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Molecular selective adsorption of nonylphenol in aqueous solution by organo-functionalized mesoporous silica

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Octylsilane-grafted hexagonal mesoporous silica removed low-concentrated nonylphenol, an endocrine disrupter, in water with high efficiency comparable to that of activated carbon, while the adsorbent showed no detectable uptake of phenol.

Mesoporous materials such as MCM-41[1] and FSM-16[2] have been extensively studied as catalyst supports and adsorbents. They have advantages for the adsorption of large molecules because of their large pore size and high surface areas. It has been reported that an as-synthesised surfactant–silica mesophase effectively absorbs 4-chlorophenol into its confined 'micelles' from aqueous solution.[3] Functionalization of the inner wall by grafting organic or organometallic groups is a promising strategy in designing the nature of pore spaces at the molecular levels.[4–8] Considering that grafted alkyl groups provide hydrophobic regions confined within the ionic surface of the inorganic phase, it is expected that control of the hydrophobicity would improve the performance of the absorbent for organic moelcules having both hydrophilic hydrophobic regions.

Alkylphenolic chemicals such as nonylphenol, which are biodegradaion products of alkylphenol polyethoxylate resin, have been found to be the major oestrogenic contaminants to induce feminising effects in fish.[9–11] The minimum effective concentration of nonylphenol was estimated *in vitro* to be in the range of 10 nM–10 μM (2.2–2200 ppb).[11] For the removal of a pollutant by adsorption with such a low concentration in sewage disposal plants, the adsorbent should have a very high molecular selectivity, otherwise many coexisting compounds with higher concentrations would saturate the capacity of the adsorbent.

Here we report that the grafting of alkylsilanes with intermediate chain lengths provides mesoporous silica with a high molecular selectivity. Octylsilane-grafted mesoporous silica effectively removed nonylphenol from water, while it showed no detectable adsorption of phenol. The capacity of the adsorbent for nonylphenol was comparable to that of an activated carbon which is currently used in sewage disposal plants and water purification plants.

Hexagonal mesoporous silica (MPS) was prepared by the following procedure: 0.011 mol of octadecyltrimethylammonium chloride was dissolved in 25 ml hydrochrolic acid (12.5 wt%) at 328 K. Then 0.011 mol of tetraethoxysilane was added with stirring to immediately give a white precipitate. After filtration, the obtained mesophase was dehydrated at 473 K for 2 h and then calcined at 813 K in air for 6 h to obtain MPS. For synthesis of alkylsilane-grafted MPS, 0.32 g of the MPS was refluxed in fresh distilled toluene with 9.6×10^{-3} mol of *n*-octyltriethoxysilane or *n*-dodecyltriethoxysilane for 48 h. Prior to the silylation, MPS was dried at 473 K for 2 h *in vacuo*. After the silylation, the samples were washed with distilled toluene and then with anhydrous methanol. During these procedures, the materials were treated in a glove-box filled with dry Ar (H_2O was monitored to be < 1 ppm). In typical adsorption experiments, 1 mg of the adsorbent was added to 10 g of an aqueous solution of nonylphenol (2100 ppb). After the adsorption with stirring for a given time, the supernatant solution was separated by centrifugation and the residual nonylphenol was analysed with an ultraviolet (UV) spectrometer at 278 nm. Blank experiments confirmed that the adsorption of nonylphenol on the flask wall was low ($< 10\%$). The data were corrected using the results of the blank tests. Adsorption of phenol in water (2000 ppb) was also measured in the same way. For comparison, an activated carbon (Calgon F-400, surface area *ca.* 1000 m^2 g^{-1}) was used.

Fig. 1 shows the N_2 adsorption isotherm for the samples synthesised in this study. The pristine MPS showed a curve with no hysteresis, which is typical for materials having cylindrical regulated pores like MCM-41. For the octylsilane-grafted MPS (C_8-MPS), the amounts of N_2 adsorption at relative pressures above 0.4 were *ca.* one third of that for MPS and the isotherm showed no hysteresis. The dodecylsilane-grafted MPS (C_{12}-MPS) gave a similar curve. This demonstrates that the alkylsilanes were grafted successfully onto the inner walls of the mesopores. Since the lengths of grafted alkylchains are shorter than the template used for the synthesis of MPS, it is expected that there are spaces at the centre of the pores. An α_s plot[12] on the basis of the N_2 isotherms of C_8-MPS (not shown) gave a shape similar to that of MPS, where the condensation of nitrogen was observed at lower α_s (*ca.* 0.6) for C_8-MPS than for MPS (α_s = *ca.* 0.8). These results demonstrated that the pores are narrower than the original ones. These spaces however, can still provide pathways for effective molecular diffusion. The inset in Fig. 1 shows the powder X-ray diffraction (XRD) pattern of C_8-MPS. This pattern shows that the mesostructure of silica (d_{100} = 35 Å) was maintained after grafting with the *n*-alkylsilane. Thermogravimetry and differential thermal analysis (TG-DTA) of C_8 and C_{12}-MPS gave exothermic weight losses due to the decomposition of alkyl groups at *ca.* 493–573 K (not shown). The molar ratios of the alkyl group to Si were

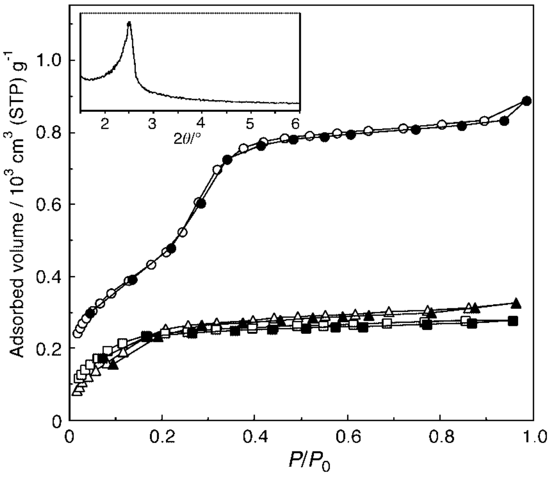

Fig. 1 N_2 adsorption isotherms of non-treated and *n*-alkylsilane-grafted mesoporous silica. Filled and open symbols represent adsorption and desorption branches, respectively. Circles, squares and triangles correspond to MPS, C_8-MPS and C_{12}-MPS, respectively. The inset shows the powder X-ray diffraction pattern of C_8-MPS.

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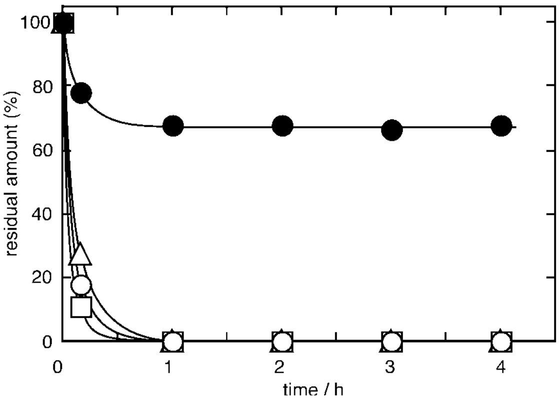

Fig. 2 Time courses of concentration of nonylphenol in water. 1 mg of adsorbent was used for 10 g of solution with an initial concentration of nonylphenol of 2100 ppb. Filled circles, open circles, open squares and open triangles correspond to MPS, C_8-MPS, C_{12}-MPS and activated carbon, respectively.

calculated from the TG data to be *ca.* 0.18 and 0.14 for C_8-MPS and C_{12}-MPS, respectively. These values are much smaller than the ratio of surfactant to Si for the as-synthesised mesophase (0.23), indicating that the materials have adequate space for molecular adsorption between the grafted alkyl groups in the mesopores.

Fig. 2 shows the time course of the concentration of nonylphenol during the adsorption. For the pristine MPS, *ca.* 30% of nonylphenol was removed. On the other hand, C_8-MPS removed nonylphenol totally within 1 h, showing that the grafting of alkyl groups is very effective in improving the performance of MPS. C_{12}-MPS and activated carbon also completely adsorbed nonylphenol within 1 h under the same conditions. A comparison between the alkyl-grafted MPSs and the activated carbon was carried out under much more severe conditions: 2 mg of the adsorbents were used for 200 g of the solution (1700–2100 ppb). The amounts of nonylphenol adsorbed at equilibrium are listed in Table 1. It was found that C_8-MPS showed a superior performance to the activated carbon. In addition, C_8-MPS was highly superior to C_{12}-MPS, while the differences of their surface areas and pore volumes were small. This indicates that the hydrophobicity of the dodecyl group is too strong while the moderate hydrophobicity of the octyl group is suitable for the effective adsorption of nonylphenol.

Table 1 Amounts of nonylphenol adsorbed on various adsorbents

Adsorbent	Concentration of nonylphenol/ppb	Amount of adsorbed nonylphenol/mol g^{-1}
C_8-MPS	6.2×10^2	6.5×10^{-4}
C_{12}-MPS	9.8×10^2	2.3×10^{-4}
MPS	1.3×10^3	9×10^{-5}
Activated carbon	6.2×10^2	5.3×10^{-4}

For comparison, adsorption of phenol in water (2000 ppb) was examined. 1 mg of absorbents were used for 10 g of solution. The activated carbon adsorbed 95% of phenol while MPS showed an uptake of 6%. On the other hand, C_8-MPS showed no detectable adsorption of phenol, while nonylphenol (2100 ppb) was completely removed under the same conditions. C_{12}-MPS gave the same results as C_8-MPS. Clearly, the grafting of alkyl group on the mesoporous silica provides a high molecular selectivity of nonylphenol against phenol.

In conclusion, MPS was made more hydorphobic by grafting alkyl chains on the inner surface of the mesopores and the resulting materials showed a high adsorption capacity for nonylphenol, an endocrine disrupter, comparable to that of activated carbon. The C_8-MPS adsorbent showed high molecular selectivity, distinguishing the hydrophobicity of molecules. These results indicate that the introduction of tuned hydrophobic regions in inorganic nanospaces is an effective strategy to design molecular selective adsorbents.

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