The results highlighted that SBA-16 mesoporous silica fitted better for the adsorption of rhodamine dye in the Henry isotherm model and that the reaction is a spontaneous and feasible one. It can be concluded that SBA-16 could be recommended as adsorbent for the removal of organic dyes from aqueous solutions.

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Author Contributions: V-CN, conceived and designed the study, oversaw the experiments, accomplished FTIR, UV-VIS and Fluorescence characterisation techniques, being also implicated in the results evaluation and in the manuscript writing. MC achieved the elemental analysis and results interpretation. FB was also involved in the elemental analysis and results evaluation. DIE performed the TG analysis and data analysis. AM performed the scanning electron microscopy measurements and results evaluation. All authors checked the results and they were implicated in the final manuscript formulation.

Conflict of Interest Statement: No conflict of interest is involved in this study.

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