

# Ureasil Gels as a Highly Efficient Adsorbent for Water Purification

Vlasoula Bekiari and Panagiotis Lianos\*

Engineering Science Department, University of Patras, 26500 Patras, Greece

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Ureasils are nanocomposite organic–inorganic materials based on a silica backbone covalently connected through urea bridges with poly(oxyalkylene) chains. Ureasil gels are synthesized by the sol–gel procedure. These gels can efficiently adsorb and retain dyes from aqueous solutions and, thus, can be employed as water purification agents. Anionic dyes bearing a sulfonate chemical group are most efficiently adsorbed, followed by hydrophobic dyes and, finally, by cationic dyes. The adsorption of anionic dyes is very impressive, because a densely colored water sample is transformed into crystal clear water by using only a small quantity of ureasil adsorbent. Variations of the adsorption efficiency have been detected by varying the poly(oxyalkylene) chain length or by using different catalysts of the sol–gel procedure. The most efficient adsorbents were gels made by the conventional sol–gel route, that is, by HCl catalysis.

## Introduction

The utilization of various adsorbents to remove organic or heavy metal pollutants from wastewaters is a very popular subject of research for obvious reasons. Besides the classical activated carbon filters, different types of other materials have been recently studied, typically natural or treated clays,<sup>1–3</sup> organically modified synthetic porous silica,<sup>4–6</sup> three-dimensional cross-linked polymers (hydrogels),<sup>7,8</sup> dendritic polymers,<sup>9,10</sup> and others.<sup>11,12</sup> A common characteristic of these agents is that they are, at least partially, hydrophilic, so they effectively interact with water; at the same time, they are insoluble in water and, therefore, can be easily recuperated. However, hydrophilic materials are not good adsorbents for organic pollutants. For this reason, it is necessary for them to contain hydrophobic pockets, which can accommodate and retain organic substances. Most complex organic polymers, such as hydrogels or dendritic polymeric structures as well as block copolymers, are usually endowed with the property to form both hydrophilic and hydrophobic domains. Natural or synthetic inorganic adsorbents on the other hand must be organically modified to obtain hydrophobic domains, and this is usually achieved by incorporating surfactants into the pores of the inorganic matrix.<sup>4–6</sup> The present work shows that a nanocomposite organic–inorganic gel, which was

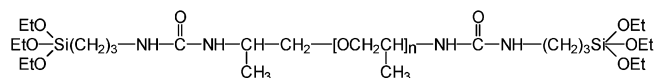
previously used for other applications,<sup>13–18</sup> is a very effective agent to remove dyes from water. It concerns the so-called ureasil,<sup>19,20</sup> a nanocomposite gel synthesized through the sol–gel technique by hydrolysis or organic acid solvolysis.<sup>21</sup> Ureasil precursors consist of a polyether chain end-capped by two triethoxysilane groups attached through urea bridges, hence the name ureasil (see Figure 1 for chemical structure). The sol–gel process acts on the siloxane groups creating a silica network. Therefore, ureasils are based on a silica backbone containing an organic subphase that can provide both hydrophilic and hydrophobic domains. This is due to the existence of polar chemical groups and the presence of poly(oxyalkylenes), which practically dissolve any organic substance, be it hydrophilic or hydrophobic. These ureasil gels are insoluble in water, but when submerged in aqueous solutions of various dyes they adsorb and retain dyes producing a really impressive result. After a few hours in contact with colored water they are capable of removing all dye content leaving crystal clear water, where any dye residues are hard to detect by any spectroscopic technique. The present work is then a study of the efficiency of ureasils as water purification agents.

\* To whom correspondence should be addressed. E-mail: lianos@upatras.gr.

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### Poly(oxypropylene)-Ureasil sol-gel precursor



### Poly(oxypropylene)-block-poly(oxyethylene)-block-poly(oxypropylene)-Ureasil sol-gel precursor

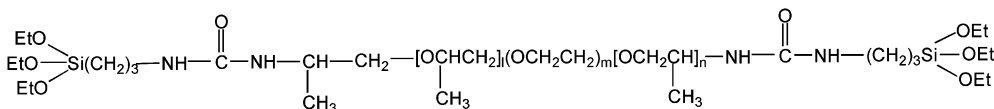


Figure 1. Chemical structures of ureasil sol-gel precursors.

## Experimental Section

**Materials.** *O,O'*-Bis(2-aminopropyl)poly(propylene glycol) of molecular weight 4000, 2000, and 230 (APPG-4000, APPG-2000, APPG-230), 3-isocyanatopropyltriethoxysilane (ICS), Acid Orange 7 (AO7), Rhodamine 6G, Basic Blue 41 (BB), Cresyl Violet (CV), Crystal Violet, sodium dodecyl sulfate (SDS), and Coumarin-153 (C-153) were from Aldrich. Pyrene, pyrene tetrasulfonate (PTS), and *O,O'*-bis-(2-aminopropyl)poly(propylene glycol)-*block*-poly(ethylene glycol)-*block*-poly(propylene glycol) of molecular weight 1900, 800, and 500 (APEG-1900, APEG-800, APEG-500) were from Fluka. All these chemicals were used as received. Amphiphilic hemicyanines, *N,N*-alkyl-4-(dimethylaminophenylethenyl)pyridinium bromide (HnHC) of three different alkyl chain lengths ( $n = 5, 7,$  and  $12$ ), were synthesized by condensation of the corresponding *N*-alkylated 4-methylpyridines with 4-dimethylaminobenzaldehyde and were purified by repeated recrystallization from ethanol.<sup>22</sup> These last reagents were graciously donated by Prof. A. Laschewsky, Potsdam University, Germany.

**Synthesis of Ureasil Precursors.** Six different unhydrolyzed ureasil precursors were prepared basically using the preparation procedure of Dahmouche et al.<sup>20</sup> APEG or APPG (frequently called Jeffamines) of various chain lengths and ICS (molar ratio [ICS]/[Jeffamine] = 2) were mixed in tetrahydrofuran (THF) under reflux (64 °C) for 6 h. The isocyanate group of ICS reacts with the amino groups of APPG or APEG (acylation reaction), producing urea connecting groups between the polymer units and the inorganic part. After evaporation of THF under vacuum, a viscous precursor was obtained, which is stable at room temperature for several months. We prepared similar hybrid precursors modified by both types of polymers with three different chain lengths for each type [poly(oxypropylene), 4000, 2000, and 230; and poly(oxypropylene)-*block*-poly(oxyethylene)-*block*-poly(oxypropylene), 1900, 800, and 500]. The respective abbreviated names used in the present work are PP4000, PP2000, and PP230 for the poly(oxypropylene)-containing precursors and PE1900, PE800, and PE500 for the poly(oxyethylene)-containing precursors. The chemical structure of the precursors appears in Figure 1 while the chemical structures of dyes can be seen in Figure 2.

**Sol-Gel Synthesis.** Three types of sol-gel synthesis procedures were employed, according to the catalyst used: HCl, NH<sub>4</sub>F, or acetic acid catalysis. In the first case, 4.5 g of precursor were mixed with 15 mL of methanol. After stirring for 5 min, 0.5 mL of 0.1 M HCl was added, and the mixture was stirred for an additional 30 min. In the second case, 0.04 M NH<sub>4</sub>F was used in the place of HCl. In the case of acetic acid catalysis, 4.5 g of precursor was dissolved in 15 mL of methanol. After stirring for 5 min, 9.6 mL of glacial acetic acid was added, and the mixture was stirred for an additional 30 min. After stirring, the fluids were put in uncovered

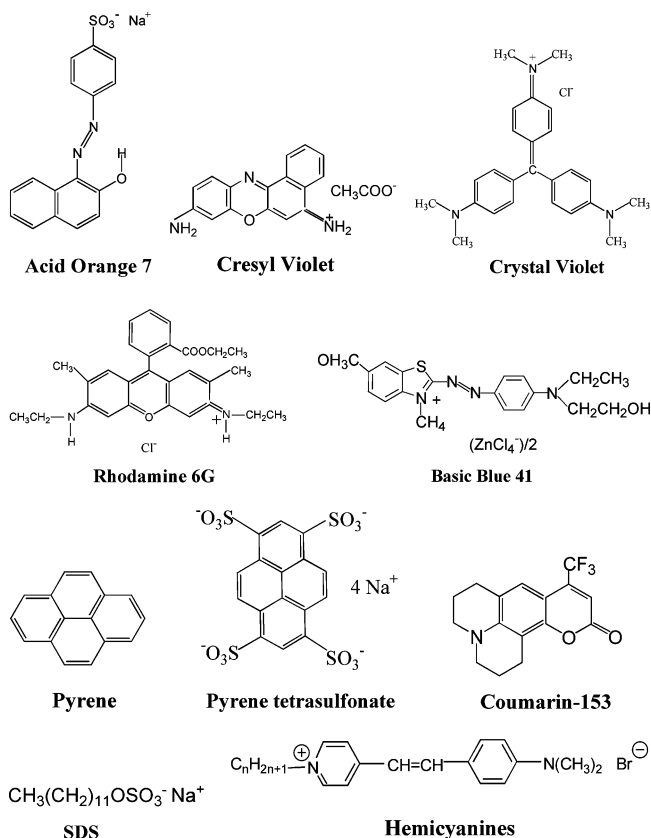


Figure 2. Chemical structures of various dyes used in this work.

square poly(methyl methacrylate) cuvettes and left to dry in air for 1 week. During this period the solvent evaporates, and the volume of the material extensively shrinks. The resulting gel is a flexible material, like soft rubber, that is easily detached from the plastic container. Its approximate shape, determined by the container used, was a cube of about a 7 mm side. It could be further cut into pieces by a knife, and it was thus ready for use.

**Experimental Methods.** Adsorption of dyes was studied by the following procedure: the adsorbent was submerged in the aqueous solution of the dye and was left to adsorb for 24 h. Then it was taken out of the solution, and the remaining dye was estimated by absorption spectrophotometry or by conductimetry. To calculate the amount adsorbed or remaining in the solution dye, we have accepted that both light absorbance and ionic conductivity are proportional to the dye concentration in the concentration range studied. To verify this hypothesis and to define the limits of the linear relationship, we have plotted absorbance or conductivity versus dye concentration in preliminary experiments. Column 3 of Table 1 shows the maximum concentration that applies to each dye studied. All samples were studied at maximum initial concentration. The whole procedure was carried out under ambient

**Table 1. Adsorption Data for PP230 Ureasil and for Various Dyes**

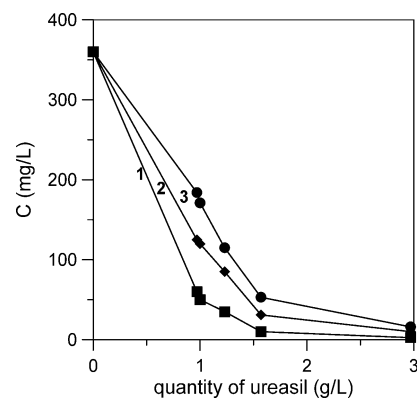
dye	$\lambda_{\max}^a$ nm	$C_0^b$ mg/L (mM)	$q_e \text{ max.}^c$ mg/g	$K_L^d$ L/g ( $10^4 \text{ M}^{-1}$ )
AO7	483	360 (1)	344	63 (2.27)
PTS	375	61 (0.1)	298	55 (3.35)
SDS		288 (1)	327	61 (1.77)
CV	596	180 (0.55)	68	13 (0.42)
Crystal Violet	590	45 (0.11)	61	11 (0.45)
Rhodamine 6G	523	47 (0.1)	65	12 (0.57)
BB	615	240 (0.5)	63	12 (0.58)
H5HC	450	94 (0.25)	73	21 (0.79)
H7HC	452	101 (0.25)	89	23 (0.93)
H12HC	453	118 (0.25)	108	26 (1.23)
pyrene	336	1 (0.005)	110	27 (0.58)
C-153	427	1.5 (0.005)	113	28 (0.86)

<sup>a</sup> Wavelength of light absorption maximum. <sup>b</sup> Initial aqueous concentration of the corresponding dye (corresponding molarity in parentheses). <sup>c</sup> Quantity of the adsorbed dye per gram of the adsorbent. <sup>d</sup> Binding constant given in L/g (in parentheses the same quantity is expressed in  $\text{M}^{-1}$ ).

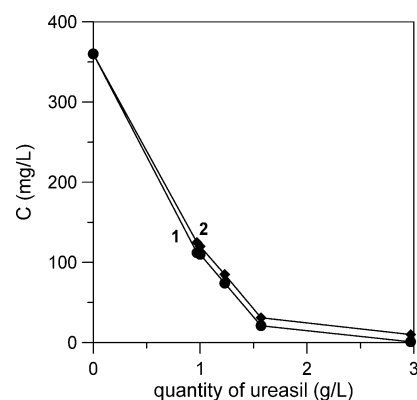
conditions. Absorption measurements were made with a Cary 1E spectrophotometer, and conductivity measurements were made with a Metrohm 660 conductometer using a thermostated cell with cell constant  $k = 0.074 \text{ cm}^{-1}$ . Finally, Fourier transform infrared (FTIR) measurements were made with Perkin-Elmer Spectrum RXI spectrometer.

## Results and Discussion

As stated in the introduction, ureasil gels are very effective in adsorbing and retaining dyes from aqueous solutions. A typical example is given in the photograph shown in the Table of Contents, where it is seen that a relatively small piece of ureasil can produce clear water by adsorbing and retaining all dye in solution. It is seen that the gel swells in solution and breaks into pieces, losing the original shape. This photograph refers to an aqueous solution of AO7 (see Figure 2 for chemical structure). AO7 and the rest of the dyes shown in Figure 2 were chosen either because they have been previously studied as typical water pollutants<sup>3,6,9,10,23–26</sup> or because they serve as representative dyes for the purposes of the present work. As an example, the efficiency of AO7 adsorption is given by the data of Figure 3, which shows the amount of dye remaining in solution after ureasil adsorbent saturation as a function of the quantity of the adsorbent. The dyes remaining in solution were monitored by absorption spectrophotometry except in the case of SDS, where we used ionic conductivity. UV–vis absorbance was measured at the absorption maximum. The absorption maximums of AO7 and of the rest of the dyes studied are listed in Table 1. Figure 3 shows AO7 adsorption efficiency of three poly(oxypropylene) ureasil gels of different polymer chain lengths. The most efficient gel is the one with the smallest polymer chain, that is, PP230. The behavior was similar to that of poly(oxypropylene)-*block*-poly(oxyethylene)-*block*-poly(oxypropylene)-containing gels while, as shown in Figure 4, no essential difference is observed by



**Figure 3.** Variation of the quantity of the nonadsorbed AO7 vs the quantity of the adsorbent for three ureasil gels: (1) PP-230; (2) PP2000; and (3) PP4000.

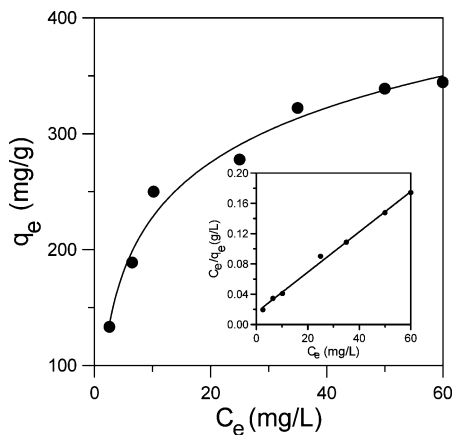


**Figure 4.** Variation of the quantity of the nonadsorbed AO7 vs the quantity of the adsorbent for two ureasil gels: (1) PP-2000 and (2) PE1900.

comparing gels of approximately the same polymer chain size. We may then conclude that the choice between these two materials makes little difference. The property that matters is chain size. It has been previously found by studying ureasil gels using fluorescent probes<sup>27</sup> and by correlation to previous findings (see references in ref 27) that ureasils are two-phase systems consisting of interpenetrating subphases, one inorganic (silica) and one organic, both organized in nanoclusters. The organization of the organic subphase is mainly governed by hydrophobic interactions. AO7 is an anionic dye, which naturally avoids hydrophobic domains, which in turn are most abundant in large-chain ureasils. Therefore, it is not a surprise that AO7 is better adsorbed by PP230, which has the smallest hydrophobic domain. Nevertheless, the differences between PP230 and PP4000, as far as AO7 adsorption is concerned and as seen from the data of Figure 3, are not spectacular. In addition, as already mentioned, negligible differences have been observed in the adsorption capacity of the presumably more hydrophobic PP2000 compared with that of the presumably less hydrophobic PE1900, as seen in Figure 4. Apparently, other factors, besides hydrophobic/hydrophilic balance, as it will be further discussed below, play a major role in dye adsorption. Figures 3 and 4 show that adsorption of AO7 by ureasil gels is indeed very efficient, because at the end there is no dye left in solution. This conclusion can be better appreciated by also studying the data of Figure 5.

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**Figure 5.** Langmuir isotherm for the quantity  $q_e$  of the adsorbed AO7 per gram of the adsorbent vs the concentration  $C_e$  of AO7 remaining in solution. Insert: plot for the analysis of the corresponding Langmuir isotherm.

Figure 5 shows a Langmuir isotherm, which is the variation of the quantity  $q_e$  of the adsorbed AO7 per gram of the adsorbent versus the concentration  $C_e$  of AO7 remaining in solution ( $C_e$  is distinguished from  $C$  to avoid the zero-point data; they are in fact equal).  $q_e$  was calculated by eq 1:<sup>6,7</sup>

$$q_e = (C_0 - C_e)V/m \quad (1)$$

where  $C_0$  is the initial dye concentration (in mg/L),  $V$  is the volume of the solution (in liters), and  $m$  is the mass of the adsorbent (in grams). The inset of Figure 5 also shows the variation of the ratio  $C_e/q_e$  versus  $C_e$ . It represents an analysis of the Langmuir isotherm, and it produces the binding constant  $K_L$  by eq 2:<sup>2,3,7</sup>

$$C_e/q_e = 1/K_L + (\alpha_L/K_L)C_e \quad (2)$$

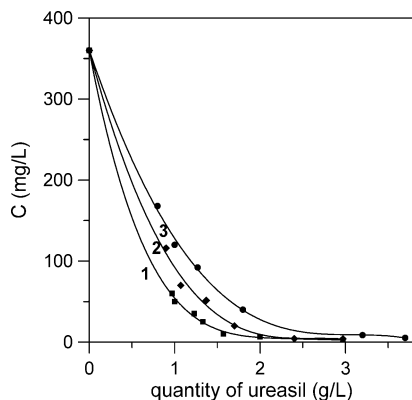
where  $K_L$  is the binding constant (in L/g) and  $\alpha_L$  is a Langmuir constant. The straight line obtained in the inset of Figure 5 shows that adsorption obeys Langmuir kinetics. Table 1 shows the values of  $q_e$  and  $K_L$  obtained for all dyes studied. For PP230 ureasil and for aqueous solutions of AO7,  $q_e$  was 344 mg/g and  $K_L$  was 63 L/g, that is,  $2.27 \times 10^4 \text{ M}^{-1}$ . These values are much higher than those recorded for other adsorbents.<sup>3,6,9</sup>

The impressive adsorption capacity of the PP230 ureasil is unfortunately not applicable to all dyes. The data of Table 1 show that not all dyes studied were adsorbed with the same efficiency. These dyes can be classified in some different categories. The highest capacity of adsorption was observed with anionic solutes, that is, AO7, PTS, and SDS, where the adsorption efficiencies were very close to each other. As seen in Figure 2, the only common characteristic of these substances, which are otherwise very different from each other, is the presence of the sulfonate group. It is then obvious that the presence of this chemical group plays the most crucial role for adsorption by PP230. A similar conclusion holds true for all six ureasils studied. It is possible that a chemical reaction might take place between the urea and the sulfonate group which could justify this high adsorption capacity. This could also explain the data of Figure 3 showing that the most efficient gel is the one with the smallest polyether chain. PP230 has a higher "concentration" of urea groups contrary to PP4000 where urea groups

are "diluted" in the more voluminous polyether chains. We have performed FTIR spectroscopic measurements on ureasils before and after AO7 adsorption. Such measurements were made on ureasil thin films on silicon wafers. It should be noted that ureasil films preserved their high adsorption capacity for ionic dyes in the film form. No evidence has been found of any modification of the IR absorption peaks after dye adsorption. IR spectroscopy then provides no conclusive evidence of strong reaction between sulfonate and urea chemical groups. The question of the existence or not of chemical reactions is still open. Ureasils demonstrated the lowest adsorption capacity for positively charged dyes, as seen in Table 1. However, adsorption capacity was still very high for cationic dyes such as BB, CV, Crystal Violet, and Rhodamine 6G ( $q_e$  ranged between 63 and 68 mg/g), compared to values previously reported for other adsorbents,<sup>3,6,9</sup> which were substantially or extensively lower. It was even higher for amphiphilic cationic dyes such as hemicyanines. In the latter case, as Table 1 shows, adsorption capacity increased with alkyl chain length. Thus, in the case of H12HC,  $q_e$  was 108 mg/g and  $K_L$  was 26 L/g (i.e.,  $1.23 \times 10^4 \text{ M}^{-1}$ ), that is, comparable with the efficiency for adsorption of anionic dyes. Obviously, the presence of the sulfonate group is a principal factor affecting adsorption, but the hydrophobic/hydrophilic balance also plays an important role. Thus the more hydrophobic H12HC is better adsorbed by ureasils than the less hydrophobic H5HC. Hydrophobicity reveals itself as an equally important factor for adsorbing dyes from water. Indeed, relatively high efficiency has been recorded with the hydrophobic dyes pyrene and coumarin, as can be also seen in Table 1. This behavior was expected, for two reasons. Hydrophobic dyes are scarcely dissolved in water, and they can easily be transferred to the adsorbent. In addition, as already stated, ureasils, which bear a poly-(oxyalkylene) subphase, create a friendly environment for dissolving dyes. Hence, there is high efficiency. Under these conditions, PP4000 ureasil should favor adsorption of hydrophobic dyes, because, as already stated, it has more hydrophobic domains.<sup>27</sup> This is indeed the case. Hydrophobic dyes are more efficiently adsorbed by PP4000 than by PP230. Thus, for a PP4000 adsorbent, H12HC gave  $q_e = 198 \text{ mg/g}$  and C153 gave  $q_e = 183 \text{ mg/g}$ , which are extensively higher than the corresponding values obtained with PP230 (108 mg/g and 113 mg/g, respectively, cf. Table 1). In any case, ureasil gels have a relatively low glass transition temperature (below  $0 \text{ }^\circ\text{C}$ );<sup>28</sup> therefore, mobility and restructuring of the poly(oxyalkylene) chains at room temperature is allowed. Subsequently, forces deriving from the hydrophobic/hydrophilic balance should definitely play a role in these materials.

Another feature of ureasils, which concerns their adsorption capacity, is related with the catalysts employed for the sol-gel procedure, because they affect the gel nanostructure. Figure 6 shows the adsorption capacity of PP230 for AO7 as a function of the catalyst used to synthesize the gel. As already stated in the experimental section, three catalysts were employed, HCl,  $\text{NH}_4\text{F}$ , and acetic acid. The most efficient gel was the one synthesized by HCl catalysis, and

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**Figure 6.** Variation of the quantity of the nonadsorbed AO7 vs the quantity of the adsorbent for PP230 ureasil gels synthesized with different sol-gel catalysts: (1) HCl; (2) acetic acid; and (3)  $\text{NH}_4\text{F}$ .

the less efficient one was the  $\text{NH}_4\text{F}$ -catalyzed one. It is known that acid or base catalysis has important effects on the structural characteristics of these gels.<sup>29</sup> Acid catalysis generally produces more finely dispersed nanoclusters, and this type of structure obviously beneficially affects adsorption capacity. Smaller differences were observed between gels obtained by the conventional sol-gel route (HCl catalysis) and those obtained by organic acid solvolysis (acetic acid catalysis). It has been previously found by  $^{29}\text{Si}$  and  $^{13}\text{C}$  NMR that the main structural features of ureasil gels synthesized by either HCl or carboxylic acid catalysis remain similar.<sup>30</sup> In this sense, small only adsorption differences are expected and the present results are along these lines.

Finally, one factor that might affect adsorbance of dyes is the solution pH, which changes the concentration of surface

silanol groups. No important variation in adsorption of most of the dyes studied was observed by varying the pH. It is possible that pH might affect the adsorption of dyes with chemical structure different from the ones studied in this work. This question deserves further investigation.

### Conclusion

Ureasil gels are very efficient as adsorbents of dyes from aqueous solutions. Dyes bearing a sulfonate group are most efficiently adsorbed, followed by hydrophobic dyes and then by dyes bearing a positive charge. The presence of the sulfonate group and the hydrophobic/hydrophilic balance in these materials are the main determining dye-adsorption factors. The efficiency of adsorption of cationic dyes by ureasil gels is comparable with the best literature data, while the efficiency becomes much higher in the case of hydrophobic and even higher in the case of anionic dyes. All six studied ureasil gels were efficient adsorbents, but differences were recorded as a function of the poly(oxyalkylene) chain size. Thus longer chains are better adsorbents for hydrophobic dyes. All gels were synthesized by the sol-gel method. In this respect, the best gels were those made by the conventional sol-gel route (HCl catalysis). Ureasil gels are serious candidates for technological applications with one drawback. Adsorption of dyes is irreversible so that these materials cannot be used twice.

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