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Efficient Removal of Anionic Surfactants Using Mesoporous Functionalised Hybrid Materials

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A new hybrid system for surfactant removal from water has been developed using mesoporous material (MCM-41) functionalised with suitable binding groups. Solid **S1**, **S2** and **S3** were prepared by reaction of the mesoporous material with *N*-methyl-*N'*-(propyltrimethoxysilyl)imidazolium chloride, (3-aminopropyl)trimethoxysilane or 4-[(triethoxysilylpropylthio)methyl]pyridine, respectively. The functionalised materials were characterised following standard solid-state techniques. The final prepared solids consist of a siliceous MCM-41-type mesoporous support with the surface decorated by imidazolium, amine and pyridine binding groups suitable for anion coordination. Equilibrium adsorption studies of linear alkylbenzenesulfonate (LAS) using **S1**, **S2** and **S3** in water have been carried out. The obtained adsorption data were correlated with a Langmuir isotherm model that gives an acceptable description of the experimental data. The maximum surfactant uptake/binding site ($mol\,mol^{-1}$) and the surfactant adsorption capacity ($mmol\,g^{-1}$) for materials **S1**, **S2** and **S3** were calculated. **S1** shows a positive-charged functionalised surface that is independent of the pH of the solution, whereas **S2** and **S3** are functionalised with neutral groups that need to be protonated in order to display electrostatic binding interactions with the anionic surfactants. Therefore, whereas the adsorption capacity of **S1** is pH-independent, **S2** and **S3** display larger LAS adsorption at acidic pH. The adsorption ability at a certain pH follows the order **S1** >> **S3** > **S2**. A remarkable maximum surfactant adsorption of 1.5 mmol per gram of material was observed for **S1** at neutral pH. **S2** and **S3** behave as poorer adsorbents and show maximum surfactant adsorption of 0.197 and 0.335 mmol per gram of material, respectively, at pH 2.

Introduction

Surfactants are amphiphilic molecules containing a hydrophilic polar head, which determines its application and its own specific properties, and a hydrophobic part that consists of hydrocarbon chains usually with a $(CH_2)_n$ motif. Surfactants are generally classified according to the charge of its hydrophilic group and have been traditionally divided into four types: anionic surfactants, cationic surfactants, nonionic surfactants and zwitterionic or ampholytic surfactants. Surfactants are one of the most common pollutants that can be found in both technogenic and natural waters. Surfactants are a well-known group of substances that have the ability to greatly reduce the surface tension of water even when used in very low concentrations. The most familiar use for surfactants is in soaps, toothpastes, laundry detergents, dishwashing liquids and shampoos. Other important uses in industrial application involve textile processing, mining flocculates, food, paints, cosmetics, petroleum recovery, emulsion polymerisation and pesticide formulation.

A rough estimate of worldwide surfactant production is 10 million tons per year, of which anionic surfactants account for about 60%.[1] Anionic surfactants are popular detergent ingredients because of their straightforward synthesis and consequently low production costs. Reported influent concentration of linear alkylbenzenesulfonate (LAS) in domestic wastewater range from 3 to 21 $mg\,l^{-1}$. Surfactants cause short term as well as long-term change in ecosystems. Thus, because of their anthropogenic origin and extensive use, it is not difficult to find these anions in aqueous environments such as lakes and rivers where they can cause serious environmental problems related to foam formation, their accumulation and dispersion, and because they can act as a transfer system for other pollutants (petroleum products, oils, pesticides and organochlorine compounds).

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Additionally, although most anionic surfactants in use today are biodegradable and nontoxic to humans, several authors have reported an effect on fish and other aquatic organisms by affecting respiratory function.[2] Apart from the efforts made to design new and improved methods for their determination, another important aspect is the study of remediation processes of this family of compounds to reduce their environmental impact in a wide range of situations.

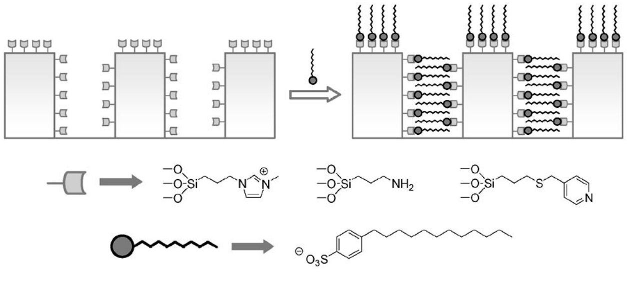
A number of methodologies for the removal of anionic surfactants have been reported such as chemical and electrochemical oxidation,[3] membrane technology,[4] the chemical precipitation and coagulation–flocculation process,[5] photocatalytic degradation[6] and various biological methods.[7] An appealing alternative to these procedures for remediation of anionic surfactants is the use of adsorption technologies. In fact, adsorption protocols of anionic surfactants from water have been extensively studied and a wide range of adsorption materials have been tested. These involve the use of activated carbons,[8] resins,[9] sand,[10] kaolinite and chrysotile,[11] silica gel,[12] zeolites,[13] alumina,[14] bentonite,[15] sediments,[16] sludge,[17] waste tyre rubber,[18] etc. Also some interesting studies comparing different adsorption materials have also been reported.[19] Despite these studies, and as far as we know, mesoporous silica materials have never been studied as suitable supports for the development of adsorption materials for anionic surfactant removal. The distinctive characteristics of functionalised mesoporous silica supports such as the very high specific surface of ca. 1200 $m^2 g^{-1}$, inertness, thermal stability, the presence of tunable pore sizes with a diameter of ca. 2–10 nm, and the possibility to easily functionalise their surface, makes these scaffolds ideal for the design of highly effective remediation materials. In fact, mesoporous functionalised solids have recently been used as scaffolding for the removal of toxic metal cations such as silver and copper,[20] gold,[21] mercury,[22,23] lead[23] and for remediation studies of the toxic fluoride,[24] nitrate and phosphate anions,[25] arsenate, selenate, molybdate and chromate oxyanions[26] and boron.[27] However, as far as we know, studies using functionalised mesoporous materials for the removal of anionic surfactants have never been carried out.

As part of our interest in the development of new functional properties using solid scaffolds[28] we report herein the functionalisation of MCM-41 supports with different anion-binding sites (i.e. imidazolium, amine and pyridine groups) and have studied the adsorption properties of these materials in the presence of anionic surfactants in water.

Results and Discussion

Design of the Removal Protocol

The design approach we followed in the synthesis of anionic surfactant adsorbents was inspired by the attractive properties of mesoporous solids (very large specific surface, capacity for functionalisation, etc) for their use as matrices in remediation protocols. Inspired by this idea, the solid "host" MCM-41 was selected. The MCM-41 mesoporous material was synthesised using the so-called "atrane route", based on the use of complexes that include triethanolamine-($TEAH_3$)-related ligands (in general "atranes" and silatranes for the silicon-containing complexes) as hydrolytic inorganic precursors and surfactants as porogen species. In a second step, the mesoporous inorganic support was treated with *N*-methyl-*N′*-propyltrimethoxysilylimidazolium chloride, (3-aminopropyl)trimethoxysilane or 4-[(triethoxysilylpropylthio)methyl]pyridine to yield solids **S1**, **S2** and **S3**, respectively. In all cases the solids were filtered off after the reaction and meticulously washed with different solvents and dried. These solids consist of a mesoporous MCM-41-type support with the surface decorated by imidazolium, amine and pyridine binding groups. Therefore, the prepared solids contained different kinds of binding sites, all of them suitable for anion coordination (vide infra) but still showing different properties. Also, the anchoring of densely packed binding groups on the internal surface of the MCM-41-based solids results in nanoscopic binding pockets that are expected to additionally result in an improvement of the coordination ability, due to cooperative effects that arise from the high density of coordinating subunits which would enhance the ability to attract anionic species into the binding pockets (Scheme 1). This enhanced coordination ability of functionalised surfaces with binding groups has been widely reported on a variety of surfaces.[29]



Scheme 1. Protocol for surfactant removal in water using mesoporous solids containing nanoscopic binding pockets.

S1 contains positively charged groups, whereas **S2** and **S3** contain amine and pyridine binding groups respectively that are expected to be protonated at acidic pH. It was expected that all three solids could coordinate anionic surfactants via Coulombic attractive forces.

Materials Characterisation

The solids were characterised with standard procedures. Figure 1 shows powder X-ray diffraction (PXRD) patterns of the calcined MCM-41 and the hybrid materials **S1**, **S2** and **S3**. PXRD of the MCM-41 phase shows the typical intense peak at $2\theta \approx 3°$, characteristic of surfactant-assisted mesoporous materials, which does not suffer important changes in the solids **S1**, **S2** and **S3**, indicating that functionalisation of the surface does not substantially damage the mesoporous structure of the silica matrix. The presence in the functionalised solids of the mesoporous structure is also confirmed from TEM analysis, in which the typical disordered hexagonal porosity of the MCM-41 matrix can clearly be observed (see for instance Figure 2 for solid **S2**).

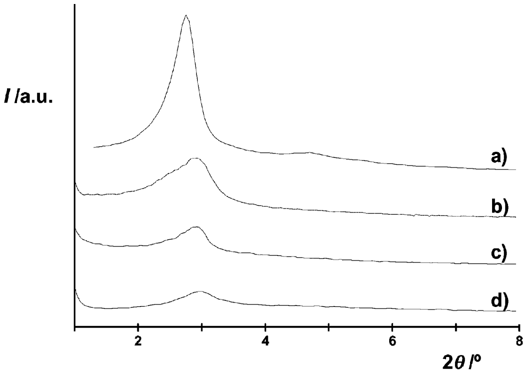


Figure 1. Powder X-ray patterns of the solid (a) calcined MCM-41, and the final solids (b) **S2** containing amine groups, (c) **S1** containing imidazolium groups, (d) **S3** containing pyridine groups.

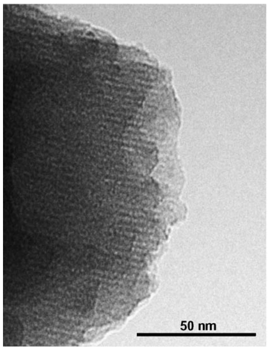


Figure 2. TEM image of solid **S2** showing the typical disordered hexagonal porosity of the MCM-41 matrix.

After functionalisation, the infrared spectra of the solids **S1**–**S3** show the expected features, that is, intense bands due to the silica matrix (1250, 1087, 802, 462 cm^{-1}), vibrations of water molecules (3420 and 1620 cm^{-1}) and vibrations of C–H at 2954–2850 cm^{-1} from the anchored organic moieties.

One important point related to the characterisation of the adsorbent materials is the determination of the degree of functionalisation and therefore the calculation of the amount of imidazolium, amine and pyridine groups on the surface of **S1**, **S2** and **S3**. This was calculated by elemental analysis and thermogravimetric studies on these solids. From elemental analysis of C, H, N, S it is possible to determine the amount of binding groups contained in the materials calculated in millimoles per gram of SiO$_2$ (mmol g^{-1} SiO$_2$) using Equation (1).

$$\alpha_A = \frac{\Delta W_{\mathrm{i}}\% \times 1000}{\Delta W_{\mathrm{SiO_2}}\% \times nM_{\mathrm{i}}} \ [\mathrm{mmol\,g^{-1}\ SiO_2}] \qquad (1)$$

where $\Delta W_i\%$ (i = C, N, S) are the weight percentages of carbon, nitrogen or sulfur, M_i is the corresponding atomic weight and n is the number of the corresponding atom type in one molecule. $\Delta W_{\mathrm{SiO_2}}\%$ is the inorganic SiO$_2$ content in weight percentage. The values of organic content as millimoles of imidazolium, amine and pyridine per gram of SiO$_2$ for the solids **S1**, **S2** and **S3** are shown in Table 1.

Taking into account these contents and the average value of the specific surface of the MCM-41 support (1092.33 m^2 g^{-1}, vide infra), the average coverage (β_A in molecules per nm^2) of the surface of the solids **S1**, **S2** and **S3** by imidazolium, amine and pyridine, respectively was calculated by Equation (2), in which α_A is the imidazolium, the amine or the pyridine content (mmol g^{-1} SiO$_2$), S the specific surface (m^2 g^{-1}) of the nonfunctionalised MCM-41 support and N_A Avogadro's number.

$$\beta_A = \alpha_A \times 10^{-3} \times S^{-1} \times 10^{-18} \times N_A = \alpha_A \times S^{-1} \times 602.3 \qquad (2)$$

A surface coverage of 1.13, 1.59 and 1.61 molecules nm^{-2} was found for the materials **S1**, **S2** and **S3**, respectively. This results in an average distance between anchored molecules of ca. 9.38 for the material **S1**, 7.92 for **S2** and 7.86 Å for **S3**.

The N$_2$ adsorption–desorption isotherms of the MCM-41 calcined material shows a typical curve for these mesoporous solids; that is an adsorption step at intermediate P/P_0 value (0.3). This curve corresponds to a type IV isotherm, in which the observed step can be related to the nitrogen condensation inside the mesopores by capillarity. The absence of a hysteresis loop in this interval and the narrow pore distribution suggest the existence of uniform cylindrical mesopores (size of 2.58 nm, volume of 0.86 cm^3 g^{-1}). The specific surface areas, volumes and pore size were calculated from a Brunauer–Emmet–Teller (BET; specific surface area) treatment of the isotherm,[30] and the Barret–Joyner–Haselda (BJH; volumes and pore size) method,[31] respectively. The application of the BET model resulted in a value for the total specific surface of 1092.33 m^2 g^{-1}. From the value of the XRD a$_0$ cell parameter (37.06 Å) and the pore diameter (2.58 nm), a value for the wall thickness of 11.26 Å was determined. Additionally, the solids **S1**, **S2** and **S3** show a considerable reduction of the total specific surface (ca. 70–80 %) as a consequence of the anchoring of the imidazolium, amine and pyridine groups on the surface.

Table 1. Millimoles of imidazolium, amine and pyridine groups per gram of SiO$_2$, average coverage and interdistance between anchored groups for the **S1**, **S2** and **S3** materials.

Solid	$\alpha_{\mathrm{I}m}$ [mmol g^{-1} SiO$_2$]	α_{amine} [mmol g^{-1} SiO$_2$]	$\alpha_{\mathrm{pyridine}}$ [mmol g^{-1} SiO$_2$]	β_{total} [molecules nm^{-2}]	Distance [Å]
S1	2.07	–	–	1.13	9.38
S2	–	2.91	–	1.59	7.92
S3	–	–	2.95	1.61	7.86

Adsorbent Behaviour

Solid **S1**, **S2** and **S3** were tested as anionic surfactant adsorbent agents in water. In a typical assay, the corresponding solid (50 mg) was suspended in 100 mL of water containing different concentrations of dodecylbenzenesulfonic acid sodium salt (LAS) at a certain pH (vide infra). The suspension was stirred, then filtered and the surfactant concentration in the solution determined by the colourimetric Methylene Blue method.[32]

The obtained adsorption data was correlated with a Langmuir isotherm model:

$$\theta = \frac{q}{q_\mathrm{m}} = \frac{KCe}{1 + KCe}$$

where q_m (mmol g^{-1}) is the maximum sorption capacity corresponding to complete monolayer coverage, Ce (mol dm^{-3}) is the equilibrium solute concentration, and K is the adsorption constant related to the affinity between the adsorbate and the surface of the solid. The Langmuir model was selected because of its simplicity and has previously demonstrated its ability to describe adsorption on mesoporous materials. Estimated model parameters for LAS adsorption using the Langmuir model, the maximum surfactant uptake/binding site (mol mol^{-1}) and the surfactant adsorption capacity (mmol g^{-1}) for materials **S1**, **S2** and **S3** are shown in Table 2. The Langmuir isotherm gives an acceptable description of the experimental data, as can be seen from the correlation coefficients (R^2).

Table 2. Adsorbent characteristics of materials **S1**, **S2** and **S3**.

Solid	Max. surfactant uptake/binding site [mol mol^{-1}]	Surfactant adsorption capacity, q_m [mmol g^{-1}]	log$K$	R^2
S1	1.08	1.52	1.94	0.954
S2	0.092	0.197	2.61	0.962
S3	0.182	0.335	2.59	0.963

Stability studies on the solids were also carried out. **S1**, **S2** and **S3** were stored at 25 °C and their activity tested two and six months after their synthesis. It was found that, even in the absence of special storage conditions, materials **S1** and **S3** preserve their activity without significant variation. In contrast, material **S2** did not conserve its adsorption activity after two months most likely due to a partial oxidation of the amines.

The hybrid support **S1** contains imidazolium salts as binding sites. Imidazolium groups have been widely reported as suitable coordination sites for anions via electrostatic forces and through $(C–H)^{+}\cdots X^{-}$ ionic hydrogen bonds.[33] In a previous paper we reported a selective and sensitive colourimetric method for the detection of anionic surfactants in water.[34] This sensing material consisted of a silica gel solid functionalised with the imidazolium groups which we found suitable to display coordination interactions with anionic surfactants. **S1** is a similar solid but additionally showing a larger surface to that of the silica gel.

Figure 3 shows the adsorption isotherms of LAS by using the solid **S1** at neutral pH. A remarkable maximum surfactant adsorption of 1.52 mmol per gram of material was observed suggesting a strong interaction between the anionic LAS and the imidazolium-functionalised surface on **S1**. From these data, for instance, removal efficiencies around 80% were observed for solutions containing 200 ppm of surfactant for 50 mg of the solid **S1**. Similar adsorption isotherms were found when using **S1** in water at pH 3 or 5 in agreement with the nature of **S1** which will show a positive charged functionalised surface that is independent of the pH of the solution. A maximum surfactant uptake/binding site ratio (mol mol^{-1}) of 1.08 for this solid was calculated suggesting the formation of a monolayer of LAS on the imidazolium-functionalised surface. We tentatively attribute this high adsorption capacity to the formation of a supported ionic liquid structure due to the presence of imidazolium groups.

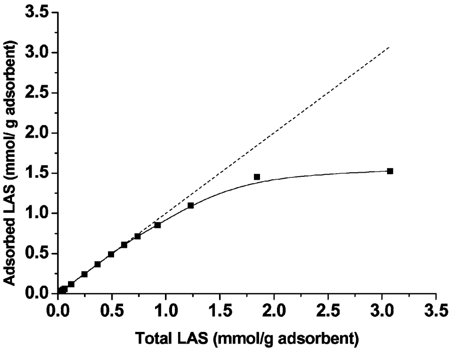


Figure 3. LAS adsorption isotherms at 25 °C and at neutral pH for functionalised solid **S1**. The dashed line corresponds to the theoretical maximum loading (100% removal efficiency of LAS).

Also kinetic studies of the adsorption process of LAS by solid **S1** have been carried out. As could be seen in Figure 4 a rapid uptake of LAS by **S1** was observed. The maximum amount of adsorbed surfactant was taken up in less than 10 minutes.

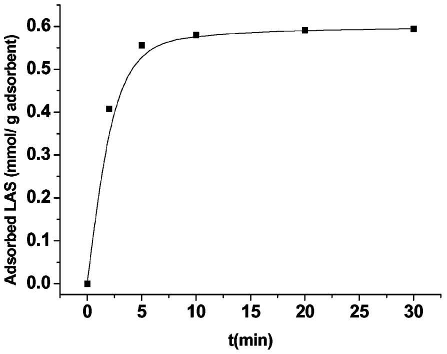


Figure 4. Kinetics of LAS (20 ppm) adsorption by solid **S1** (10 mg) at 25 °C and at neutral pH.

S2 contains amino groups within the mesoporous binding pockets. Polyamine/polyammonium binding groups have been extensively explored for the design of synthetic receptors able to interact with a large variety of inorganic, organic and biologically important guests,[35] providing hydrogen bonding and electrostatic interactions with anions. The adsorption experiments were carried out in water at pH 5, 3 and 2. A rapid analysis of **S2**, showed that this solid displayed adsorption abilities in the order pH 2 > 3 > 5. Accordingly, the adsorption isotherms of LAS with the solid **S2** at pH 2 were determined (see Figure 5). A maximum anionic surfactant adsorption of 0.197 mmol per gram of material was observed. From these data, removal efficiencies larger than 75% were observed for solutions containing 40 ppm of surfactant and 50 mg of the solid **S2**. This maximum surfactant adsorption found for **S2**, is remarkably lower than when using the imidazolium-functionalised solid **S1**, pointing out the importance of the functional binding site. In order to understand this different behaviour it has to be taken into account that, whereas imidazolium is positively charged in all the studied pH range, the NH_2 groups are neutral and need to be protonated to the corresponding ammonium moieties in order to display significant electrostatic interactions with the anionic LAS. A secondary amine has a p*K*a of ca. 9.5. However, we believe that this p*K*a value will be significantly modified when a number of polyamines are densely anchored on the siliceous mesoporous surface. Thus, prediction models on protonation of amines show that it is more difficult to protonate amines placed close to an already protonated ammonium group and this is why, for instance, stepwise p*K*a values in polyamines decrease as the number of protonated amines increases.[36] Thus, although the p*K*a values of aliphatic amines (monoamines) are typically around ca. 9–10, a densely packed surface containing NH_2 groups would behave as a polyamine and therefore a monolayer of amines such as we have in **S2** would behave as having a very wide range of p*K*a values; i.e. the amines will behave from very basic (first protonations) to poorly basic (last protonations). We have reported previously the preparation of amine-functionalised mesoporous surfaces and have observed that 100% protonation for instance can only be achieved at quite acidic pH values.[37] These reported titration experiment studies also showed that there was a gradual protonation as a function of the pH rather than a complete and simultaneous amine protonation at acidic pH values. In this case **S2** shows a maximum surfactant uptake/binding site (mol mol^{-1}) ratio of 0.092 indicating that only 9% of the total amines on the mesopores are able to give strong enough interactions with the anionic LAS at pH 2 and suggesting that not all the amines are protonated at the mesopores. Additionally, it has to be taken into account that some kind of interaction could also occur between polyamines and the silanol groups at the silica surface that would inhibit possible polyammonium–LAS interactions.

In further studies the adsorption of LAS by solid **S3** was investigated. **S3** contains pyridines that represent a neutral group that can only be expected to interact with anionic surfactants when protonated. Moreover, pyridine is much less basic than primary aliphatic amines, showing typical p*K*a values of ca. 5.21. Additionally, as explained above for amines, the anchoring of the pyridine derivative to give a densely packed surface results in the existence of a range of molecules having different p*K*a values due to the close proximity between binding sites. Figure 5 shows the adsorption isotherms of LAS with the solid **S3** at pH 2. Only a maximum anionic surfactant adsorption of 0.335 mmol per gram of material was observed. This corresponds to a surfactant uptake/binding site (mol mol^{-1}) ratio of 0.182 indicating that only 20% of the pyridines on the mesopores are able to efficiently coordinate the anionic LAS at this pH and strongly indicating that, as in the case of **S2**, relatively few groups are protonated in the inner surface of the mesoporous scaffold. Additionally, the lower maximum adsorption capacity of **S2** vs. **S3** may be related to the possible interaction of the small and flexible propylamines in **S2** with residual silanol moieties at the surface, whereas this interaction would be inhibited in **S3** which contains more rigid pyridine groups.

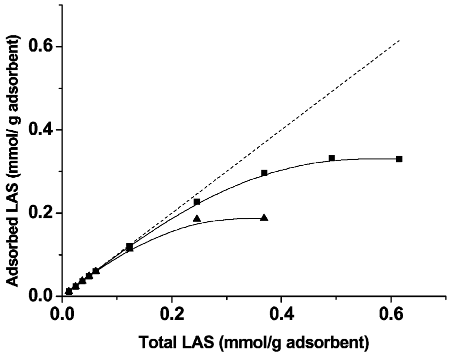


Figure 5. LAS adsorption isotherms at 25 °C and at pH 2 for functionalised solid **S2** (▲) and **S3** (■). The dashed line corresponds to the theoretical maximum loading (100% removal efficiency of LAS).

From the LAS adsorption studies it is clear that **S1** is the best suited for adsorption applications. For this material a remarkable maximum surfactant adsorption of 1.52 mmol per gram of material (0.5 g LAS g^{-1}) was observed. This maximum absorption is remarkably higher than those reported for the adsorption of anionic surfactant using activated carbon (ranging from 0.027 to 0.53 g LAS g^{-1}) and comparable with the adsorption capacity presented by certain resins (for instance the maximum capacity for Amberlite XAD-4 was reported to be 0.59 g LAS g^{-1} and the interval of maximum adsorption for resins range from 0.42 to 1.21 g LAS g^{-1}). However, **S1** displays a lower adsorption capacity than those reported for certain synthetic clays, that is LDH (layered double hydroxide) which ranges from 1.74 to 1.81 g LAS g^{-1}.[19]

In summary, although **S2** and **S3** showed poor LAS adsorption capability, **S1** is a potent LAS adsorbent at neutral pH. Thus, for instance, the absorption capacities using **S1** are higher than those reported for activated carbon. Additionally, **S1** shows comparable adsorption capacity with certain resins but displays a lower adsorption capacity than those reported for certain synthetic clays.

Conclusions

We have shown for the first time that functionalised mesoporous materials can act as adsorbents for the removal from water of anionic surfactants. In particular we have prepared solids **S1**, **S2** and **S3** that contain imidazolium, amine and pyridine groups, respectively. Organic contents of ca. 2–3 millimole of binding groups per gram of SiO_2 have been obtained in the final solids. Solids **S1**, **S2** and **S3** were tested as anionic surfactant adsorbent agents in water at different pH values. The adsorption ability at a certain pH follows the order **S1** >> **S3** > **S2**. A remarkable maximum surfactant adsorption of 1.5 mmol per gram of material was observed for **S1** at neutral pH suggesting that in this solid a strong interaction between the anionic LAS and the imidazolium-functionalised surface occurs. **S2** and **S3** are functionalised with neutral groups that need to be protonated in order to display electrostatic binding interactions with the anionic surfactants. Therefore, whereas the adsorption capacity of **S1** is pH-independent, **S2** and **S3** display larger LAS adsorption at acidic pH. **S2** and **S3** show maximum surfactant adsorption of 0.197 and 0.335 mmol per gram of material at pH 2. The high loading capacity found for solid **S1** and the possibility of obtaining these solids with a controlled macrostructure (by formation of different shaped monoliths) in order to minimize pressure drop, makes this or similar functionalised mesoporous scaffolds promising candidates as new materials for anionic surfactant remediation in certain applications.

Experimental Section

Methods: Thermogravimetric analyses (TGA), X-ray, TEM, IR, elemental analysis, N_2 adsorption–desorption and UV/Vis spectroscopy techniques were employed to characterise the synthesised materials. Thermogravimetric analyses were carried out with a TGA/SDTA 851e Mettler Toledo balance, using an oxidant atmosphere (air, 80 mL min^{-1}) with a heating program consisting of a ramp of 10 °C min^{-1} from 393 to 1273 K and an isothermal heating step at this temperature during 30 min. N_2 adsorption–desorption isotherms were recorded with a Micromeritics ASAP2010 automated sorption. The samples were degassed at 120 °C in vacuo overnight. The specific surface areas were calculated from the adsorption data in the low pressure range using the BET model. Pore size was determined following the BJH method. X-ray powder diffractograms were performed with a Bruker AXS D8 advance diffractometer using Cu-K_α radiation. IR spectra were recorded with a Jasco FT/IR-460 Plus between 400 and 4000 cm^{-1} in KBr pellets. UV/Vis spectroscopy was carried out with a Lambda 35 UV/Vis spectrometer (Perkin–Elmer Instruments).

Reagents: For the preparation of the pyridine derivative, (3-mercaptopropyl)triethoxysilane was provided by Fluka, sodium ethoxide (NaOEt) 21 wt.-% in ethanol and 4-(bromomethyl)pyridine hydrobromide were purchased from Sigma–Aldrich. For the synthesis of the imidazolium derivative, *N*-methylimidazole was provided by Acros Organics and 3-(chloropropyl)trimethoxysilane was purchased from Fluka. The organosiloxane derivative, (3-aminopropyl)trimethoxysilane for the synthesis of the solid **S2** was provided by Sigma–Aldrich. For the synthesis of the mesoporous material, tetraethyl orthosilicate (TEOS), *n*-cetyltrimethylammonium bromide (CTAB), and triethanolamine ($TEAH_3$) were provided by Aldrich. Sodium hydroxide was purchased from Scharlab.

For the adsorption experiments and the determination of concentrations of surfactant in the used samples, sulfuric acid, sodium hydroxide and sodium dihydrogen phosphate were provided by Scharlab, dodecylbenzenesulfonic acid sodium salt (LAS) was obtained from Fluka and the dye, methylene blue (MB), was purchased from Riedel-de Haën.

Synthesis of *N*-Methyl-*N′*-(propyltrimethoxysilyl)imidazolium Chloride: The *N*-methyl-*N′*-(propyltrimethoxysilyl)imidazolium chloride was prepared following a slightly modified procedure to that recently reported by Valkenberg et al.[38] A mixture of *N*-methylimidazole (6.57 g, 80 mmol) and 3-(chloropropyl)trimethoxysilane (15.89 g, 80 mmol) was stirred in a dry 100-mL flask under nitrogen flow at 95 °C for 24 h. After cooling at room temperature, the resulting liquid product was extracted with diethyl ether. The final compound was obtained as a yellow liquid (13.73 g, 70% yield). ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 0.55 (t, J = 8.0 Hz, 2 H, -CH_2-Si-), 1.81 (qt, J = 7.6, 8.0 Hz, 2 H, CH_2-CH$_2$-Si-), 3.46 (s, 9 H, CH_3-O-), 3.83 (s, 3 H, -N-CH_3), 4.11 (t, J = 7.6 Hz, 2 H, -N-CH_2-CH$_2$-), 7.69 (s, 1 H, Me-N-CH-CH-), 7.75 (s, 1 H, CH-CH-N-CH$_2$-), 9.11 (s, 1 H, N-CH-N-) ppm. ^{13}C NMR (75 MHz, [D$_6$]-DMSO, 25 °C): δ = 5.39 (-CH$_2$-Si-), 23.35 (-CH$_2$-CH$_2$-Si-), 35.71 (CH$_3$-O-), 50.1 (-N-CH$_3$), 50.93 (-N-CH$_2$-) 122.17 (-CH-CH-N-CH$_2$-), 123.59 (Me-N-CH-CH-), 136.62 (-N-CH-N-) ppm. HRMS calcd. for $C_{10}H_{21}N_2O_3Si$: 245.1321, found 245.1320.

Synthesis of 4-[(Triethoxysilylpropylthio)methyl]pyridine: (3-Mercaptopropyl)triethoxysilane (382 µL, 1.58 mmol) and sodium ethoxide (1.28 mL, 3.95 mmol) were added to a dry 100-mL flask with ethanol (40 mL) and the mixture was stirred for 45 min. After this time, 4-(bromomethyl)pyridine hydrobromide (0.5 g, 1.98 mmol) was added and the mixture refluxed for 48 h under argon flow. Then the ethanol was eliminated under vacuum and the resulting solid was extracted with dichloromethane. The final product was obtained as a reddish solid (0.23 g, 35.3% yield). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 0.55 (t, J = 8.0 Hz, 2 H, -CH_2-Si-), 1.07 (t, J = 6.9 Hz, 9 H, CH_3-CH$_2$-O-), 1.53 (qt, J = 7.4, 8.0 Hz, 2 H, -CH_2-CH$_2$-Si-), 2.3 (t, J = 7.4 Hz, 2 H, -S-CH_2-CH$_2$-), 3.55 (s, 2 H, C$_5$H$_4$N-CH_2-S-), 3.6 (qd, J = 6.9 Hz, 2 H, CH$_3$-CH_2-O-), 7.12 (dd, J = 4.5, 1.5 Hz, 2 H, C$_5$$H_4$N-CH$_2$-S-) ppm. 8.38 (dd, J = 4.5, 1.5 Hz, 2 H, C$_5$$H_4$N-CH$_2$-S-). ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C): δ = 9.67 (-CH$_2$-Si-), 18.10 (CH$_3$-CH$_2$-O-), 22.55 (-CH$_2$-CH$_2$-Si-), 34.35 (-S-CH$_2$-CH$_2$-), 34.88 (C$_5$H$_4$N-CH$_2$-S), 58.19 (CH$_3$-CH$_2$-O-), 123.74 (C_5H$_4$N-CH$_2$-S-), 147.83 (C_5H$_4$N-CH$_2$-S-), 149.55 (C_5H$_4$N-CH$_2$-S-) ppm. HRMS calcd. for $C_{15}H_{28}NO_3SSi$: 330.1559, found 330.1557.

Synthesis of MCM-41: The MCM-41 mesoporous support was synthesised by following the so-called atrane route.[39] In a typical synthesis, the molar ratio of the reagents in the mother liquor was fixed to $TEAH_3$/TEOS/CTAB/NaOH/H_2O = 7:2:0.52:0.5:180. $TEAH_3$ (25.79 g, 0.173 mol) and sodium hydroxide (0.49 g, 0.012 mol) previously dissolved in water (2 mL) were added to a flask. The mixture was stirred and heated to 120 °C, and then cooled to 70 °C. TEOS (11 mL, 0.049 mol) was added to the mixture and the mixture was heated to 120 °C to remove ethanol released during formation of the atrane complexes. Then, cetyltrimethylammonium bromide (CTAB, 4.68 g, 0.013 mol) was slowly added. Finally, the liquid was cooled to 70 °C and then water (80 mL, 4.4 mol) was added with vigorous stirring. The mixture was subsequently aged at room temperature for 24 h. The resulting solid was collected by filtration, washed with water and dried at 70 °C. To prepare the final porous material (MCM-41), the as-synthesised solid was calcined at 550 °C using an oxidant atmosphere for 5 h in order to remove the template phase.

Synthesis of S1: In a typical synthesis, template-free MCM-41 (1.00 g) was suspended in anhydrous acetonitrile (40 mL) inside a round-bottomed flask connected to a Dean–Stark trap apparatus in an inert atmosphere. The suspension was refluxed (110 °C) in azeotropic distillation collecting 10 mL in the trap in order to remove the adsorbed water. After this, an excess of *N*-methyl-*N′*-(propyltrimethoxysilyl)imidazolium chloride (2.81 g, 10 mmol) was added to the suspension at 50 °C and stirred for 13 h at this temperature. Finally, the solid **S1** was filtered off, washed with acetonitrile (100 mL) and dried at 70 °C for at least 12 h.

Synthesis of S2: In a typical synthesis, template-free MCM-41 (1.00 g) was suspended in anhydrous acetonitrile (40 mL) inside a round-bottomed flask connected to a Dean–Stark trap apparatus in an inert atmosphere. The suspension was refluxed (110 °C) in azeotropic distillation collecting 10 mL in the trap in order to remove the adsorbed water. Afterwards the mixture was heated at 50 °C, an excess of (3-aminopropyl)trimethoxysilane (1.75 mL, 10 mmol) was added to the suspension and the mixture was stirred for 13 h. Finally, the solid **S2** was filtered off, washed with acetonitrile (100 mL) and dried at 70 °C for 12 h.

Synthesis of S3: In a typical synthesis, template-free MCM-41 (1.00 g) was suspended in anhydrous acetonitrile (40 mL) inside a round-bottomed flask connected to a Dean–Stark trap apparatus in an inert atmosphere. The suspension was refluxed (110 °C) in azeotropic distillation collecting 10 mL in the trap in order to remove the adsorbed water. After this, an excess of the 4-[(triethoxysilylpropylthio)methyl]pyridine (3.29 g, 10 mmol) was added to the suspension at 50 °C and the mixture was stirred for 13 h at this temperature. Finally, the solid **S3** was filtered off, washed with acetonitrile (100 mL) and ethanol (100 mL). Then, the final solid was dried at 70 °C for 12 h.

Surfactant Removal Studies: In a typical experiment, 50 mg of the corresponding solids (**S1**, **S2** or **S3**) were placed in water (100 mL) containing a certain concentration of dodecylbenzenesulfonic acid sodium salt (LAS) and the suspension was stirred overnight. Then, the solid was filtered off and the remaining concentration of LAS in the solution was determined using the standard colourimetric Methylene Blue method. This colourimetric method comprises three successive extractions of the LAS from an acid aqueous medium containing excess Methylene Blue into chloroform, followed by an aqueous backwash and measurement of the blue colour in the $CHCl_3$ by spectrophotometry at 652 nm.

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