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Use of Ureasil gels to extract ions from aqueous solutions

Vlasoula Bekiari, Panagiotis Lianos *

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

Abstract

Nanocomposite organic–inorganic gels synthesized through the sol–gel procedure by using Ureasil precursors can be employed as efficient sorbents for retaining metal cations and small anions from aqueous solutions. Sulfate or sulfonate as well as nitrate ions demonstrate a high affinity for Ureasils. High affinity was also demonstrated by trivalent metal cations. This affinity was explained by the presence of urea and of ether groups in Ureasils, which have the ability to complex many different types of ionic species.
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1. Introduction

A simple and efficient procedure to remove toxic metals from water is to use sorbents, which adsorb and retain these pollutants. Several such sorbents, natural, modified or synthetic, have been tried in the past, for example, modified natural clays [1], multiply branched hydrophilic polymers like hydrogels [2,3], sugar industrial waste [4], mesoporous oxides [5], etc. The common characteristic of these sorbents is that they are hydrophilic, i.e. they efficiently interact with water, but they are insoluble in water, so as to be easily removed. In a recent publication [6], we have found that a nanocomposite organic–inorganic gel, obtained by sol–gel condensation from a Ureasil precursor, can efficiently retain organic substances from water. In the present work, we show that the same sorbent is equally efficient to remove metal cations and small anions from aqueous solutions. Ureasil precursors consist of a polyether chain end-capped by two triethoxysilane groups attached through urea bridges, hence the name Ureasil (see Fig. 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, which is capable to dissolve practically any organic species or small ions. This is due to the presence of the polyether chain and of the strong polar chemical groups on the two sides of the molecule. These Ureasil gels are insoluble in water but when submerged in aqueous solutions of various ions they adsorb and retain them. In the case of metal ions making colored solutions, one can observe by bare eye the retaining of the ions, which move from water to the sorbent and color it. The present work is then a study of the efficiency of Ureasils as water purification agents.

2. Experimental

2.1. Materials

O,O'-Bis(2-aminopropyl)polypropyleneglycol of molecular weight 230 (APPG-230) or 4000 (APPG-4000), 3-isocyanato-propyltriethoxysilane (ICS) and various salts were all from Aldrich and were used as received.

2.2. Synthesis of Ureasil precursors

The unhydrolysed Ureasil precursor was prepared basically using the preparation procedure of Dahmouche et al. [7]. APPG-230 or APPG-4000 (frequently called Jeffamines) 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 (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. This precursor is

* Corresponding author.
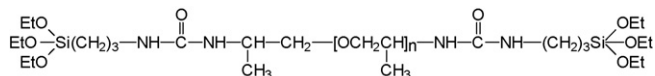 *E-mail address:* lianos@upatras.gr (P. Lianos).

Fig. 1. Structure of the Ureasil sol–gel precursor ($n = 3$ for PP230 and 68 for PP4000).

abbreviated in this work as PP230 (or PP4000, when applied). Their chemical structure appears in Fig. 1.

2.3. Sol–gel synthesis

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 30 more minutes. After stirring, the fluid was put in uncovered square PMMA 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 quantity of gel obtained for 4.5 g of precursor was approximately 3 g. 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 7 mm side. It could be further cut into pieces by knife and it was thus ready for use. The usual size of pieces used in this work was about 2 mm × 2 mm.

2.4. Experimental methods

Adsorption was studied by the following procedures: first, 15 ml aqueous solutions of 4 mM of various metal salts were made by using the following substances: $Cr(NO_3)_3$, $Co(NO_3)_2 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, CuCl, $Ni(CH_3CO)_2 \cdot 4H_2O$, Na_2SO_4, $NaNO_3$ and NaCl. Then, various quantities of the sorbent were submerged in the aqueous metal salt solutions and were left to adsorb for 24 h. Finally, the sorbent with retained material was taken out of the solution and the remaining in solution salt was estimated either by absorption spectrophotometry or by conductimetry or both. In order to calculate the amount of adsorbed or remaining in solution metal, we have accepted that both light absorbance or ionic conductivity is proportional to ion concentration in the concentration range studied. To verify this hypothesis and to define the limits of linear relationship, we have plotted absorbance or conductivity versus salt concentration in preliminary experiments. Fig. 2 shows, as an example, the case of Cr^{3+}. In the case of SO_4^{2-}, there was no absorption of light in the UV–vis range and conductivity values did not offer a linear range of measurements. For this reason, the quantity of sulfate ions was measured by reaction with $BaCl_2$, which leads to the formation of a suspension of $BaSO_4$. When the quantity of the reactants is small, the products stay in suspension and they cause a zone of cloudiness in the visible range (maximum at 420 nm). Thus light absorbance at 420 nm can lead to calculation of the number of reacting sulfate ions. The corresponding calibration curve gave a linear range only at concentration ≤0.4 mM. For this reason, as seen in Table 1, while all cations were studied at 4 mM, for SO_4^{2-} the concentration was only 0.4 mM. However, as it will be seen below, results based on conductivity values are also given for comparison. In addition, data are supplied for other anions, also based on conductivity values. The major
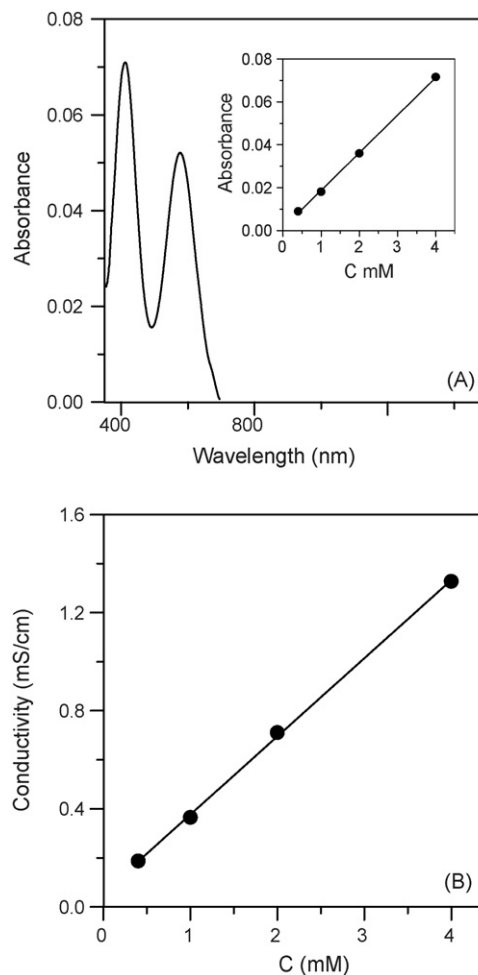

Fig. 2. Calibration curves for aqueous solutions of Cr^{3+}: (A) absorption spectrum of 4 mM Cr^{3+} and variation of maximum absorbance with cation concentration; (B) variation of conductivity with cation concentration.

Table 1
Adsorption data for PP230 Ureasil and for various ions

Ion	λ_{max}[a] (nm)	C_0[b] (mM)	$q_{e\,max}$[c] (mmol/g)	K_L (10^4 M^{-1})
Cu^+	360	4	0.09	0.21
Cu^{2+}	810	4	0.12	0.38
Ni^{2+}	403	4	0.13	0.42
Co^{2+}	512	4	0.14	0.45
Fe^{3+}	505	4	0.19	0.55
Cr^{3+}	570	4	0.20	0.58
SO_4^{2-}	420[d]	0.4	1.16	0.92
SO_4^{2-}	–	0.4	1.90[e]	1.13[e]
NO_3^-	–	0.4	1.72[e]	1.07[e]
Cl^-	–	0.4	0.85[e]	0.78[e]

[a] Wavelength of light absorption maximum in the case of substances with UV–vis absorbance.
[b] Initial concentration of the corresponding ion.
[c] Quantity of the adsorbed ion per gram of the adsorbent.
[d] Absorbance after reaction with $BaCl_2$.
[e] These values are based on conductivity measurements, which are obtained with a lot of error and they are possibly smaller.

problem with detection of ions by conductivity is that conductivity measurements reflect ionic conductivity of both monitored ions and their counter ions. Therefore, they do not represent the studied ion itself but provide data calculated with a lot of error. All samples were studied at maximum applicable concentration. Absorption measurements were made with a Cary 1E spectrophotometer and conductivity measurements with a Metrohm 660 conductometer using a thermostated cell with cell constant $k = 0.074\,\mathrm{cm}^{-1}$. The whole procedure was carried out under ambient conditions.

3. Results and discussion

As already said in Section 1, Ureasil gels are nanocomposite organic–inorganic materials composed of a silica backbone with polyether chains covalently bound through urea bridges. The organic and the inorganic subphases are mixed in the nanoscale and for this reason it is hard to characterize these materials by microscopy. Most information is usually indirectly obtained by employing spectroscopic techniques [8,9]. Differential scanning calorimetry measurements have been previously made [9] and showed that T_g of Ureasil gels decreases with increasing polyether chain length. When the chain is long, T_g is mainly affected by polyether T_g value, which ranges between -50 and $-25\,^\circ\mathrm{C}$. When the chain is short then the system is more rigid and T_g can climb as high as $50\,^\circ\mathrm{C}$ [9]. Both PP230 and PP4000 used in the present work were rather soft rubbery materials. When a piece of this material was submerged in a water solution containing ions, the latter were adsorbed at high percentages.

Fig. 3A gives the variation of the residual cation concentration as a function of the quantity of sorbent introduced into the solution. It is seen that as the quantity of sorbent increases, less and less metal ions are left in solution. For Ureasil concentration about 25 g/L the system arrives at equilibrium. The equilibrium concentration is very sensitive to the original ion concentration. Thus in the case of sulfate ions (Fig. 3B), which were initially 10 times less concentrated than metal ions (i.e. 0.4 mM as opposed to 4 mM), it took almost 100 times less sorbent to arrive at equilibrium. The time evolution of adsorption is shown by the inset of Fig. 3A. Equilibrium was reached in about 24 h. Adsorption capacity also greatly varies from one metal ion to the other (Fig. 3A). In order to use a uniform means of comparison between the behavior of these ionic species, it is common practice to express data with the help of Langmuir isotherms [6]. Fig. 4 shows a Langmuir isotherm, that is the variation of the quantity q_e of the adsorbed Cr^{3+} per gram of the adsorbent versus the concentration C_e of Cr^{3+} remaining in solution. q_e was calculated by Eq. (1) [5,6,10]:

$$q_e = \frac{(C_0 - C_e)\,V}{m} \tag{1}$$

where C_0 is the initial ion concentration (mmol/L), V the volume of the solution (L) and m is the mass of the sorbent (g). The inset of Fig. 4 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) [1,10,11]:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{\alpha_L}{K_L}\right) C_e \tag{2}$$

where K_L is the binding constant (L/g) and α_L is a Langmuir constant. The straight line obtained in the inset of Fig. 4 shows that
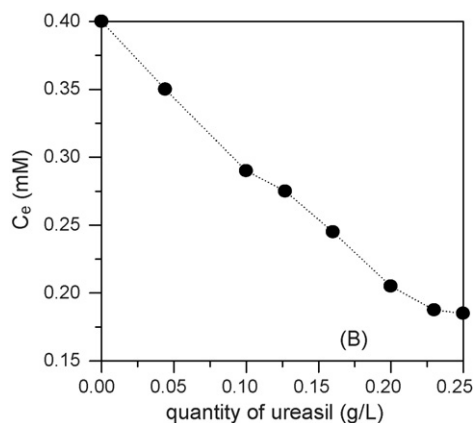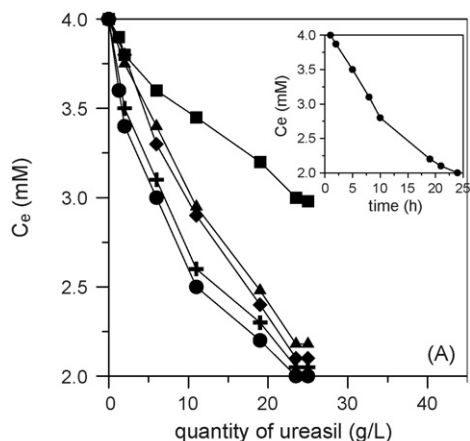

Fig. 3. Variation of the residual ion concentration after adsorption vs. sorbent concentration: (A) metal ion solutions: (■)Cu^+; (▼) Ni^{2+} and Cu^{2+}; (♦) Co^{2+}; (✚) Fe^{3+}; and (●) Cr^{3+}; (B) sulfate solution. Inset of (A) shows the residual quantity of Cr^{3+} vs. time in the presence of 25 g/L sorbent.
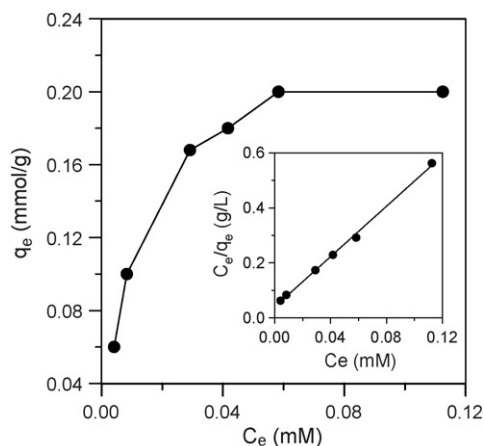

Fig. 4. Langmuir isotherm for the quantity q_e of the adsorbed Cr^{3+} per gram of the adsorbent vs. the concentration C_e of Cr^{3+} remaining in solution. Inset: plot for the analysis of the corresponding Langmuir isotherm.

adsorption obeys Langmuir kinetics. Table 1 shows the values of q_e and K_L obtained for all ions studied. Both $q_{e\,max}$ and K_L are listed in Table 1 and they both represent the capacity of PP230 Ureasil gel as ion-adsorbing material from aqueous solutions. These values have been calculated with 1% error. In the case of Cu^+, the concentration of this monovalent ion was monitored by absorption spectrophotometry, which is well distinguished from light absorption by divalent Cu^{2+}. No transition of monovalent to divalent copper was detected during the process of detection. $q_{e\,max}$ and K_L progressively increased in going from monovalent to trivalent cations and they further increased in the case of sulfate anions. The values corresponding to metal ion removal are comparable with values found by other researchers, who used different types of sorbent, for example, modified clays [1] or mesoporous silica [5]. However, PP230, which was previously found to be a powerful sorbent for dyes bearing a sulfonate group [6], proves itself equally powerful to adsorb small sulfate ions themselves. Indeed, as seen in Table 1, $q_{e\,max}$ as well as K_L in the case of sulfate ions were by far larger than in the case of metal ions. q_e max and K_L for sulfate ions were found even higher when they were calculated through conductivity measurements. However, as already said, conductivity values contain a lot of error since they represent both the conductivity due to SO_4^{2-} and of its counter ion Na^+. As seen in Table 1, $q_{e\,max}$ and K_L were also very high in the case of nitrate anions while for Cl^- adsorbance was also high but substantially smaller than in the case of sulfate anions.

What makes sulfate groups demonstrate such affinity for Ureasil gels and why trivalent ions also demonstrate higher affinity than monovalent ions? As seen in Fig. 1, each Ureasil molecule contains two urea bridges. It is known, particularly by works dealing with biological macromolecules [12], that sulfate or sulfonate groups interact with urea groups [13] forming strong hydrogen bonds through sulfonate or sulfate oxygens. These bonds serve important biological functions by complex formations between proteins. It is then concluded that the affinity of sulfate (or sulfonate [6]) groups to Ureasils is due to the presence of the $-NH-CO-NH-$ groups. We further believe that the relatively high affinity of nitrate groups is also due to complexation of nitrate oxygens with urea groups. On the contrary, it seems that cations are attracted by the poly(oxypropylene) chain and complexed by ether oxygens. This could explain why trivalent cations are better adsorbed than monovalent cations. Indeed, when PP230 was substituted by an homologue bearing a much longer poly(oxypropylene) chain, i.e. PP4000 ($n = 68$), for Cr^{3+} adsorbance q_e became 0.28, i.e. substantially larger than the corresponding value obtained with PP230, which was 0.20. This shows that the polyether chain does play a major role in cation adsorption. Of course, partial attraction by urea carcoxylic oxygen [13] cannot be excluded. Unfortunately, FTIR spectroscopy did not offer a clear-cut information on this subject. It is then indirectly concluded that ether oxygens play a major role for the adsorption of positive ions. The different mechanisms of ion adsorption give Ureasils substantial capacity of selectivity. Selectivity has been observed between cations of different valence. Higher valence cations are more strongly adsorbed. Anions are also more efficiently adsorbed than cations. Thus when a solution contains a mixture of cations of different valences, preference is demonstrated for those of the highest valence. The pH of the solution did not substantially affect the above properties. In alkaline pH, cations precipitate. Therefore, it makes no sense to use sorbent. In acidic pH, we detected negligible variation of the adsorbing efficiency of Ureasils.

An obvious question that could be finally asked is whether Ureasil sorbents can be regenerated and reused. When sorbent with adsorbed cations was treated with an alkaline solution, partial elution of the adsorbed material was observed. Ureasils are then not completely regenerated. This is a disadvantage. However, the other capacities of this material described above may make it interesting for applications.

4. Conclusions

Ureasil gels, i.e. nanocomposite organic–inorganic gels based on a silica backbone with attached polyether chains covalently attached through urea bridges, can be employed as efficient sorbents for retaining ions from aqueous solutions. Cations demonstrate an affinity for Ureasils, which increases with cation valence. Ureasils are particularly efficient sorbents for sulfate, sulfonate and nitrate ions since these ions have a strong affinity for the urea groups of Ureasils.

Acknowledgements

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