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Use of Ureasil gels to extract ions from aqueous solutions

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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.

Keywords: Ureasil; Adsorption of ions

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-isocyanatopropyltriethoxysilane (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

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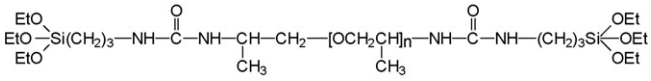

Fig. 1. Structure of the Ureasil sol–gel precursor ($n = 3$ for PP230 and 68 for PP4000).

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

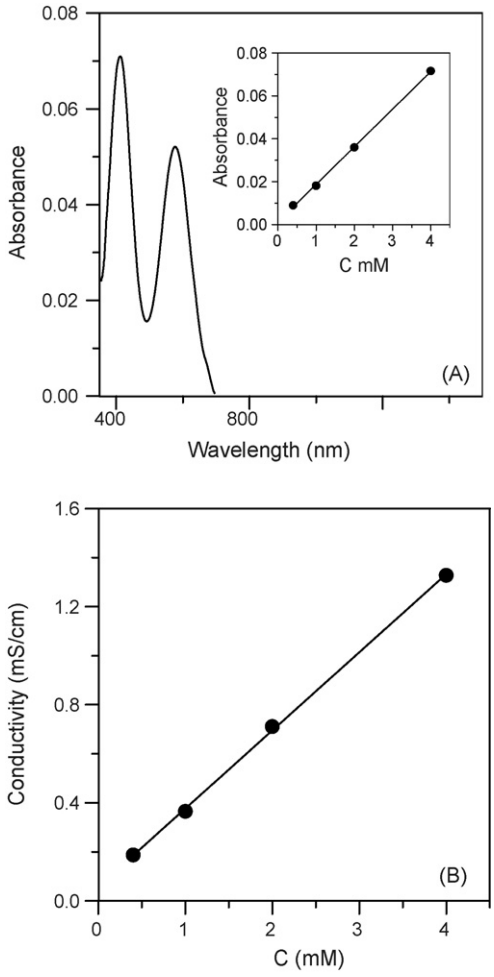

Fig. 2. Calibration curves for aqueous solutions of Cr^{3+}: (A) absorption spectrum of 4 mM Cr^{3+} and variation of maximum absorbance with cation concentration; (B) variation of conductivity with cation concentration.

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.