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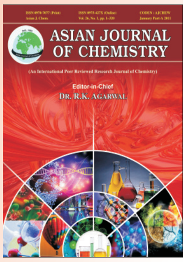

Organic-Inorganic Hybrid Materials Based on Mesoporous Silica MCM-41 with β-Cyclodextrin and its Applications

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This study explained the covalent attachment of β-cyclodextrin on MCM-41 through two different methods. In both methods, a diisocyanate was used as a linker. The modified mesoporous silicates characterized by Fourier transform infrared spectroscopy, thermal analysis and elemental analysis. The FTIR spectra and TGA analysis verified that the β-cyclodextrin was covalently attached to the mesoporous silica while the preservation of the MCM-41 channel system was checked by X-ray diffraction and nitrogen adsorption analysis. These materials were then used to evaluate the sorption properties of some organotin compounds (tributyltin, triphenyltin and dibutyltin). The results showed that mesoporous silica MCM-41 functionalized with β-cyclodextrins, using toluene di-iso-cyanate as a linker (MCM-TDI-β-CD), is a more highly effective sorbent for organotins especially for triphenyltin, compared to mesoporous silica MCM-41 functionalized with β-cyclodextrins using 3-chloropropyltriethoxysilane and toluene di-iso-cyanate as linkers (MCM-PTS-TDI-β-CD).

Keywords: MCM-41, β-Cyclodextrin, Organotins.

INTRODUCTION

The synthesis of porous materials with tailored properties is among the most attractive areas of study in material science[1-5]. The pioneering mesoporous silica material having regular pore channels ranging from 20-100 Å was reported in 1992[6,7]. Since then, the mesoporous inorganic materials synthesis through the use of a structure-directing template has been included in several discussions[8]. Currently, a new generation of the mesoporous hybrid silicates possessing organic groups on their surface was created through grafting or anchoring organic guests on the surface of the mesopore channel[9-12] or directly to the organic groups by condensation of organo trialkoxy silanes along with tetra alkoxysilanes [$Si(OEt)_4$ or $Si(OMe)_4$][13-19]. This novel group of hybrid mesoporous materials holds an attractive interest in the field of environmental remediation and chromatographic separation because of the presence of high surface areas and organic functional groups[20].

β-Cyclodextrins (β-CDs) are described as cyclic oligosaccharides comprising of 6 D-glucopyranose units linked by α-(1,4)-linkage. They can be represented in a spatial way as a torus having wide and narrow openings, respectively corresponding to secondary and primary hydroxyl groups and having the capability of encapsulating compounds because of the hydrophobic character of the internal cavity[21]. This unique feature has been used in pharmaceutical, food, cosmetic and textile industries and has long been utilized in the field of catalysis, environmental remediation, chemical sensing and enantiomeric separations[21,22]. Particular applications call for the immobilization of cylodextrins or cyclodextrin derivatives in an insoluble support. Various studies concerning the same, have been conducted with the help of organic materials[23], metal surfaces[24,25] or inorganic oxide supports. From the latter supports, mesoporous silica is the most commonly utilized for the production of functionalized materials owing to their great physical strength and chemical inertness[26-30].

A variety of coupling agents have also been utilized to functionalize mesoporous silica like organosilanes with particular functional groups; for instance, chloride, carboxylic acid, thiol and amine. Isocyanates are considered to be highly reactive with -OH groups, leading to the formation of urethane bonds[31], depending upon the diisocyanate utilized, at least as strong as those obtained with the organosilane binders[32].

Organotins compounds are invaluable organometallic pollutants which are utilized as follows; as antifouling paints, PVC stabilizers, pesticides and additives several industrial, chemical and agricultural applications[32]. The increasing use of tin compounds in the last few years has led to a high degree of organotins compounds widely detected in environmental matrices[33]. Additionally, the high toxicity of the organotins compounds poses increasing environmental concerns. Hence, in several countries, the utilization of triorganotin compounds including tributyltin and triphenyltin is legally banned or restricted. The adsorption method has been viewed among the most effective and economical ways to remove organic and inorganic pollutants from aqueous solutions.

In this work, mesoporous silica MCM-41 was functionalized with β-cyclodextrins molecule by post-grafting methods using: (a) a linking agent consisting on an organosilane (3-chloropropyltrimethoxysilane-ClPTS) and a diisocyanate (toluene di-isocyanate) (Fig. 1, route a), further designated as method 1; (b) a diisocyanate as a linker (Fig. 1, route b), designated as method 2. Both methods used toluene 2, 4-di-isocyanate as a coupling agent, being one of the isocyanate endings attached to the organosilane -OH ending (**method 1**), or to the silica surface (**method 2**), while the other isocyanate ending remains available for reaction with β-cyclodextrins.

Our general approach is similar to previous work in functionalization of mesoporous silica MCM-41 with calix[4]arene derivatives[34]. However, in this work we use β-cyclodextrins as organic modifier, deferent linking agent and evaluate its organotins adsorption capacities.

EXPERIMENTAL

Mesoporous silica [Aldrich, surface area 993 m^2/g, average diameter of 2.9 nm] as silica sources and β-cyclodextrins [$C_{42}H_{70}O_{35}$, 99 %, Acros] was the organic modifier. 3-Chloropropyltriethoxysilane [$C_9H_{21}ClO_3Si$, 95 %, Aldrich] and toluene 2, 4-di-isocyanate [$C_9H_6N_2O_2$, 98 %, Aldrich] were the organic linker. Triethylamine [$C_6H_{15}N$, SAFC] was used as catalyst while di-*n*-butylamine [$C_8H_{19}N$, 99 %, Acros] and hydrochloric acid [HCl, 37 %, fisher] were used to determine isocyanate groups. Toluene [fisher, dried before use by using molecular sieves], ethanol [fisher] and acetone [fisher] were used as solvents. Water was purified using Milli-Q purification equipment.

For sorption experiments, tributyltin chloride ($C_{12}H_{27}ClSn$, 96 %, aldrich), triphenyltin chloride ($C_{18}H_{15}ClSn$, 97 %, fluka) and dibutyltin chloride ($C_8H_{18}C_{l2}Sn$, 96 %, aldrich) concentrations were adjusted by successive dilutions with Milli-Q water of an 8.42 mM solutions in methanol stored at 4 °C in the dark. A methanolic stock solution of organotins compound was used because of the very low solubility of organotins in water.

Fourier transform infrared spectra (FTIR) were recorded on a Perkin Elmer FTIR Specrum RX1 ATR with a KBr pellet technique. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out from 50 to 900 °C at a heating rate of 20 °C/min in a nitrogen atmosphere using Perkin Elmer TGA 4000 analyzer. In addition, elemental analyses were performed on a Perkin Elmer CHNS-2400 analyzer and nitrogen adsorption-desorption experiments were carried out at 77.40 K on a Quantachrome Autosorb Automated Gas Sorption system. Moreover, the Brunauer-Emmett-Teller (BET) surface area (SBET) was calculated from the linearity of the BET equation while the volume and pore diameters were calculated from the pore size distribution curves using the Density functional theory DFT method. The X-ray powder diffraction (XRD) patterns were obtained on a Bruker AXS D-8 Advance diffractometer using Cu K radiation (λ = 0.154056 nm) at 40 kV and 30 mA within the 2θ range of 2 to 10.

An agilent technology 7500 series ICP-MS was used to determine organotins in aqueous solutions. The ICP-MS condition is shown in Table-1. Finally, a calibration curve was constructed through a series of Sn standard solutions for which a good linear relationship was observed.

TABLE-1
ICP-MS CONDITIONS

Parameter	Value
RF power (W)	1550
Sampling depth (mm)	8
Carrier gas flow (L/min)	0.9
Make-up gas flow (L/min)	0.28
O_2/Ar mixed gas	0
Chamber temperature	2 °C
Nebuliser	Babington
Cones	Ni

Synthesis methods

Preparation of 3-hydroxypropyltrimethylsilyl functionalized MCM-41: The surface functionalization of MCM-41 was carried out by a procedure described by Feng *et al.*[9] as shown in Fig. 1 (route a). The MCM-41 support was dehydrated (125 °C, overnight) and a self-assembled monolayer of the initial silane was produced by suspending 1 g of MCM-41 in 40 mL of toluene in a 100 mL round bottom flask. The suspension was stirred vigorously for 5 min before adding 0.30 mL of deionized water and the stirring continued for 2 h. A slight excess of the silane (10 % v/v), 2.18 mL of 3-chloropropyltriethoxysilane corresponding to 9.07 mmol, was added and the solution refluxed for 6 h. The solids were then filtered and washed copiously with toluene and acetone to remove unreacted silane and dried overnight. The so obtained modified material was denoted as ClPTS-MCM. The chlorine groups present in the ClPTS -MCM were hydrolyzed into hydroxyl groups, by heating 1 g of solid material with a solution of methanol: water (1:1) for 2 h at 60 °C[37]. Finally, the hydrolysed material (OHPTS-MCM) was filtered and dried at 110 °C overnight.

β-Cyclodextrin anchoring: β-Cyclodextrin was anchored on the MCM-41 surface by using toluene di-isocyanate as a linking agent [Fig. 1, route (a) and (b)].The materials were prepared by refluxing the hydroxyl modified material, OHPTS-MCM (route a)) and the unmodified MCM-41 (route b)) with excess of toluene di-isocyanate (dried by molecular sieve 24 h), in a dry nitrogen atmosphere at 80 °C for 4 h[35]. After cooling down the material was filtered, washed and dried overnight. 1.8 mmol and 2.0 mmol β-cyclodextrin (calculated from section determination of isocyanate groups) were added into modified mesoporous silica with toluene di-isocyanate (route a and b, respectively) (1 g) suspension with toluene (dried by molecular sieve 24 h). Subsequently, few drops of triethylamine were added and the reaction temperature was kept at 80 °C for 24 h under stirring. The so obtained modified materials were filtered, washed by toluene and acetone and dried under vacuum. The materials obtained by the OHPTS/TDI-method (route a) were denoted as MCM-PTS-TDI-β-CD and those obtained by the TDI-method (route b) were outlined as MCM-TDI-β-CD.

Determination of isocyanate groups: The content of isocyanate groups of the reaction system was determined by titration 200 mg of MCM-TDI and MCM-PTS-TDI samples and 20 mL of 0.1 mol/L di-*n*-butylamine in toluene were charged into a flask and the mixture was stirred at room temperature for 1 h. The unreacted di-*n*-butylamine was back titrated with 0.1 mol/L HCl using bromophenol blue as an indicator. The content of isocyanate groups was calculated by the eqn. 1:

$$\text{Isocyanate group (mmol/g)} = 0.1\ (V_o - V_s)\frac{f}{w} \qquad (1)$$

where V_o (mL) is the titer of 0.1 mol/L HCl for blank; V_s (mL), the titer of 0.1 mol/L HCl for the sample; f, the factor of 0.1 mol/L HCl; and w, the weight of the sample in gram (g).

Sorption studies: Mesoporous silica-grafted β-cyclodextrin (0.01 g) was shaken with 10 mL of aqueous solution containing of organotins solution with known concentration (C_o) at 180 rpm in a 50 mL Teflon reactors (FEP, Nalgene) since prior studies showed that this material does not compete for organotins sorption and does not leach organotins compounds[36]. Batch experiments were performed at room temperature for 1 h and filtered off (0.45 μm Millipore filter). The concentration of organotins remaining (C_e) in aqueous phase after the sorption was then determined by ICP-MS. The amount of organotins sorbed by modified mesoporous silica with β-cyclodextrin (q) was calculated as

$$q = \frac{(C_o - C_e)V}{w} \qquad (2)$$

where q is the amount of organotins adsorbed (mg/g), C_o is the initial aqueous concentration of organotins (mg/L), C_e is the concentration of organotins after shaking for a certain period of time (mg/L), V is the solution volume (L) and w is the mass of modified mesoporous silica (g).

The per cent sorption of organotins (S %) was calculated by;

$$S\ \% = \left[\frac{Co - C_e}{C_o}\right] \times 100$$

RESULTS AND DISCUSSION

β-Cyclodextrin was anchored on the MCM-41 support, using toluene di-isocyanate as a linking agent. Moreover, two different methodologies were used. In the first method (Fig. 1a) designated as the OHPTS/TDI-method, the MCM-41 was functionalized, through a post-synthetic method, with 3-chloropropyltrimethoxysilane. The chlorine groups were hydrolyzed into hydroxyl groups, which react with one of the terminal isocyanate groups of the linking agent, forming urethane links. The other terminal isocyanate functionality reacted with the free hydroxyl group present in the β-cyclodextrin. In the second method (Fig. 1b), designated as the toluene di-isocyanate method, β-cyclodextrin was covalently attached to the unmodified MCM-41 support using (toluene di-isocyanate) as linker. The isocyanate groups at *para*-positions in toluene di-isocyanate would bind with the hydroxyl groups on the surface of mesoporous silica preferentially whereas those at the *ortho*-positions would be preserved due to steric hindrance within the toluene di-isocyanate molecule[37]. The mole amount of the isocyanate groups that reacted with mesoporous silica can be regarded as that of toluene di-isocyanate that reacted with mesoporous silica. The amounts of toluene di-isocyanate that reacted with mesoporous silica are largely dependent on the amount of hydroxyls on the mesoporous silica surface so in the case of excess of toluene di-isocyanate, the amounts of toluene di-isocyanate that reacted with silica were invariable[38]. Excess toluene di-isocyanate was used serving two functions; as a solvent to disperse silica and as reactant in order to drive the reactions to completion and was easily removed after reaction by centrifugation and prolonged washing with anhydrous toluene. The isocyanate groups at *ortho*-positions in mesoporous silica-toluene di-isocyanate were reacted with hydroxyl group at β-cyclodextrin.

FTIR analysis: The spectrum of the unmodified MCM-41 (Fig. 2a), as well as the modified materials, is dominated by strong bands characteristic of the support matrix, indicating that the support framework remained unchanged. These bands are due to the surface hydroxyl groups, in the range of 3770-3300 cm^{-1} and to lattice vibrations, in the range 1300-750 cm^{-1}. Bands at about 1215, 1085, 807 and 480 cm^{-1} are assignable to the asymmetric and symmetric stretching [ν_{as}(Si-O-Si) and ν_s(Si-O-Si)] of the support framework. The band present at about 970 cm^{-1} is attributable to ν(Si-OH) vibrations[39-41].

After anchoring of 3-chloropropyltriethoxysilane (MCM-ClPTS) and subsequent hydrolysis (MCM-OHPTS), new weak bands arise at 2960 and 2850 cm^{-1} probably due to the aliphatic ($-CH_2$) stretching of the propyl chain of the silylating agent, which suggest that the modification of the support material was achieved[39].

The addition of excess toluene di-isocyanate to the MCM-OHPTS and MCM-41 resulted in the incorporation of isocyanate functionalities on the surface of the MCM- OHPTS (Fig. 2b) and mesoporous silica (Fig. 2c). This was evidenced by the appearance of a clearly discernible band at 2282 cm^{-1} corresponding to asymmetric stretching of the appended terminal isocyanate groups and the appearance of an aromatic C-C stretch at 1560 cm^{-1} in the FTIR spectrum. The signals corresponding to the C=O and C-N stretches of the formed carbamate linkages between the hydroxyl group and the isocyanate functionality at 1637 and 1202 cm^{-1} merged with the band of surface hydroxyl groups of mesoporous silica and Si-O-Si band respectively. The surface isocyanate functionalities could then be treated with β-cyclodextrin in dry toluene at 80 °C for 24 h. These functionalization reactions were again followed by FTIR spectroscopy to monitor the appearance and disappearance of some peak (Fig. 2d,e). The absence of the -NCO characteristic band, at about 2282 cm^{-1}, indicates that both functional groups of 1,4-diisocyanatobutane have reacted[42,43]. In addition, the bands at 2927 and 2850 cm^{-1} are more intense and a new band arises at 1425 cm^{-1}, which may be due to the ($-CH_2$) bending[42].

Thermogravimetric analysis: Thermogravimetric analysis of functionalized mesoporous silica MCM-PTS-TDI-β-CD and MCM-TDI-β-CD were determined (Fig. 3). Functionalized

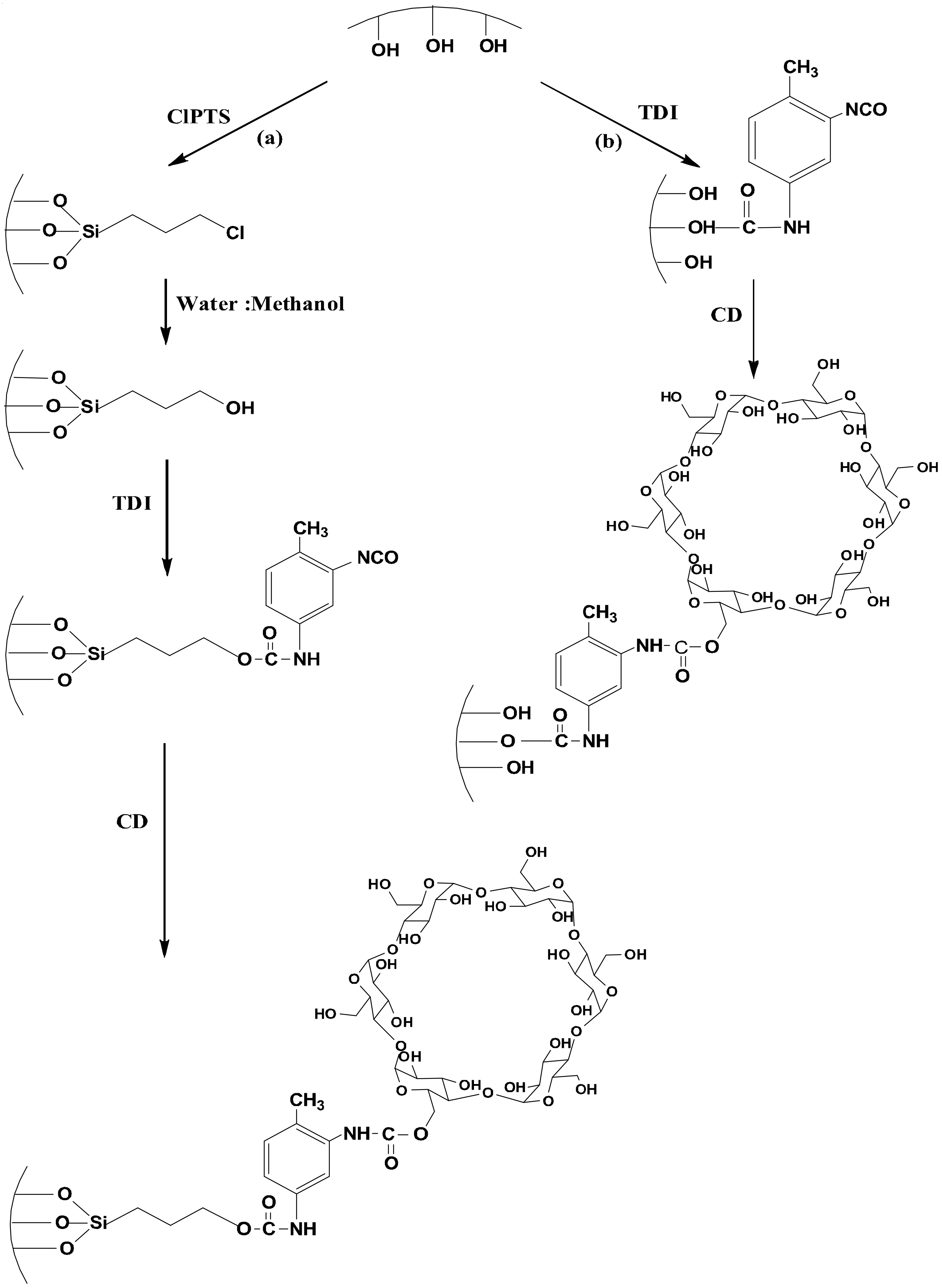

Fig. 1. Preparation of modified mesoporous silica with β-cyclodextrin

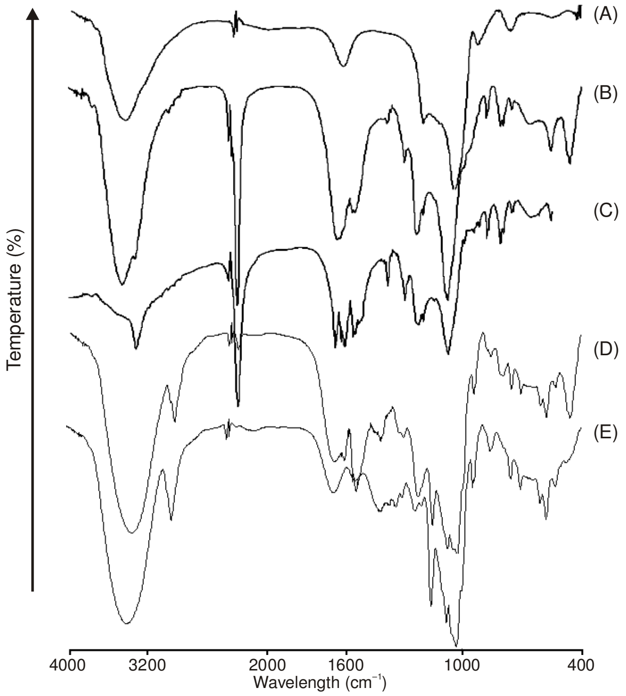

Fig. 2. FTIR spectra of MCM-41 (A), MCM-PTS-TDI, (B) MCM-TDI (C), MCM-PTS-TDI-β-CD (D) and MCM-TDI-β-CD (E)

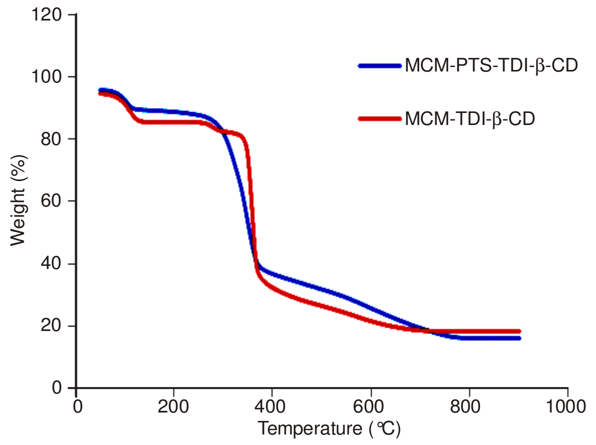

Fig. 3. TGA-DTA analysis of MCM-PTS-TDI-β-CD and MCM-TDI-β-CD

mesoporous silica curves exhibited a stage of weight loss below 100 °C due to the loss of the adsorbed water. After initial loss of adsorbed water, the removal of the linkers was conducted (Table-2). The removal of β-cyclodextrin started at 310 °C and continued up to 600 °C. An additional weight loss occurred at higher temperatures due to further condensation of the silicate walls, as observed in other mesoporous silicates.

TABLE-2
THERMOGRAVIMETRIC ANALYSIS RESULTS OF MCM-PTS-TDI-β-CD AND MCM-TDI- β -CD

	Temp. (°C)	Weight -loss (%)	Assignment
MCM-PTS-TDI-β-CD	50-120	6.7	Moisture
	150-400	53.2	PTS Carbamate group and β-CD
	400-700	20.1	β-CD
MCM-TDI-β-CD	50-120	9.2	Moisture
	240-310	3.5	Carbamate group
	310-800	63.8	β-CD

Elemental analysis: Covalent attachment of the β-cyclodextrin to MCM-PS-TDI, according to (Fig. 1), was monitored by several techniques. The elemental analysis of the samples (Table-1) shows a gradual increase in the carbon content after the modification step. After the reaction of MCM-PS with toluene di-isocyanate, the percentages of C and N increases from 3.13 and 0.14 % to 20.82 and 5.03 %, respectively, indicating the success of the modification step. After reaction with β-cyclodextrin content increased even further (Table-3), showing that the β-cyclodextrin were attached to the silicate surface.

TABLE-3
RESULTS OF ELEMENTAL ANALYSIS FOR CLPTS-MCM, MCM-PTS-TDI-β-CD, M-TDI, MCM-TDI-β-CD

	C (%)	H (%)	N (%)
MCM-ClPTS	3.13	3.24	0.14
MCM-ClPTS-TDI	20.82	4.21	4.43
MCM-PTS-TDI-β-CD	39.01	6.60	1.21
MCM-TDI	18.64	3.04	5.93
MCM-TDI-β-CD	36.41	5.21	4.72

XRD diffraction: Fig. 4 shows the low angle range of XRD patterns for the modified materials. The pure MCM-41 starting material (not present), exhibits the peak patterns characteristic of mesoporous silica materials with hexagonal symmetry: three well resolved Bragg reflections for 2 h values between 2 and 4, $5^{\bullet}$, one very intense due to the (100) reflection and two weaker peaks due to (110) and (200) reflections (6). Upon functionalization of MCM-41 with β-cyclodextrin, the XRD patterns of the samples show weak (100) peaks and weaker (110) and (200) peaks. The change in the (100) peak intensities and the small shift to higher 2θ values suggests that β-cyclodextrin is present on the internal pore walls of MCM-41[44], leading to an increase of phase cancellation between scattering from the walls and the pore regions[45,46]. It also can be noticed that the (100) peak became broader in case of MCM-TDI-β-CD, indicating a slight alteration of the ordering of the mesoporous structure.

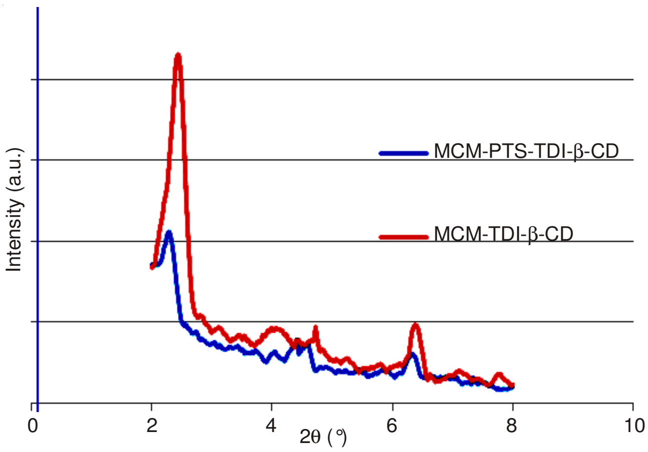

Fig. 4. XRD analysis of MCM-PTS-TDI-β-CD and MCM-TDI-β-CD

Nitrogen adsorption-desorption analysis : In order to further investigate the channel structure of these materials, the characterization of the nitrogen adsorption-desorption was also carried out. The corresponding isotherms are presented in Fig. 5. The material MCM-TDI-β-CD exhibit the typical type-IV isotherm according to the IUPAC classification and it corresponds to the characteristic of mesoporous materials with highly uniform size distributions, while MCM-PTS-TDI-β-CD exhibits the type-II isotherm. Type-II isotherm is characteristic for non porous or macroporous adsorbent with strong adsorbate-adsorbent interactions. Adsorption isotherms are of Type-II in the IUPAC classification that represents monolayer/multilayer adsorption. This suggests that adsorption of N_2 for the sorbent materials is moderate or, on the other hand, the main adsorption process may be ascribed to a van der Waals force. Generally, the isotherm shows that the amount of N_2 adsorbed increases as the relative pressure increases up to a saturation point. A complete adsorption of N_2 as a monolayer onto the surface of sorbent material is shown by the plateau of the adsorption isotherm. After this point, a large uptake of N_2 is observed close to the saturation pressure and it is assumed that multilayer adsorption takes place (*i.e.*, implying the presence of mesopores)[47].

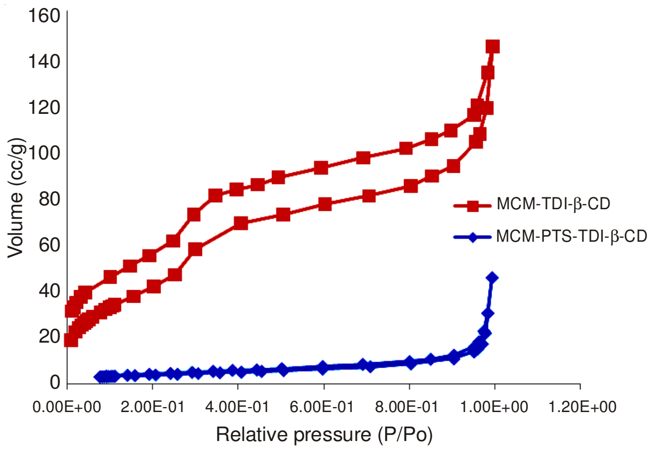

Fig. 5. Nitrogen adsorption-desorption isotherms of (◆) MCM-PTS-TDI-β-CD and (🟥) MCM-TDI-β-CD

The BET isotherm (Fig. 5) of the modified sample MCM-TDI-β-CD shows hysteresis loops type H_2 which describes materials that are frequently disordered with poor-defined pore size and shape indicating bottleneck constrictions[48]. The structure data of these mesoporous materials (BET surface area, total pore volume and pore diameter) are summarized in Table-4. The prepared materials showed a decrease in the BET surface area, which suggests the presence of bulky materials inside the support porous system[49].

TABLE-4
STRUCTURAL PARAMETERS OF MCM-41,
MCM-PTS-TDI-β-CD AND MCM-TDI-β-CD

Sample	S_{BET} (m^2/g)	V(cm^3/g)	D (nm)
MCM-41	993	0.86	2.9
MCM-PTS-TDI-β-CD	14	0.023	6.7
MCM-TDI-β-CD	147	0.17	4.48

Evaluation of sorption capabilities: In this study we aim to evaluate the sorption abilities of mesoporous silica-grafted with β-cyclodextrin toward some selected organotin compounds. We performed solid-liquid sorption studies of organotins compounds (tributyltin, triphenyltin and dibutyltin) by using MCM-PTS-TDI-β-CD and MCM-TDI-β-CD as sorbents. The sorption capacities and sorption percentages were calculated through eqn. (2) and (3), respectively and they are provided in Figs. 6 and 7, respectively. These data were obtained by using a 0.01 g of the grafted mesoporous silica for sorption of organotins compounds from aqueous solution. The equilibrium concentration of tin in the aqueous phase was determined by ICP-MS.

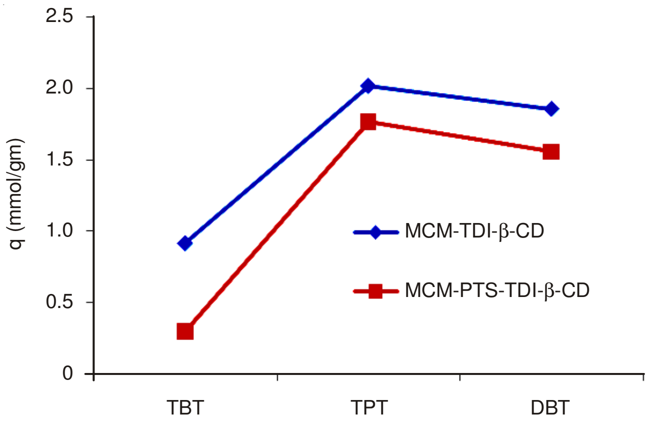

Fig. 6. Sorption capacities (q) of MCM-PTS-TDI-β-CD and MCM-TDI-β-CD towards organotins compounds.

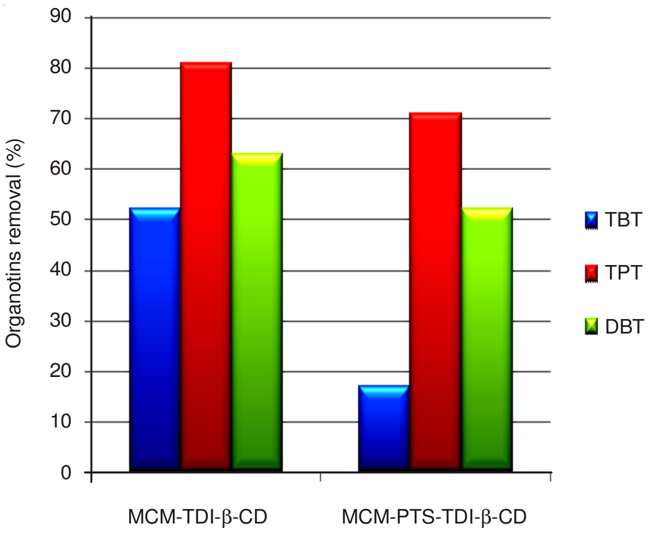

Fig. 7. Sorption percentages of organotins compounds by MCM-PTS-TDI-β-CD and MCM-TDI-β-CD

The sorption data revealed that MCM-TDI-β-CD and MCM-PTS-TDI-β-CD are effective sorbents and the sorption efficiency of MCM-TDI-β-CD is higher than MCM-PTS-TDI-β-CD for organotins compounds. Fig. 7 show that the MCM-TDI-β-CD can remove 52 % tributyltin, 81 % triphenyltin and 63 % dibutyltin from aqueous solution whereas MCM-PTS-TDI-β-CD can only remove 17 % tributyltin, 71 % triphenyltin and 52 % dibutyltin. The reason for MCM-TDI-β-CD has a larger removal capacity compared to MCM-PTS-TDI-β-CD might be due to the larger specific surface area of the former.

On the whole, MCM-TDI-β-CD and MCM-PTS-TDI-β-CD are revealed to be useful sorbents especially MCM-TDI-β-CD for triphenyltin. This also indicates that the grafting of a β-cyclodextrin based compound onto a mesoporous silica based support is a good approach.

Conclusion

In this work, we report the successful anchoring of β-cyclodextrin onto the MCM-41 surface, using two methods. In the first method, the MCM-41 surface was functionalized with 3-chloropropyltriethoxysilane (ClPTS). The chlorine groups were hydrolysed into hydroxyl groups, which reacted with one of the terminal isocyanate groups of the linking agent (TDI), forming urethane links. The other terminal isocyanate functionality reacted with the free hydroxyl group present in the β-cyclodextrin. In the second method, toluene di-isocyanate was directly used as a binder. Urethane bonds were formed between a terminal isocyanate group and the silanol groups present on the unmodified MCM-41 surface. Different characterization techniques such as FTIR, XRD, CHN, BET and TGA showed evidences that the β-cyclodextrin was covalently attached to the MCM-41 surface and that its channel structure remained unchanged. The sorption studies of some organtins compounds were performed by MCM-TDI-βCD and MCM-PTS-TDI-βCD as sorbent materials. From the sorption results it appeared that MCM-TDI-βCD is a more effective sorbent than MCM-PTS-TDI-βCD and especially for triphenyltin triphenyltin. Overall, the grafting of a mesoporous silica MCM-41with a β-cyclodextrin has become a useful approach for organtins compounds removal from aqueous media by sorption.

ACKNOWLEDGEMENTS

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