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ORIGINAL CONTRIBUTION

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Adsorption of octadecyltrimethylammonium chloride and adsolubilization on to cellulosic fibers

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Abstract The coadsorption of different organic solutes on cellulosic fibers treated with octadecyltrimethylammonium chloride (ODTMA) has been studied. In the absence of ODTMA cellulosic fibers had little tendency to retain organic compounds. The enhanced solute incorporation was ascribed to the adsolubilization of these compounds on the aggregated domains of the adsorbed surfactant molecules at the solid/liquid interface. The specific shape of solute coadsorption isotherms indicated that the adsolubilization process may be regarded as a partition phenomenon between the aqueous bulk phase and the adsorbed surfactant aggregates. The decrease in solute uptake at the cellulose/water interface above the CMC of ODTMA was ascribed to micelle formation in the bulk solution and to the ensuing micellar solubilization of organic solutes. Preliminary experiments performed using vertical fixed bed columns showed that modified cellulosic fibers can be conveniently used as substrate for treating organic pollutants.

Keywords Adsolubilization · Coadsorption · Cellulosic fibers Organic solutes

Introduction

The uptake of poorly water-soluble solutes by adsorbed surfactant layers at the solid/liquid interface has recently come to academic researchers' notice [1, 2]. This phenomenon, known as adsolubilization, has attracted much interest in both applied and academic research [2, 3, 4, 5]—adsolubilization may be exploited in wastewater treatment for removal of organic pollutants using surfactant-treated particles such as clays [6, 7, 8, 9], it can be a precursor to the formation of thin polymeric films by admicellar polymerization [10], and other applications have been found in pharmacology for drug carrier targeting [11].

Investigation carried out on surfactant adsorption on various charged surfaces revealed the formation of aggregated structures, namely hemimicelles and admicelles, on the solid/liquid interface below the critical micelle concentration [12, 13]. Hemimicelles have been viewed as a local surfactant monolayer oriented with their head groups in contact with the aqueous media whereas admicelles are associated with the formation of a surfactant bilayer bearing the lower layer head groups adsorbed on the surface and the head groups of the top layer oriented toward the solution [13, 14]. The use of AFM [15, 16] and small-angle neutron scattering [17] has provided a clear evidence of the morphology of the adsorbed surfactant at the solid/liquid interface. Different patterns of aggregative structures have been observed, viz: monolayer, bilayer, cylindrical network, and even spherical aggregates. A transition from one structural type to another often occurs when the surfactant concentration is varied. However other factors such as the surface charge, electrolyte concentration, and surfactant type play an important role in determining the shape of the aggregates [15, 17, 18, 19].

The hydrocarbon chains of the aggregated layer provide hydrophobic domains which are able to incorporate organic solutes which, otherwise, could not be adsorbed on the substrate in the absence of adsorbed surfactant. This partition process between the hydrocarbon core of admicellar structures and the aqueous medium is the main mechanism of the adsolubilization phenomenon [20, 21, 22, 23, 24, 25]. To the best to our knowledge most reported studies on adsolubilization have focused on charged inorganic substrates. The effect of different conditions such as surfactant concentration, pH, ionic strength, on the adsolubilization mechanisms have been extensively investigated [26, 27, 28, 29], indicating that the maximum adsolubilization capacity increases as the substrate surface charge and available surface area increase. Thus the adsolubization of about 200 μmol g^{-1} organic solute needs very fine particles with a mean diameter lower than 0.5 μm, which are too difficult to handle.

We have reported in previous work that the surface properties of cellulosic fibers, i.e. their natural hydrophilic character, can be modified by coating the fibers' surfaces with a thin polymeric film by admicellar polymerization [30]. In this work we have continued to explore the suitability of cellulosic fibers for use as a novel organic substrate for adsolubilization. The effect of the organic solute structure on the maximum amount adsolubilized has been investigated in order to determine the effectiveness of cellulose modification with a cationic surfactant in promoting the selective adsorption of organic solutes from aqueous media.

Materials and methods

Materials

The fibers used in this work were commercial microcrystalline cellulose (Technocel-150DM). Their average length was about 250 μm and their specific surface area in the dry state, measured by the BET technique using nitrogen as probe, was found to be 2.5 m^2 g^{-1}. The presence of negative surface charge was confirmed by ξ potential measurement which gave −10 mV. The amount, determined by conductivity measurements, was approximately 55 μmol COO^- equivalents g^{-1}. The extent of crystallization determined by powder X-ray diffraction was about 72%.

Octadecyltrimethyl ammonium chloride (ODTMA) ($C_{21}H_{44}NCl$) from Aldrich (99% pure) was used as received. Its critical micelle concentration (CMC) measured by surface tension measurement (Kruss K10T) at 25 °C was 2.4×10^{-3} mol L^{-1}, a value which is in agreement with literature values [27].

All the organic solutes used were of analytical grade.

Adsorption and adsolubilization isotherms

The adsorption isotherms of the cationic surfactant ODTMA were determined in the presence of 1% (*w*/*w*) cellulose dispersed in water with different concentrations of ODTMA. The suspensions were stirred for 24 h at room temperature to reach adsorption equilibrium. The coadsorption of organic solutes was performed as follows. A series of aqueous solutions of the desired ODTMA concentration was prepared, after 24 h equilibration in presence of 1% (*w*/*w*) cellulosic fibers to enable adsorption of the surfactant, organic solute at the desired concentration was added using a micro-syringe for liquid solutes and by weighing for powdered materials. The sample was then shaken for 4 h to reach adsolubilization equilibrium.

Dispersions were centrifuged at 2500 rpm for 15 min. The supernatant concentrations of organic solute and ODTMA were analyzed simultaneously by UV spectroscopy and colorimetric titration, respectively. For poorly soluble solutes (solubility lower than 10^{-3} mol L^{-1}), the adsolubilized amounts were determined by UV spectroscopy after their extraction from the cellulose fibers with ethanol.

Colorimetric titration of the cationic surfactant ODTMA with a starch solution and iodine is based on the aptitude of ionic linear surfactants to form stable inclusion complexes [31, 32, 33]. The starch–surfactant complex is formed by enclosing the hydrocarbon chain of the surfactant in the cylindrical cavity of the helical chains of the amylose (Fig. 1). The stability of the complex is ensured by steric effects and by dispersive interaction between the methylene groups of the surfactant and the glucose rings.

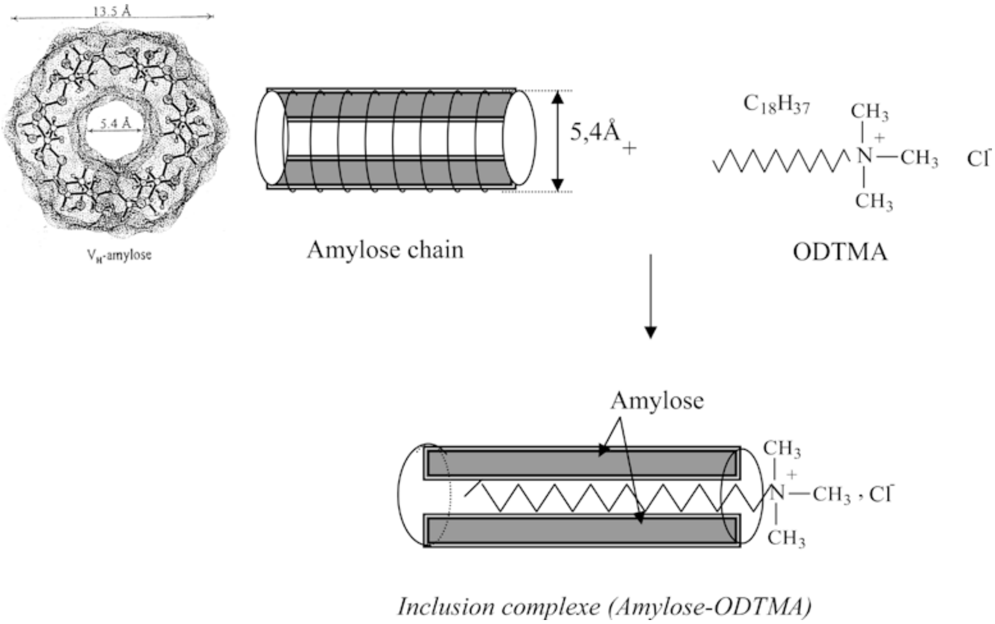
An excess amount of freshly prepared starch solution was added to the ODTMA solution and excess amylose was back-titrated by measuring absorbance at 590 nm after addition of iodine solution. UV and colorimetric analysis were both performed on the basis of previous calibrations.

Results and discussion

ODTMA adsorption on cellulose fibers

Adsorption isotherms of ODTMA surfactants on to cellulosic fibers plotted on linear–linear and linear–log scales are presented in Figs. 2a and 2b. The data are presented as the amount of ODTMA adsorbed as a function of the surfactant equilibrium concentration. The linear-linear plot showed an initial steep rise, followed by a gentle increase of bound surfactant until a plateau region. The steep rise in the adsorption isotherm reveals the high affinity of the cationic surfactant for the cellulosic substrate. To magnify the low concentration domain region adsorption isotherms were plotted on linear–log scales (Fig. 2b). A typical S-sigmoid curve which can be divided in three different regions was obtained. The occurrence of three regions I, II, and III is a recurrent features of adsorption phenomenon with an aggregation process. At very low ODTMA bulk concentration (region I), the amount adsorbed increases slowly with increasing surfactant concentration; in this domain ODTMA is adsorbed as individual ions almost exclusively by an ion-exchange mechanism. In region II, a sharp increase in surfactant adsorption is observed, indicating the onset of lateral interaction among adjacent hydrocarbon surfactant tails, which gives rise to the formation of aggregate structures. In region III a decrease in the adsorption isotherm slope is observed because the packing of surfactant molecules gives rise to electrostatic repulsive forces among charged head

Fig. 1 Schematic illustration of the amylose–ODTMA inclusion complex



groups which reduces the extent of further surfactant adsorption. Beyond this region no more surfactant is adsorbed and free solution micelles are formed. It is worth to noting that the maximum amount of ODTMA adsorbed (320 μmol g^{-1}) far exceeds the surface charge of the fibers (approx. 55 μmol COO$^-$ groups g^{-1}); the negative charge on the cellulosic fibers originates from the presence of carboxyl moieties derived from hemicellulose and from oxidative bleaching. This result suggests that the driving force of surfactant self-assembly on the solid/liquid interface is hydrophobic interaction between a hydrocarbon surfactant tail, which reduces the extent of hydrocarbon contact with water molecules, and hence the free energy of the system. It seems that the surface charge is only essential in the first step of the adsorption process where it promotes adsorption through an ion-exchange mechanism. Analysis of the effect of pH on the adsorption isotherm indicates that in the pH range 5–9, adsorption isotherms do not change appreciably, because neither ODTMA or the cellulosic substrate undergo modification of the extent of their ionization. The cellulosic substrate remains negatively charged in this pH domain, because the carboxyl groups remain fully ionized up to a pH 5.

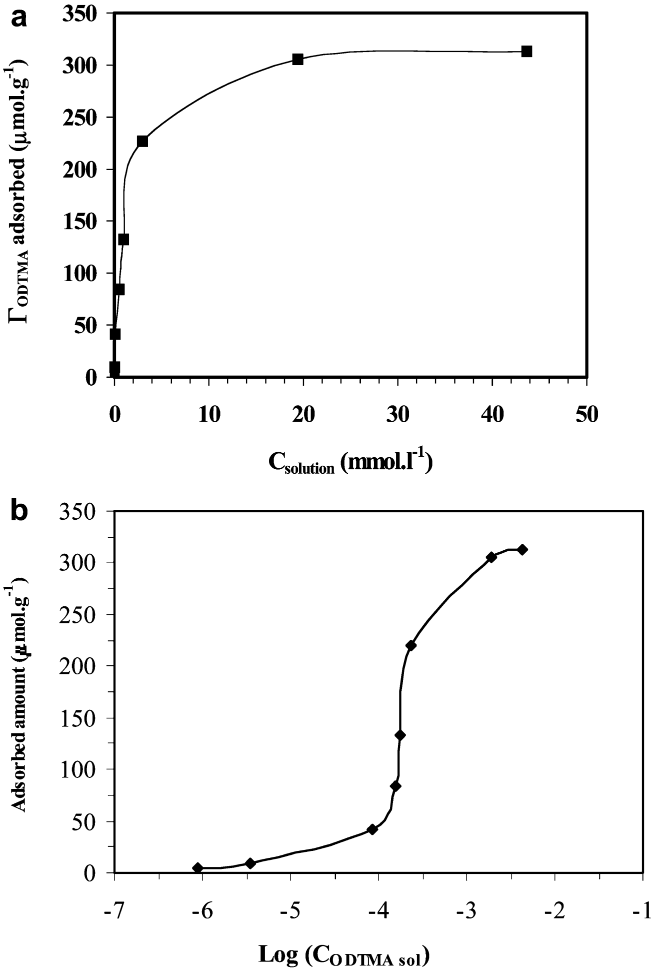


Fig. 2 Adsorption isotherm of ODTMA on to cellulosic fibers at pH 6.8–7, (**a**) on linear–linear scale, (**b**) on linear–log scale

Adsolubilization behavior of organic solute

Figure 3 reports simultaneously the adsorption of ODTMA and the coadsorption of 2-naphthol at constant concentrations of 5×10^{-3} mol L^{-1} which was added after surfactant adsorption. The data are presented as the number of moles of adsorbed solute per gram of cellulose fibers, as a function of the free equilibrium

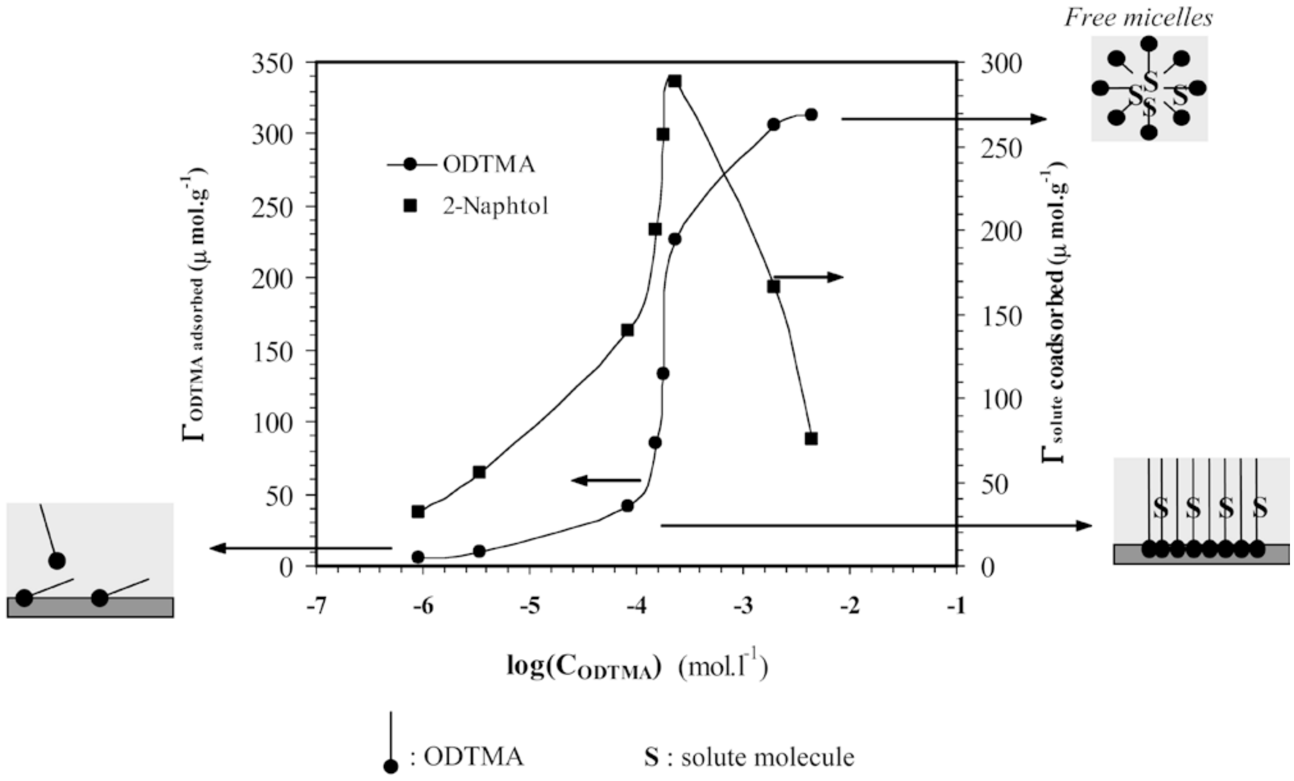


Fig. 3 ODTMA adsorption isotherm and 2-naphthol coadsorption isotherm as a function of equilibrium ODTMA concentration at pH 6.5–7

surfactant concentration. In the absence of adsorbed ODTMA surfactant the solute is not adsorbed to any measurable extent on the cellulose. When adsorption of the surfactant begins, retention of 2-naphthol occurs and increases with the amount of ODTMA adsorbed up to a certain surfactant concentration close to the CMC, then levels off rapidly to a very small value. We infer that the large enhancement of solute uptake is the result of an adsolubilization process within the system ODTMA/cellulose. Indeed, analysis of the adsorption isotherms of ODTMA with and without any solute indicates that the coadsorption of 2-naphthol does not lead to any surfactant desorption, therefore uptake of the solute must be because of its accumulation within the aggregated surfactant domains. The decrease of 2-naphthol coadsorption beyond a critical ODTMA concentration close to CMC suggests that once free micelles were formed the solute was preferentially incorporated by these microreservoirs, rather than being adsorbed by surfactant present on the fibers.

The kinetics of ODTMA adsorption and 2-naphthol coadsorption have been determined. In this procedure the solute was introduced 24 h after surfactant addition. Figure 4 indicates that ODTMA adsorption equilibrium is reached after10 h; the relatively long equilibrium time and the high amount adsorbed is probably a result of diffusion of ODTMA within the micropores of the fibers. Indeed, if we assume that the adsorbed surfactant molecules are oriented perpendicularly to the surface and that the surface which is covered by one ODTMA molecule is about 60–70 Å^2 [34] the surface of cellulose substrate could be estimated to be about 110 m^2 g^{-1}, which is much higher than 2.5 m^2 g^{-1} obtained from

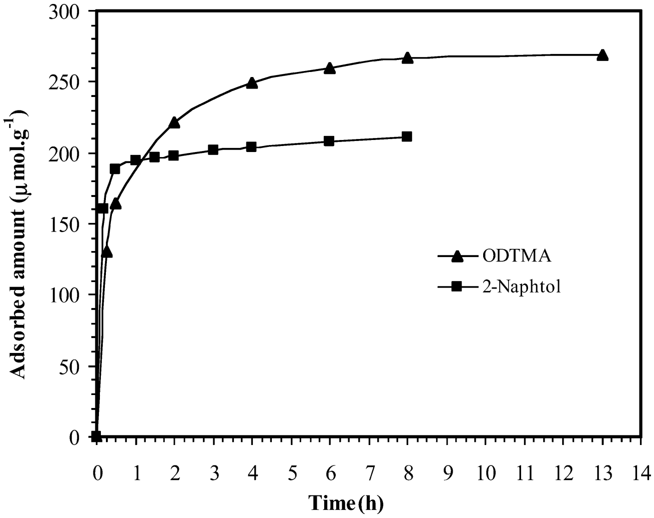


Fig. 4 Time evolution of the adsorbed and coadsorbed amounts of ODTMA and 2-naphthol: C_0(ODTMA) = 3×10^{-3} mol L^{-1}, C_0(2-naphthol) = 2×10^{-3} mol L^{-1}

BET measurement. This discrepancy can be rationalized by considering that the use of an aqueous swelling media favored expansion of the bulk micropores of the cellulosic fibers [35] with a consequent increase in both the available interaction area and the accessibility of this restricted area to surfactant molecules. The coadsorption of 2-naphthol is markedly more rapid and is achieved within 0.5 h. It is probable that adsorption of ODTMA favors the expansion of the inner part of the bulk micropore fiber, thus diffusion of the solute molecules is promoted.

One may ask whether 2-naphthol adsolubilization is merely a result of interaction between the hydroxyl group and the surfactant ammonium head groups. To rule out this hypothesis a series of organic solute of different structure were studied. As shown in Fig. 5, in all instances similar trends are observed for all the components irrespective of their structure. Markedly enhanced solute uptake is noted up to a critical ODTMA concentration of about 0.25 mmol L^{-1}, which seems to be independent of the organic solute. Above the ODTMA CMC a continuous decrease of the amount coadsorbed is equally apparent for all the solutes. The maximum amount of solute adsolubilized varies from 170 to 300 μmol g^{-1}. This result strongly supports the fact that adsolubilization of solutes is a consequence of their accumulation on the hydrophobic core of adsorbed surfactant aggregates, and not an issue of a specific interaction between the head surfactant groups and the polar moiety of solute.

To analyze the coadsorption process quantitatively, we may consider that the organic solute is partitioned between the adsorbed surfactant pseudophase and the aqueous media. The partition equilibrium can be represented by the equilibrium:

$$\text{Cellulose/ODTMA} + \text{solute} \rightleftarrows \text{Cellulose/ODTMA/solute}$$

Referring to this concept, the partition coefficient may be defined as:

$$K_{\text{adsol}} = \frac{C^{\text{S}}_{\text{adsol}}}{C^{\text{S}}_{\text{sol}} \cdot C^{\text{ODTMA}}_{\text{adso}}}$$

where $C^{\text{S}}_{\text{adsol}}$, $C^{\text{S}}_{\text{sol}}$, and $C^{\text{ODTMA}}_{\text{adsol}}$ are, respectively, the amount adsolubilized, the free solute concentration, and the concentration of ODTAM adsorbed.

Plotting $C^{\text{S}}_{\text{adsol}}/C^{\text{S}}_{\text{sol}}$ vs $C^{\text{ODTMA}}_{\text{adsol}}$ gives a clear-cut idea of the validity of this model in the present context. The linearity of the plots for different solutes, shown in Fig. 6, confirmed that the partition approach is suitable for solute coadsorption by cellulosic substrate. It should be specified that only the region below the CMC was taken into account. The partition coefficients of a large series of organic solutes are reported in Table 1. For all the solutes tested K_{adsol} values are relatively high (over 1000); this reveals the high affinity of ODTMA-treated cellulosic fibers for organic solutes.

To study the dependence on solute concentration of the coadsorption effect on ODTMA-treated cellulosic fibers, we measured, at fixed surfactant coverage, below the CMC, the maximum amount adsorbed, for various solute concentrations. Examples of the coadsorption isotherms for different solutes are shown in Fig. 7. For low concentrations adsorption of the solute is almost total, the fairly steep slope of the isotherms denotes again the high affinity of the organic solute for the modified cellulosic fibers. The Langmuir model was used

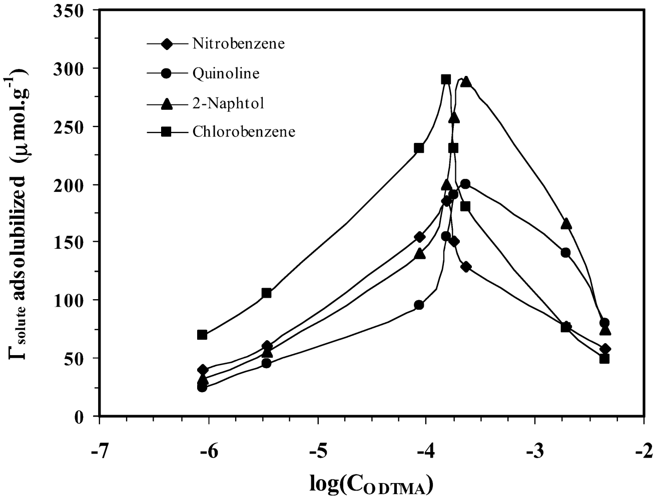


Fig. 5 Coadsorption isotherms of different organic solutes on to cellulose fibers after treatment with ODTMA, at pH 6.5–7

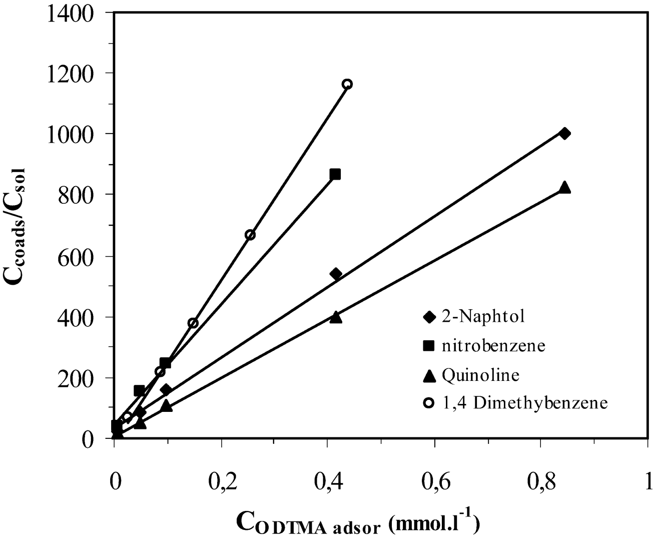
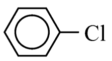
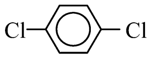
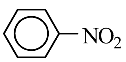
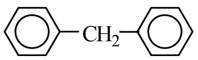
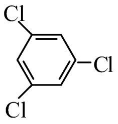
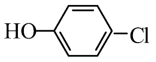
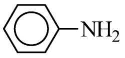
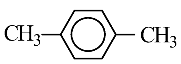
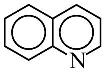
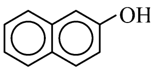


Fig. 6 Variation of the coadsorbed solute fraction ($C^{\text{S}}_{\text{adsol}}/C^{\text{S}}_{\text{sol}}$) with the adsorbed ODTMA amount $C^{\text{ODTMA}}_{\text{adsol}}$

Table 1 Results related to the coadsorption of different organic solutes on ODTMA treated cellulosic fibers

Organic solute	K (g.l^{-1})	C_{adsol}^{max} (µmol.g^{-1})	K_{adsol} (l.mol^{-1})	K_{OW}	Solubility (mmol.l^{-1})
Benzene 	2750	396	8925	135	22.9
Chlorobenzene 	4903	336	6467	840	4.46
Dichlorobenzene 	6185	223	7618	2400	0.4
Nitrobenzene 	1771	194	1924	31	16.9
Diphenylmethane 	9067	306	6748	12300	0.09
Trichlorobenzene 	6360	187	5015	10470	0.22
Chlorophenol 	2305	169	987	144	89.12
Aniline 	779	368	785	8	389
Dimethylbenzene 	3630	232	2395	1320	1.73
Quinoline 	957	374	1027		
2-Naphtol 	1426	295	1162	780	5

K_{OW}: the ocatnol-water partition coefficient

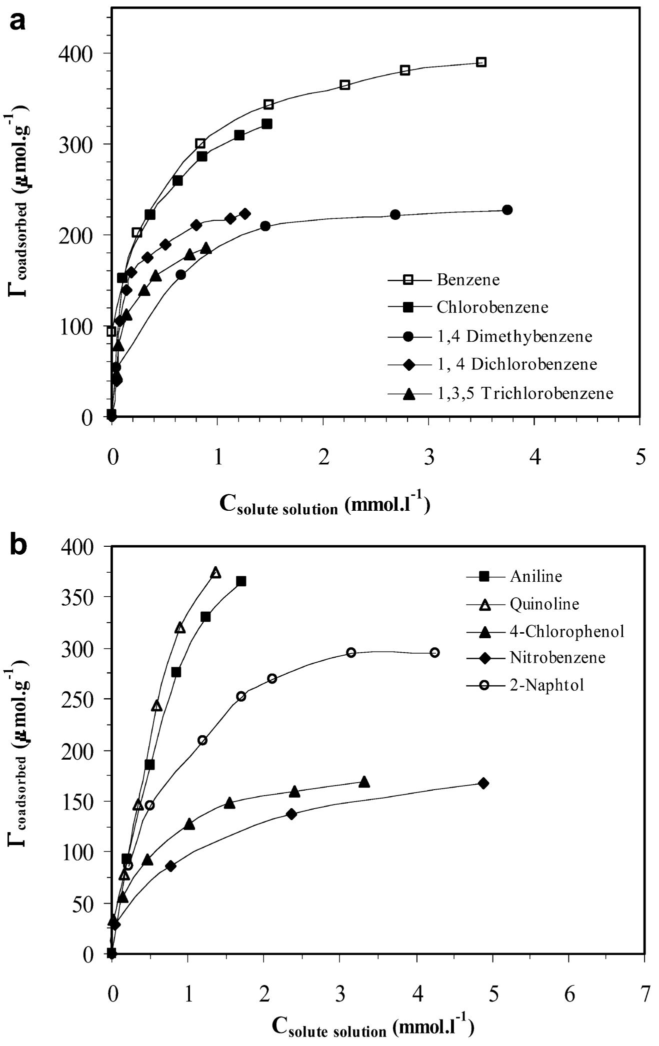


Fig. 7 Coadsorption isotherms of different organic solutes on cellulosic fibers at a constant coverage of ODTMA (C_0(ODTMA) = 2.5×10^{-3} mol L^{-1}): (**a**) benzene, chlorobenzene, 1,4-dimethylbenzene, 1,4-dichlorobenzene, 1,3,5-trichlorobenzene; (**b**) aniline, quinoline, 4-chlorophenol, nitrobenzene, 2-naphthol

to describe each isotherm. According to this model the following equation can be written:

$$C^{S}_{adsol} = \frac{KC^{max}_{adsol}.C^{S}_{sol}}{1 + KC^{S}_{sol}}$$

where C^{S}_{adsol}, C^{S}_{sol}, and C^{max}_{adsol} are, respectively, the adsolubilized amount, the free solute concentration, and the maximum amount adsolubilized. K is the Langmuir equilibrium constant. The goodness-of the model fit was evaluated by plotting the linearized form of the Langmuir equation:

$$\frac{C^{S}_{sol}}{C^{S}_{adsol}} = \frac{1}{KC^{max}_{adsol}} + \frac{C^{S}_{sol}}{C^{max}_{adsol}}$$

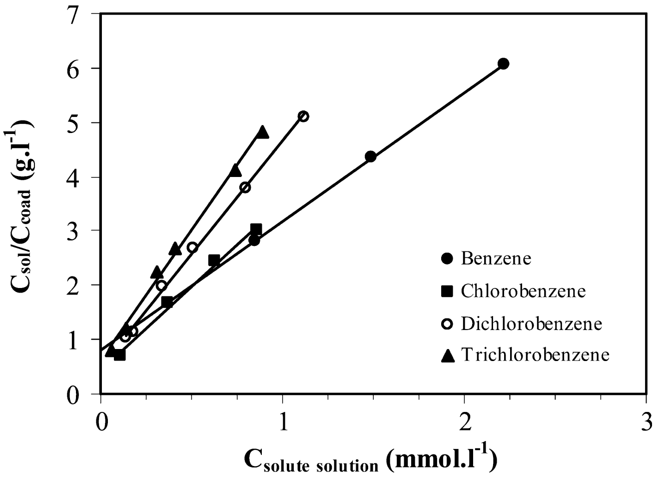


Fig. 8 Application of the Langmuir approach to the cellulose samples treated with ODTMA

For all the solutes studied, a linear plot is obtained with a regression coefficient close to unity (Fig. 8). From each curve, the adsorption equilibrium constant K and the maximum concentration of coadsorbed solute were evaluated, as summarized in Table 1. These results suggest the following remarks:

1. The values of C^{max}_{adsol} deduced graphically were close to those observed at the plateau value in the coadsorption isotherms. For the different solutes tested C^{max}_{adsol} varied from 200 to 390 μmol g^{-1}.
2. The equilibrium constant K value varies from 1000 to 9000. This relatively high value is in tune with the high affinity of ODTMA-treated cellulose fibers toward organic solutes. Except for benzene and chlorobenzene, the K value is as much higher as the solute solubility is lower. This result is expected if we consider that the adsolubilization process is a result of partition of the organic solute between the hydrophobic domain generated by the aggregated surfactant tails and the aqueous medium.
3. No clear trends between K and K_{adsol} equilibrium coefficient and K_{OW} (the octanol–water partition coefficient) or the water solubility could be observed. In all instances high values of the equilibrium coefficients were noted for the poorly soluble organic compounds. However, solute hydrodynamic volume seems to be a factor which probably affects the adsolubilization equilibrium coefficient. More work is needed to give a clear idea about the influence of this property.

To show the potential of ODTMA-modified cellulosic fibers to remove organic solutes from water, we performed measurements in continuous flow using vertical fixed bed columns filled with cellulosic fibers. Columns of 8 mm×100 mm (diameter×height) packed with 0.5 g cellulosic fibers previously treated with 160 μmol L^{-1} ODTMA were fed by an aqueous

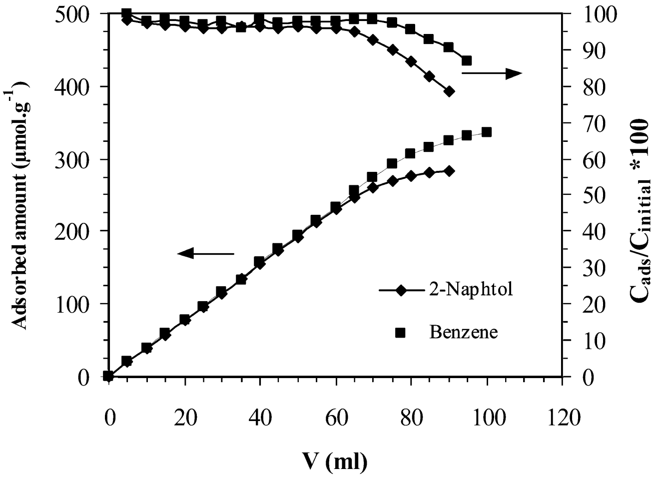


Fig. 9 Plot of the amount of solute adsorbed and the corresponding immobilized fraction vs the eluted volume: solute concentration and feed flow are 10^{-3} mol L^{-1} and 2 mL min^{-1}, respectively

solution of organic compounds (10^{-3} mol L^{-1}) at a constant flow rate (2 mL min^{-1}) and the eluted solution was analyzed to determine the amount of the trapped solute. Results shown in Fig. 9 reveal that the organic compounds were efficiently immobilized on to the fibers. Indeed, the fraction of the trapped solute is close to 100% if the saturation level of the fibers is not reached; the maximum amount retained is, moreover, close to that found from batch experiments.

We believe the process of adsolubilization by modified cellulosic fibers might be exploited to remove organic pollutants and toxic substances in wastewater. However, it is necessary to undertake chemical grafting of the adsorbed surfactant on to the cellulosic substrate in order to avoid possible desorption of molecular surfactant from the surface, and to make possible the re-use of the fibers after the solute elimination. This study is under progress in our laboratory.

Conclusion

The adsorption of ODTMA on to cellulosic fibers has been studied; the shape of the adsorption isotherm suggests some cooperativity in the adsorption. This behavior may be attributed to hydrophobic aggregation of the surfactant molecules on the solid surface. The subsequent coadsorption of different organic solutes has also been investigated. It was found that ODTMA adsorption greatly enhances uptake of the organic solute. The enhanced solute incorporation was ascribed to the adsolubilization of the organic solutes by the cellulose substrate. Adsolubilization capacity depends principally on the amount of surfactant adsorbed.

Thermodynamic analyses of the adsolubilization showed that the phenomenon can be analyzed in terms of a partition equilibrium of the solute between the adsorbed aggregative domains of ODTMA and the bulk media. The relatively high values of both the partition coefficient and the adsorption constant indicate the high potential of the modified cellulosic fibers for immobilization of organic compounds.

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