

THE ADSORPTION PROPERTIES OF SURFACE-MODIFIED MESOPOROUS SILICA MATERIALS WITH β -CYCLODEXTRIN

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ABSTRACT

The adsorption properties of surface-modified mesoporous silica materials containing β -cyclodextrin (CD ICS) were studied using two types of gas phase adsorbates (N_2 and CH_3Cl), along with a dye molecule (*p*-nitrophenol; PNP) in an aqueous solution. The CD ICS materials possess an ordered silica mesostructure framework that depends on the type of surfactant template and the level of loading of β -CD. Incremental variations in the uptake of gas phase adsorbates and PNP from an aqueous solution were observed, according to the composition of CD ICS materials. For materials with similar CD loading, the surface area (SA) and pore volume doubled, as the surfactant from dodecylamine to hexadecylamine was varied. The SA of the CD ICS materials decreased by *ca.* 1.5-fold as the CD loading varied from 2% to 6%. The sorption capacity (Q_e ; mmol/g) of PNP increased from 61% to 84% as the CD loading increased from 2% to 6% and as the alkyl chain length of the surfactant template varied from C12 to C16. The adsorption properties of CD ICS materials with CH_3Cl in the gas phase and for PNP in aqueous solution adopt a multi-layer adsorption profile, as described by the BET isotherm model.

Keywords: 4-Nitrophenol; Adsorption; β -Cyclodextrin; Methyl Chloride; Mesoporous Silica; Surface functionalization

1. INTRODUCTION

Porous materials are widely used as adsorbents, catalysts and catalyst supports, due to their large surface area (SA) and pore volume (PV) characteristics. Zeolites are microporous crystalline aluminosilicate materials with uniform pores in the range of 0.5–2.0 nm with structurally well-defined pores and channels. Zeolites have applications as molecular sieves and as catalysts for the cracking of crude-oil (Cejka et al., 2010), however; the adsorption properties of zeolites in an aqueous solution become attenuated because the competition between adsorbate and solvent is somewhat limited, due to their small pore-size distribution (PSD). Thus, there is an ongoing research interest in the development of mesoporous materials with tunable PSD and surface functionalization, due to their utility in adsorption-based applications, such as catalysis, molecular sieving, chemical sensing, and environmental remediation (Valtchev et al., 2011; Rurack & Martinez-Manez, 2010; Mitzi, 2008; Bergna & Roberts, 2005; Levy & Zayat, 2015).

Since the discovery of mesoporous silica materials such as MCM-41 (Beck et al., 1992) efforts have been directed toward the incorporation of organic functionality within such framework materials. The incorporation of organic moieties onto silica enables tuning of the surface

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properties such as the hydrophile-lipophile balance (HLB), surface binding affinity, and the surface reactivity toward oxidation and hydrolytic processes. Surface modification can be achieved by post-synthetic grafting of organic groups onto the channel walls *via* the pendant –Si-OH groups or by direct co-condensation of symmetric tetraalkoxy-substituted orthosilicate precursors such as TEOS [Si(OEt)₄] with asymmetric reagents of the type RSi(OEt)₃ (Lim et al., 1998; Lim & Stein, 1999), where *R* is an organic functional group. Both methods have a disadvantage of non-uniform distribution of the *R*-group in the pores and limited surface coverage. In order to achieve greater and uniform surface coverage, monographs on the synthesis of periodic mesoporous organosilica have been reported (Valtchev et al., 2011; Rurack & Martinez-Manez, 2010; Mitzi, 2008; Bergna & Roberts, 2005; Levy & Zayat, 2015). The polymerization of bridged silsequioxane monomers, (RO)₃Si-B-Si(OR)₃, or the copolymerization of TEOS with (RO)₃Si-B-Si(OR)₃ in the presence of surfactant affords MCM-41 type materials, where the *R*-group becomes an integral part of the channel walls. Subsequent removal of the surfactant yields a periodic mesoporous organosilica material, similar to hexagonal mesophase silica (HMS) without notable channel blockage (Levy & Zayat, 2015; Hatton et al., 2005). A new family of mesoporous hybrid silica materials with covalently bound cyclodextrin (CD) was reported (Huq et al., 2001; Liu et al., 2004; Liu, & Lambert, 2004; Zolfaghari, 2016; Yang et al., 2014; Alam et al., 2013) with relatively high SA and PV. The microporous cavities are provided by the CD moiety for these surface functionalized materials.

Cyclodextrins (CDs) (Crini, 2014) represent an important class of cyclic oligosaccharides composed with variable numbers ($n=6-8$) of D-glucopyranosyl units connected by α -1,4-linkages. β -CD (β -CD $n=7$) is among the most widely studied of the CDs due to its availability and relatively low cost. Continued interest in the science and technology of CDs is attributed to their remarkable ability to form inclusion complexes with appropriately sized guest molecules and ions in solution and in the gas phase. Inclusion complex formation results in variation of the physicochemical properties of the guest molecule; solubility profile, chemical stability toward heat, light, and oxidizing conditions, and vapour pressure. Thus, CDs are widely used in formulation of pharmaceuticals, food and flavors, cosmetics, packaging and textiles. Some examples of reviews include research on the application of CDs in biocatalysis, agriculture, environmental remediation, and chemical separation, (Crini, 2014; van de Manakker et al., 2009; Morin-Crini, & Crini, 2013). The utility of CDs in polymer materials includes research in filtration and solid phase extraction processes (Morin-Crini, & Crini, 2013; Wilson et al., 2014; Mohamed et al., 2015).

Concerns regarding the fate and transport of toxic waterborne organic compounds, such as phenols (Pratt et al., 2010; Udoetok et al., 2016) and petrochemical derivatives (Mohamed et al., 2015) by inadvertent release in aquatic environments are an issue of emerging global concern for the ecosystem and human health. Among the various physical and chemical treatment processes, adsorption represents a green strategy for environmental remediation of waterborne contaminants (Qu, 2008). Surface-modified silica materials containing CDs are of considerable interest due to the unique host-guest chemistry of CDs and their utility as sorbents in solid state separation technologies, especially functionalized organosilica compounds (Alam et al., 2013; Crini & Morcellet, 2002). Recently, the preparation of modified mesoporous silica materials (CD ICS) was reported using surfactant templates with variable alkyl chain length (C12-C16) and variable β -CD content, according to Figure 1 and 2 (Wilson et al., 2010). The objective of the present study was to investigate the adsorption properties of CD ICS materials in an aqueous solution with a model dye probe (*p*-nitrophenol; PNP) along with methyl chloride in the gas phase. It will be shown that CD ICS materials have improved textural properties with improved surface modification of the silica framework via β -cyclodextrin, as compared with

previous reports (Huq et al., 2001; Bibby & Mercier, 2003). The potential utility of these materials as promising adsorbents for waterborne and atmospheric contaminants was studied.

2. EXPERIMENTAL

2.1. Materials

Acetic acid, sodium acetate, epichlorohydrin, HCl, NaOH, sodium hydrogen phosphate, *p*-nitrophenol (PNP) were obtained from Sigma-Aldrich Canada Ltd. (Oakville, ON). All the chemicals used were ACS grade unless specified otherwise and these were used as received without further purification. The preparation of HMS silica materials containing β -CD was carried out, according to a reported procedure (Bibby & Mercier, 2003). The detailed preparation and characterization of CD ICS materials, according to Figures 1 and 2, are reported elsewhere (Bibby & Mercier, 2003; Mahmud, 2007). The sample ID and the relative composition (w/w%) for the CD ICS materials is given in Table 2 (*vide infra*).

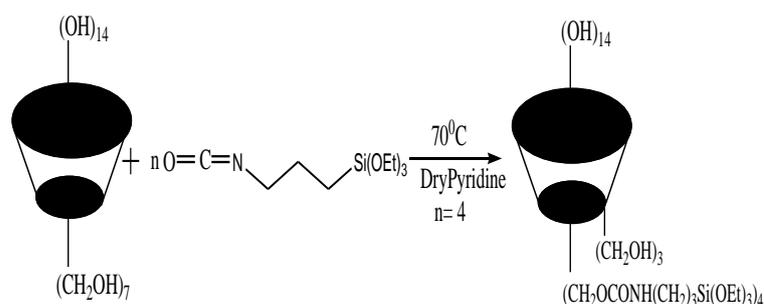


Figure 1 Covalent coupling of β -CD with triethoxysilane (3-isocyanatopropyltriethoxysilane) where the product is hereafter referred to as CD-ICL, where the degree of substitution onto β -CD is estimated to be $n=4$

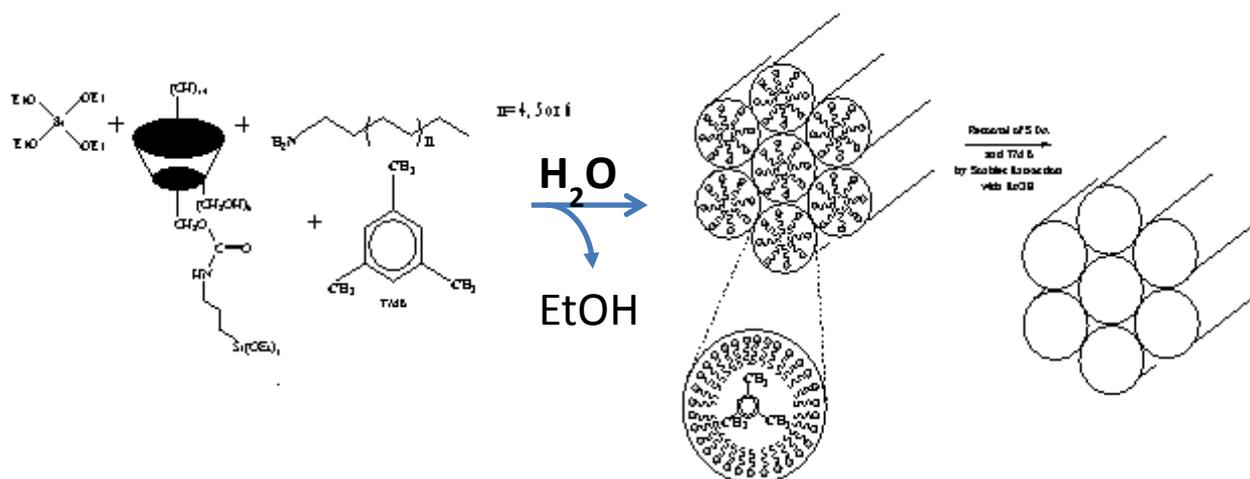


Figure 2 An overview of the synthesis of surface modified hexagonal mesophase silica (HMS) containing β -CD. Note that the respective components are not drawn to scale.

2.1. Methods

2.1.1. Nitrogen adsorption

Nitrogen adsorption-desorption isotherms of the adsorbent materials were measured at 77 K using a Micromeritics ASAP 2000 SA analyzer. Samples were ground in a small crucible and passed through a 40 mesh size sieve prior to measurement with degassing at 383 K at 10^{-6} mm Hg until stable vacuum pressures were achieved. SA and PV were determined according to a reported procedure (Wilson et al., 2011).

2.1.2. CH_3Cl adsorption

All samples for adsorption measurements were ground into powders and passed through a 40 mesh sieve. Gas adsorption was performed at equilibrium and 295 K where the volume of gas was adsorbed at variable relative pressures (p/p°) up to the saturation vapour pressure (p°) of methyl chloride at ambient conditions. All samples were degassed at 110°C and 10^{-6} mm Hg prior to the start of each isotherm and the uptake of CH_3Cl was obtained using a modified Langmuir gas adsorption as described elsewhere (Wilson et al., 2010; Mahmud, 2007).

2.1.3. Solid-solution adsorption studies

A stock solution of 10^{-4} M PNP was prepared in 0.1M $\text{CH}_3\text{CO}_2\text{H}/\text{CH}_3\text{CO}_2\text{Na}$ buffer at pH 5.0. Variable amounts of adsorbent were dosed in 10 mL of adsorbate solution and equilibrated with shaking for 24 h (hours) until equilibrium at 295 K. The solid phase was filtered and the concentration of PNP in the filtrate solution was measured by UV-Vis spectroscopy.

2.1.4. Models and equations

The isotherms results herein are presented as plots of the amount of adsorbate uptake (Q_e) per weight of adsorbent according to Equation 1.

$$Q_e = \frac{(C_o - C_e) \times V}{m} \quad (1)$$

C_o is the initial concentration of adsorbate (PNP), C_e is the residual PNP concentration after adsorption, V is the volume of solution, and m is the weight of adsorbent. The data was fitted with several types of isotherms (Table 1) as follows; Langmuir, Freundlich and Brunauer-Emmet-Teller (BET) models (Atkins & de Paula, 2009). The sum of square of errors (SSE) was used as a criterion of the "best fit" where a lower value of SSE (Equation 2) yielded a "best-fit".

$$SSE = \sqrt{\frac{(\sum (Q_{e,calc} - Q_{e,expt})^2)}{N}} \quad (2)$$

The SSE was minimized across all data where $Q_{e,expt}$ is an experimental value, $Q_{e,calc}$ is the calculated value according to the respective isotherm model, and N is the number of experimental data points.

Table 1 Adsorption isotherm models (Atkins & de Paula, 2009)

Model	Equation	Comment
Langmuir	$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m}$	Monolayer adsorption
BET	$\frac{C_e}{Q_e(C_o - C_e)} = \frac{1}{Q_m k} + \frac{C_e(k-1)}{C_o Q_m} \left(\frac{C_e}{C_o} \right)$	Multi-layer adsorption
Freundlich	$\log Q_e = \frac{1}{n} \log C_e + \log K_f$	Heterogeneous adsorption model

The parameters in Table 1 are defined as follows: Q_e is the amount of adsorbate adsorbed (mol g^{-1}), C_e is the equilibrium concentration (M) of adsorbate in solution, Q_m is the maximum adsorption for monolayer coverage (mol g^{-1}), C_o is the initial concentration of adsorbate (M), b is the adsorption equilibrium constant (M^{-1}), k is a constant related to the heat of adsorption, K_f

and n are the Freundlich constants for adsorption capacity and intensity (Atkins & de Paula, 2009).

3. RESULTS & DISCUSSION

3.1. Organosilica Materials Design

Bibby and Mercier (2003) incorporated CDs within mesoporous silica frameworks using a triethoxysilane linker (APS β -CD) with a C12 surfactant (Figure 3). In this study, the ICL linker (3-isocyanatopropyltriethoxysilane) was used to form a conjugate with β -CD denoted as CD ICL (Figure 1). The CD ICL precursor represents a substituted form of TEOS [$\text{RSi}(\text{OEt})_3$; where R contains β -CD], as seen in Figure 3. CD ICL was utilized because the urethane bond linker and β -CD were anticipated to have greater stability towards hydrolysis as compared with APS β -CD illustrated in Figure 3.

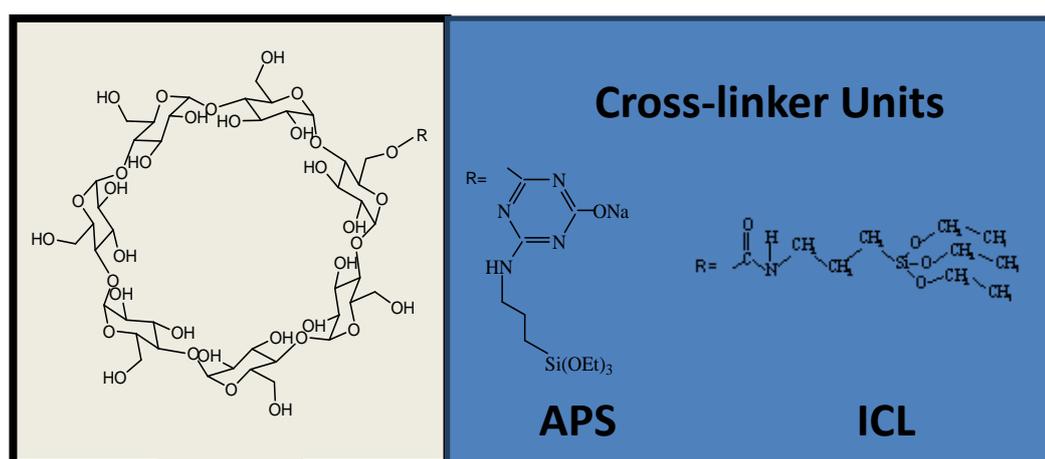


Figure 3 Molecular structure of CD APS and CD ICL, according to the silica-based cross-linker used in the co-condensation with TEOS to form hybrid silica materials with grafted β -CD. The relative size of cross-linker and β -CD are not drawn to scale.

As outlined in Figures 1 and 2, the incorporation of an organic functional group in a mesoporous silicate framework can be achieved by introduction of an asymmetric orthosilicate through conjugation of β -CD with 3-isocyanatopropyltriethoxysilane (CD-ICL). The sol-gel reaction of TEOS with CD-ICL affords a direct synthesis pathway to surface modified hexagonal mesophase silica containing β -CD (Figure 2), referred to hereafter as CD-ICS materials (Bibby & Mercier, 2003; Mahmud, 2007). Figures 1 and 2 illustrate a facile and efficient approach for obtaining CD-ICS materials whilst affording surface accessibility and stable attachment of β -CD to the silica framework *via* the urethane coupling. The product identity of the materials was supported by a range of materials characterization methods; IR/Raman/solids ^{13}C CP MAS NMR spectroscopy, PXRD, TGA, and MALDI TOF mass spectrometry, described elsewhere (Mahmud, 2007).

3.2. Solid-Gas Isotherm Results: Nitrogen Adsorption

The heterogeneous adsorption properties of the CD ICS materials were studied by adsorption from the gas phase and in an aqueous solution, respectively. The use of N_2 gas adsorption isotherms is a routine method for obtaining textural (SA and PV) properties and these are well established for meso- and micro-porous materials (Mahmud, 2007; Wilson et al., 2011). A complete listing of the adsorption isotherms are presented elsewhere (Mahmud, 2007). The presence of textural mesoporosity is verified by well-defined hysteresis loops in the range of p/p^0 from 0.3 to 1.0. A comparison of the adsorption isotherms of materials was prepared using

different surfactants (C12 to C16) reveal that CD-ICS materials prepared with templates with shorter alkyl chain possess greater textural versus framework mesoporosity. An opposite trend occurs for surfactants with longer alkyl chains, in agreement with observations reported elsewhere (Tanev & Pinnavaia, 1996). Table 3 summarizes the textural properties of CD ICS and CD HMS (Figure 3) materials as determined from nitrogen adsorption results.

Table 2 Textural properties of CD-ICS and CD HMS materials estimated from nitrogen adsorption at 77 K

Material	β -CD (w/w%)	Surfactant (SDA)	SA (m ² /g)	PV (cm ³ /g)
CD ICS 2(12)	2	C12	630.3	0.67
CD ICS 4(12)	4	C12	504.3	0.51
CD ICS 6(12)	6	C12	307.0	0.21
CD HMS 2% ^a	2	C12	547.0	0.51
CD ICS 2(14)	2	C14	680.1	1.16
CD ICS 4(14)	4	C14	505.4	0.52
CD ICS 6(14)	6	C14	591.8	0.42
CD HMS 4% ^a	4	C14	319.0	0.26
CD ICS 2(16)	2	C16	906.5	1.18
CD ICS 4(16)	4	C16	832.1	0.90
CD ICS 6(16)	6	C16	656.8	0.47
CD HMS 6% ^a	6	C16	197.0	0.21

^aObtained from (Huq & Mercier, 2001). C12, C14, and C16 refer to the SDA surfactants dodecylamine, tetradecylamine, and hexadecylamine, respectively.

In general, the CD ICS materials have greater surface area (SA) and pore volume (PV) when compared with CD HMS materials. The enhanced textural properties of CD ICS are also related to use of the ICL linker employed in this study as compared with a more bulky linker (APS β -CD) reported elsewhere (Huq & Mercier 2001). As for the case of CD ICS materials, the dependence of SA on the type of structural directing agent (surfactant) and CD loading of the various mesoporous silica materials containing β -CD was evaluated according to the SAPV in Table 2. Accordingly, a general decrease in SA and PV occurs as the β -CD loading increases for CD-ICS materials prepared with a common surfactant. A comparison of CD-ICS materials prepared using C12 with variable CD loading (2% to 6%) shows a decrease in SA (630.3 to 307.0 m²/g) along with a decrease in PV (0.67 cm³/g to 0.21 cm³/g). Similar trends were observed for CD-ICS materials prepared using C14 and C16, suggesting that β -CD incorporation likely occurs within the pore channels. At similar CD loadings, the framework mesoporosity increases as the surfactant alkyl chain length increases. A comparison of CD ICS 2(12) and CD ICS 2(16) shows that the SA increases (630.3 m²/g to 906.5 m²/g) with an increase in PV (0.67 cm³/g to 1.18 cm³/g) as the surfactant alkyl chain length increases (C12 to C16). Similar trends were observed for other CD loadings in other CD-ICS materials, according to the textural properties in Table 2.

3.3. Solid-Gas Isotherm Results: CH₃Cl Adsorption

Selected examples of isotherm adsorption results for CD-ICS materials with gaseous methyl chloride and PNP in aqueous solution were provided for CD ICS 2(12) and CD ICS 4(12) in a previous study (Wilson et al., 2010). A limited comparison of the uptake results for CD-ICS materials at 4% and 6% loading of β -CD were made with several carbonaceous and cross-linked polymers containing β -CD with methyl chloride (*cf.* Figure 1 and Table 1 in Wilson et al., 2010). The results in this study cover a wider range of CD ICS materials according to the

list of materials given in Table 2. CH₃Cl is an industrial pollutant (Wilson et al., 2010) with behaviour representative of many volatile organic compounds (VOCs) and its uptake properties are complementary to the nitrogen adsorption results due to its different physicochemical properties, such as polarity and molecular size.

In general, the CH₃Cl gas adsorption isotherm of CD ICS materials is well-described by the BET and Freundlich models. The trends are understood in terms of the heterogeneous surface properties of the CD ICS materials due to the limited surface attachment of β-CD, along with the tendency of CH₃Cl to form multilayers, as evidenced by its relatively high uptake in Table 3. Examples of representative uptake results in Table 3 are given for two types of CD ICS materials with variable CD loading. Additional isotherm results for the other CD ICS are reported elsewhere (Mahmud, 2007). The adsorbent surface area (SA) estimated from CH₃Cl and N₂ adsorption isotherms of CD ICS 4(12) and CD ICS 6(14) are listed according to the Langmuir and BET models. The variable SA values for each model may be attributed to an underestimation of the adsorption at low pressure and an overestimation at higher pressure conditions. Consequently, the SA values calculated from the BET isotherm are generally lower than the experimental values from N₂ adsorption. By comparison, the SA values in Table 3 by the Langmuir model correspond more closely to the BET estimates obtained by nitrogen adsorption results.

Table 3 Estimates of adsorbent surface area according to CH₃Cl adsorption at 295 K and comparison with N₂ BET results

Adsorption Isotherm Model	CD ICS 4(12) (m ² /g)	CD ICS 6(14) (m ² /g)
Langmuir isotherm	521	560
BET isotherm	85	81
BET isotherm (N ₂ adsorption) ^a	504	591

^a BET surface area from N₂ adsorption were obtained at 77K

The BET derived SA for CH₃Cl adsorption is lower than the SA obtained from the N₂ adsorption results (Table 2). This difference may be attributed to the nature of the backfill gas (CH₃Cl vs. N₂) and relative temperature conditions for each experiment (295 K vs. 77 K). The anticipated number of multi-layers formed in the case of CH₃Cl adsorption is lower than that for the case of N₂ adsorption. As well, N₂ is a smaller gas species than CH₃Cl, aside from differences in their relative polarity. As a result, the BET SA value calculated from CH₃Cl adsorption is lower than that obtained from N₂ adsorption which may be attributed to the differences in micropore filling of each respective gas due to the Kelvin effect.

3.4. Solid-Solution Isotherm Results: PNP Adsorption

In previous studies, it was shown that PNP is a useful UV-vis dye probe for estimating the textural properties of adsorbent materials. Dye concentration can be monitored by spectrophotometry at variable conditions and PNP serves as a suitable model compound that represents typical wastewater contaminants for agrochemical, textile, and pharmaceutical industries. Figure 4 is a representative plot of adsorptive uptake (Q_e; mmol/g) versus the equilibrium concentration of PNP. The adsorption isotherms for other CD ICS materials with variable CD loadings prepared using surfactant templates with variable chain length are qualitatively similar in appearance (Mahmud ST., 2007) to Figure 4. In general, the uptake is low across the experimental range of concentrations up to a critical value, where a sharp rise is observed. The concentration dependence of Q_e was evaluated using the Langmuir, Freundlich

and BET isotherm models. The uptake properties for the various CD ICS materials are well-described by the BET model, in accordance with the multi-layer adsorption profile.

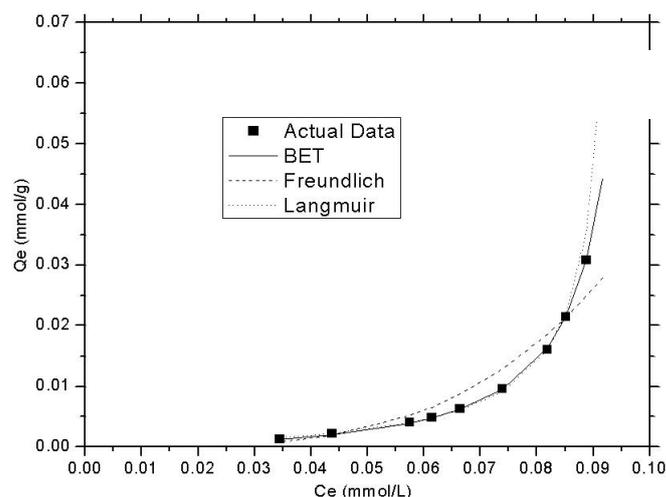


Figure 4 Adsorption isotherm result for CD ICS 4(12) with *p*-nitrophenol (PNP) at pH 5.0 in 0.1 M $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ buffer at 295 K. The lines correspond to the “best fit” results according to each isotherm model.

A comparison of adsorption behaviour of CD ICS materials prepared using the same surfactant (template) at variable levels of CD loading reveal differences in the relative uptake toward PNP at these same conditions (results not shown). As the CD loading increases the C_e values for PNP decrease at a fixed dosage of adsorbent material. By contrast, the uptake properties of pristine HMS silica (containing no CD) toward PNP show negligible uptake at similar conditions, in agreement with previous reports (Huq et al., 2001; Bibby & Mercier, 2003). In a manner similar to CD HMS materials, the observed uptake for CD ICS materials in this study with PNP can be attributed to the formation of stable host-guest complexes between β -CD and PNP ($K \approx 10^2 \text{ M}^{-1}$) (Wilson & Guo, 2012). The overall increase in uptake for PNP is relatively constant with some variation due to the CD loading level (2%-6%). As noted above, a decrease in the SA and PV results as the CD loading increases beyond a certain level that is accompanied by a decrease in sorptive uptake. The attenuated uptake is understood in terms of two interrelated effects; *i*) the decreased surface accessibility of the CD sites, and *ii*) the loss of mesoporosity of the silica framework at higher CD loadings. Both effects are anticipated to attenuate the adsorption of PNP. The role of surfactant template on the adsorption properties of CD ICS materials is evidenced by changes in C_e for PNP. The value of C_e decreases from $3 \times 10^{-2} \text{ M}$ to $5 \times 10^{-3} \text{ M}$ for CD ICS materials at a fixed CD loading with variable surfactant chain length (C12 to C16). The variation in uptake agrees with the greater textural mesoporosity, in agreement with N_2 adsorption results (Table 3). An increase in the surfactant chain length enhances the SA and PV for such silica materials, in accordance with the colloidal properties of the hexagonal mesophase for variable chain length (C12-C16) surfactants.

The CD-ICS materials show favourable sorption affinity towards PNP as compared with the CD HMS materials, according to the comparison listed in Table 4. In the case of the C12 surfactant template, the adsorption capacity is 2- to 3-fold greater than the corresponding CD HMS materials. The offset may reflect the greater overall surface accessibility of β -CD in CD ICS materials according to the nature of the ICL linker (Figure 3) employed herein.

Figure 5 illustrates the UV-vis absorbance spectra of PNP in the presence and absence of APS at variable doping levels.

Table 4 Comparison of the PNP uptake with CD ICS and CD HMS materials at 295 K

Adsorbent Material	PNP Uptake ($\mu\text{mol/g}$)	Removal PNP ($\text{mol}\%$) ^b
CD ICS 2(12)	5.7	61%
CD HMS 2% ^a	3.3	Not reported
CD ICS 4(12)	6.2	65%
CD HMS 4% ^a	2.1	Not reported
CD ICS 6(12)	6.5	68%
CD HMS 6% ^a	3.4	Not reported
CD ICS 6(14)	6.6	73%
CD ICS 6(16)	7.6	84%

^a Obtained from (Huq et al., 2001); ^b $C_0 = 10.0 \times 10^{-2}$ M; and ^b wt. adsorbent = 500 mg

The λ_{max} at *ca.* 320 nm is characteristic of PNP in its non-ionized form. As the content of APS increases, the peak at 400 nm for ionized PNP increases in intensity. The λ_{max} at 400 nm is typically observed for the phenolate form of PNP at elevated pH values. The mixture of non-ionized and ionized forms of the PNP was suppressed by carrying out the sorption experiments in aqueous solutions buffered at reduced pH = 7.45, where this pH lies above the pK_a (*ca.* 7.1) for PNP. Evidence of shifts in the protolytic equilibria was observed in an independent study for cross-linked forms of β -CD where the cross-linker units contain amide linkages. The occurrence of hydrogen bonding between PNP and the amide functionality was found to shift the equilibria of PNP from its protonated to ionized form due to the base character of the amide group (Wilson et al., 2011). The adsorptive interaction between PNP and APS was also supported by IR spectroscopy. The IR spectra of CD HMS were taken before and after adsorption with PNP after recovery from an aqueous solution. After the adsorption of PNP, the IR bands around 1600 cm^{-1} due to C=N stretching frequency and 1512 cm^{-1} due to C-C aromatic skeletal vibration of cyanuric chloride from APS β -CD were attenuated. A concomitant increase of the vibrational band around 1080 cm^{-1} due to Si-O-Si stretching from silica network is observed in Figure 6.

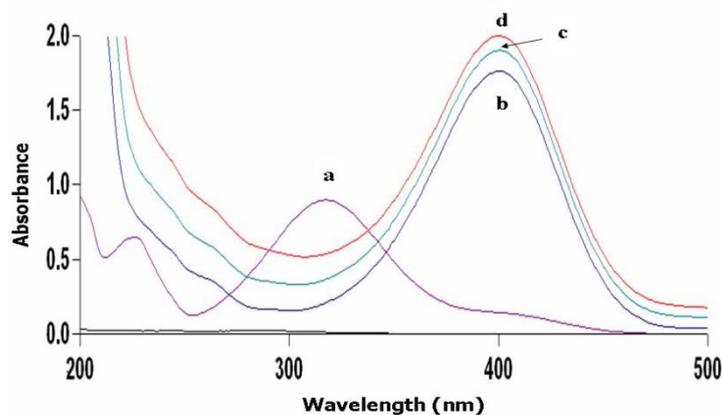


Figure 5 UV-Visible spectra showing the effect of APS on the absorbance properties of PNP at pH 5: a) 10^{-4} M neutral PNP without APS; b) 100 μL (~ 100 mg) APS with 10 ml 10^{-4} M PNP; c) 200 μL (~ 200 mg) APS with 10 ml 10^{-4} M PNP; d) 300 μL (~ 300 mg) APS with 10 ml 10^{-4} M PNP

Thus, it is important to carry out complementary studies when possible to provide a further understanding of the nature of the active adsorption sites for such complex materials. According to the adsorption and spectroscopic results for the APS β -CD/PNP system, it is concluded that two adsorption sites contribute to the uptake of PNP to a variable extent. Contributions arising from the linker site (APS) and the inclusion sites of β -CD likely play a key role for the adsorption properties of this system.

According to adsorption isotherm results presented herein, there are differences between CD HMS and CD ICS materials, according to the nature of the linker which anchors β -CD to the silica framework (Figure 3). In the case of CD ICS materials, increases in the adsorption properties occur as the chain length of the surfactant template varies (C12-C16) along with the CD loading (2%-6%). The role of framework mesoporosity is understood in terms of the increase of the channel diameter of the silica framework; however the effects of variable CD loading on textural mesoporosity are complicated by two opposing effects. If one assumes that the inclusion sites of β -CD are accessible, the adsorptive uptake typically increases as the CD content increases, along with micropore contributions from the CD. In the case of CD ICS materials, the potential of blockage within the channel mesopores results in attenuated accessibility of the β -CD inclusion sites, ignoring the mechanical instability of the silica framework at such higher CD loadings.

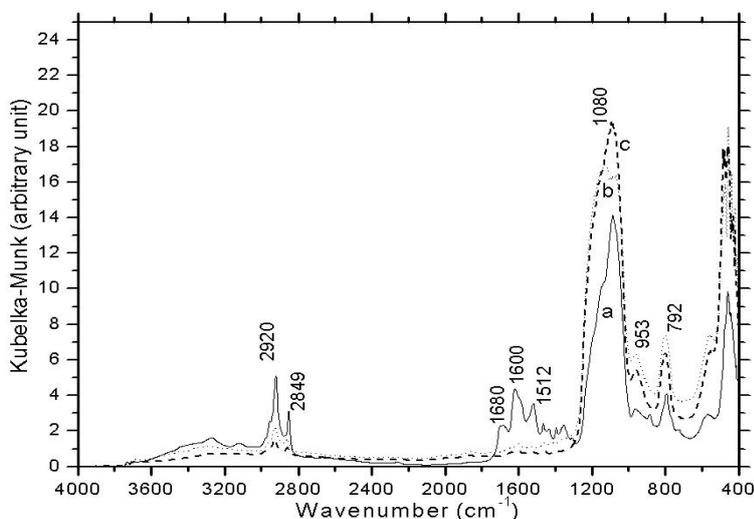


Figure 6 IR spectra of CD HMS: a) before adsorption of PNP; b) after adsorption of PNP (ambient pH); c) after adsorption of PNP at pH 7.45 (0.1 M $\text{KH}_2\text{PO}_4/\text{NaOH}$ buffer) at 295 K

The aforementioned challenge of increasing the loading capacity of adsorbents containing β -CD was discussed elsewhere (Mohamed et al., 2010; Mohamed et al., 2015). Cross-linked forms of β -CD are susceptible to attenuated access of the inclusion sites of CD at higher levels of cross-linking in a parallel manner as observed for CD ICS materials at higher CD loadings. The use of a dye adsorption method in conjunction with a systematic NMR study (Wilson & Guo, 2012) of cross-linked β -CD materials resolved a decade long knowledge gap related to the structure and function of such cross-linked adsorbents. Cross-linking may result in the formation of multiple binding sites such as inclusion and non-inclusion domains (*cf.* Figure 1 in Pratt et al., 2010) that are strongly influenced by steric effects, in accordance with the level of cross-linking (Figure 7). Depending on the relative HLB of the framework components in Figure 7, it can be appreciated that the multiple adsorption sites contribute to the observed adsorption properties, according to the nature of the adsorbate. This study reveals that surface modified silica

materials with variable HLB can be achieved by careful selection of the components; cross-linker, polysaccharide, and reactant ratios. The end result affords unique adsorbent materials with tunable textural and adsorption properties.

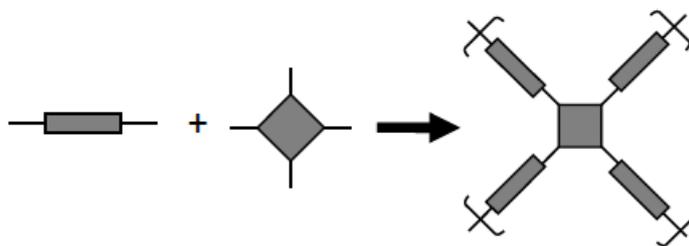


Figure 7 A 2-D illustration of the cross-linking reaction between a cross-linker (rectangle) with a multi-functional polysaccharide (square) to form a framework material with tunable adsorption properties

4. CONCLUSION

Silicate materials containing mesoporous channels were prepared using amine-based surfactant templates with variable alkyl chain length (C12-C16). The surface of the mesopores were modified by incorporation of asymmetric orthosilicates *via* coupling ICL with β -CD at different loading levels (2%-6%) to yield surface modified with β -CD. The heterogeneous adsorption properties of CD ICS materials were examined using gas (N_2 and CH_3Cl) adsorption along with PNP in an aqueous solution. Nitrogen adsorption-desorption isotherms reveal that templation with surfactants of increasing alkyl chain length to yield larger pores with higher SA and PV. The BET provides a good fit for the gas adsorption isotherms and solution uptake results for PNP. Composite materials of the type described herein will contribute positively to adsorbent technology that demands materials with high mechanical strength as in the case of tunable ceramic materials. The ability to prepare surface-modified silica materials reveals that the adsorption properties can be tuned by incorporation of macrocyclic host components, such as β -CD. Further efforts are underway to improve the level of β -CD incorporation, since such materials are potentially useful adsorbents for the controlled removal of waterborne and atmospheric contaminants.

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