THE INCREASED TERMAL STABILITY ASSOCIATED WITH HUMIC ACID ANCHORED ONTO SILICA GEL

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Abstract

Commercial humic acid (HA) was anchored onto silica gel (SiAPTS) previously modified with 3-aminopropyltrimethoxysilane (APTS). HA was anchored onto SiAPTS through two routes: adsorption and covalent chemical immobilization onto the surface. The adsorption occurred by adding SiAPTS to HA in an aqueous solution, producing SiHA1, while chemical immobilization was performed by reacting HA suspended in N,N-dimethylformamide with SiAPTS, to yield SiHA2. The infrared spectra confirm HA immobilization using both procedures and the termogravimetric results showed that the anchored compounds have significantly thermal stability increased. While natural HA presents a thermal stability up to $200^{o}C$, the anchored compound presents a thermal stability near to $750^{o}C$.

Keywords: humic acid, silica, thermogravimetry

Introduction

Humic acid (HA) is one of the main components of the organic mass in soils and also of the dissolved part of organic carbon in a natural aquatic environment [1]. This material is constituted by a mixture of weak-acid polyeletrolites, which comprise a complex class formed by organic macromolecules, exhibiting a large range variety of molar-mass distributions, substructures and functionalities [2–3]. Knowledge of HA acid-base equilibrium gives useful information to discuss its complexation with heavy metal ions [4], its bonding abilities with organic pollutants, such as pesticides [5] and the chemistry involved in the catalysis of degradation in the environment [6].

During the course of sorption investigations, HA is isolated, purified and used in laboratory studies. However, these studies are often partially impeded by the fact that it is difficult to separate HA from aqueous solutions. One way to avoid this difficulty is to attach it onto an inorganic support. The procedure is feasible because on immobilization the solute is easily separated from the supernatant by sedimentation or centrifugation.

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Immobilized HA can be explored in a wide range of environmental conditions such as pH, ionic strength and column experiments, wherein operations are employed to recover the starting material [7–8].

Among a series of supports that can be used to immobilize HA, silica gel clearly plays a significant role due to its ability to anchor organic chains designed to embrace desired functional groups [9]. For this purpose, the use of silylant agents in many reactions is a common route of immobilizing molecules, in which chelating functional groups belonging to the covalent chains are bound to the surface, in order to attain special properties [9–10].

The success of the immobilization of functional groups on silica supports is mainly due to attachment of a silylant agent containing trialkoxysilyl groups, which are chemically reactive toward the free silanol groups disposed on the active surface [9–13]. On the other hand, subsequent reactions can expand the previously bound organic chain, during which desired functional groups can be introduced [13–17].

The present investigation reports on thermal stability studies of two synthetic methodology of the commercial humic acid immobilized by two different methodologies onto a silica gel surface previously modified with 3-aminotrimethoxysilane.

Experimental

The silylant agent 3-trimethoxysilylpropylamine (APTS) was used without purification. Silica gel was activated in a stream of dry nitrogen and a specific area of 425.5 ± 15.8 $m^2\,g^{-1}$ was determined by BET method [9, 10].

Samples of humic acid (Sigma) were suspended in water and dialyzed in order to reduce the salt content [18]. The external water was replaced twice during 5 h and then every 12 h until no chloride could be detected. Subsequently, HA was dried in vacuum at 55°C. The total acidity and carboxylic acidity was determined by potentiometric titration [19] as recommended, with some modification of the original procedure [20], presenting 2.54 and 4.94 mmol of carboxylic and total acidity per gram of HA, respectively.

Activated silica gel (45.0 g) suspended in 100.0 cm^3 of dry xylene was refluxed and mechanically stirred for 1 h under dry nitrogen. To this suspension 15.0 cm^3 of APTS was added dropwise. The mixture was refluxed for another 72 h and the solid was filtered, then washed with water and ethanol [21], to give solid SiAPTS, which was dried in vacuum at room temperature for several hours [9, 21].

HA (30.0 mg) was solubilized in 30.0 cm^3 of a 0.10 mol dm^{-3} NaOH aqueous solution. SiAPTS (1.00 g) was added to this solution, the pH was adjusted to 7.5, and the suspension was stirred for 20 h at room temperature. Before drying, the sample was rinsed several times, first using 0.20 mol dm^{-3} NaCl at pH 7.5 and then with water at the same pH. The solid was centrifuged, rinsed several times with NaCl 1.0 mol dm^{-3} at pH 10 to remove unbounded HA and with 1.0 mmol dm^{-3} HCl to protonate the SiAH1 [7, 8]. The final product, SiHA1, was dried at 120°C for 5 h in vacuum.

A mixture of SiAPTS (1.0 g) and HA (300 mg) were suspended in 30.0 cm^3 of N,N-dimethylformamide (DMF) and stirred for 20 h at 120°C. SiAH2 was rinsed re-

peatedly with DMF and centrifuged until the supernatant became colorless [7, 8]. The product SiAH2 was dried at 120°C for 5 h in vacuum.

Elemental analyses were obtained on a Perkin Elmer PE-2400 elemental analyzer. Infrared spectra of solid samples in the 4000 to 400 cm^{-1} range were performed in KBr pellets, with resolution of 4 cm^{-1}, by accumulating 25 scans on a Bomem series spectrophotometer. Thermogravimetric curves were obtained with samples of around 10 mg of the solid on a DuPont 1090B thermogravimetric analyzer model in a dynamic atmosphere, using a dry nitrogen flux, with heating from room temperature up to 900°C at a heating rate of 0.17°C s^{-1}.

Results and discussion

The synthetic procedure to anchor the humic acid on the inorganic support can be summarized by the reactions: i) activated silica gel (SiOH) with 3-aminopropyl-trimethoxysilane (APTS) to form the SiAPTS product as shown in reaction 1 [9, 10, 21] and ii) this product reacted with HA to give the final product SHA1, as presented in reaction 2.

A simple adsorption occurred through hydrogen bond formation between carboxylate groups present on HA and the protonated amine pedant groups of the
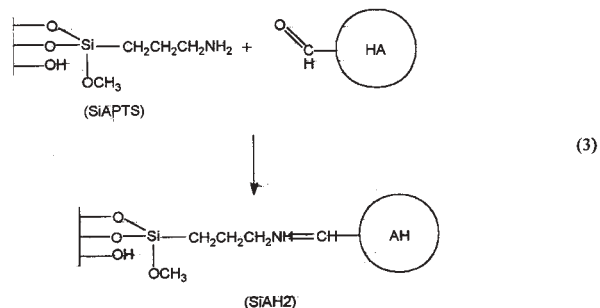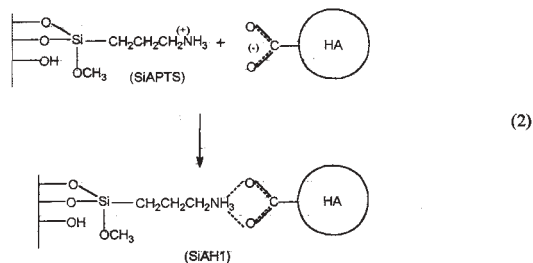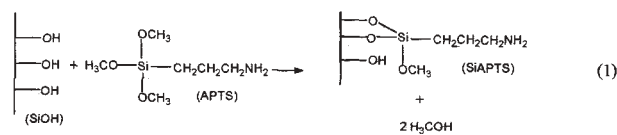
SiAPTS at pH 7.5. On the other hand, the HA is also immobilized, to yield the product SiHA2, as illustrated in reaction 3, through the reaction between aldehyde groups present on HA and pendant amine groups on the SiAPTS surface, by forming a Schiff base.

Elemental analysis showed that both surfaces presented a similar amount of anchored HA compound, as shown in Table 1. The complexity in HA structural features does not enable the determination the number of moles anchored onto silica surface. However, the carbon content is a good indication of the amount of HA anchored. Based on the carbon elemental analyses, a similar amount of HA is linked onto the silica surface after both kinds of immobilizations.

Table 1 Percentages of carbon (C) and nitrogen (N) for humic acid (HA) and the anchored surfaces SiHA1 and SiHA2

Sample	C/%	N/%
HA	56.34±0.71	4.91±0.56
SiHA1	12.31±0.91	2.42±0.34
SiHA2	12.56±0.45	2.43±0.16

The infrared spectra of samples are presented in Fig. 1 and some differences in frequencies can be observed. Thus, the SiAPTS spectrum presents typical peaks due to silanol and siloxane stretching frequencies at 900 and 1100 cm^{-1}, respectively. A weak CH stretching frequency appeared at 2950 cm^{-1}, which confirmed the attachment of the silylant agent on the surface [10, 21]. Large broad bands between 3500 to 3000 cm^{-1} are assigned to O–H stretching for silanol groups and hydrogen bonded water molecules on the surface. These broad bands are also presented in other spectra with much higher intensity, as a consequence of water, phenol, alcohol and
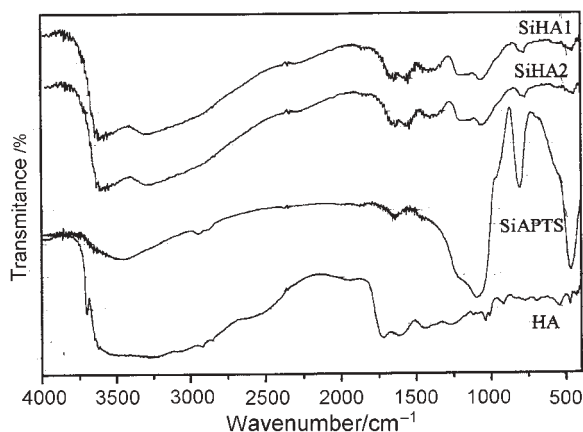

Fig. 1 Infrared spectra of humic acid (HA) and the anchored surfaces SiAPTS, SiHA1 and SiHA2

carboxylic groups, and also amines and amides N–H stretching from the HA molecule [22].

The success of HA anchoring on the SiAPTS surface can be observed in the SiHA1 and SiHA2 spectra, where peaks characteristic of HA are presented, such as i) broad bands between 1700 to 1650 cm^{-1}, assigned to C=O of amides, ketones, ester and carboxylic acid groups, ii) other broad bands at 1600–1500 cm^{-1} assigned to C=O of aldehyde, ketone, quinone groups, COO$^-$ symmetric stretching frequencies and iii) C=C aromatic group which are characteristic for HA molecules [22]. The broad bands between 1400 to 1300 cm^{-1}, attributed to C–O phenol groups, OH deformation and COO$^-$ antisymmetric stretching are also characteristic for HA molecules [22]. These data confirm that HA was immobilized onto SiAPTS using both procedures.

The thermogravimetric curves for all samples are presented in Fig. 2a and the corresponding DTG curves in Fig. 2b. The corresponding mass loss values are listed in Table 2. The characteristic mass losses related to physically adsorbed water were detected between 100 to 180°C for all curves, being a lesser value of 7.0% for SiAPTS and a larger value of 85.5% for the HA compound. After this common step, all samples showed a decomposition stage, in which HA curve presented an abrupt
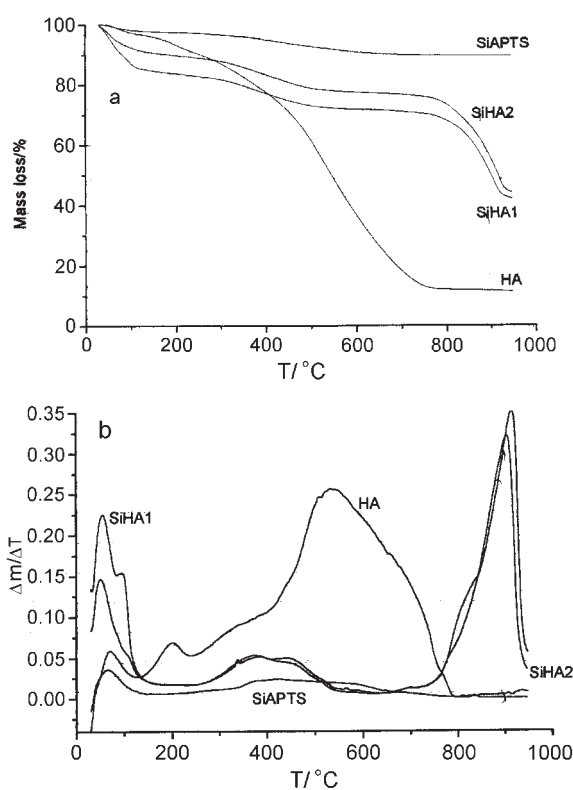
Fig. 2 a – TG and b – DTG curves of humic acid (HA) and the anchored surfaces SiAPTS, SiHA1 and SiHA2

organic mass loss, leaving only a residue near to 10%. For SiAPTS the anchored organic mass corresponded to about 5%. However, SiHAX (X=1, 2) curves presented very close mass losses steps, as shown in the derivative curves of Fig. 2b. A small loss started at 260°C assigned to decomposition of end chain groups of the bonded HA compound, such as: carboxylic, aldehydes, amides, amines, alcohol and phenol groups, followed by the next step at 740°C, assigned to decomposition of the organic matter of HA [22]. These decomposition data listed in Table 2. corroborate the HA immobilization onto silica gel and show a dramatic increase in thermal stability, yielding highly stable anchored surfaces, without damage by solvent attack, as reported before [2, 7, 8].

Table 2 Percentages of mass losses (Δm) and the respective temperature range (T) for humic acid (HA) and anchored surfaces SiAPTS, SiHA1 and SiHA2

Sample	$\Delta m/\%$	$T/\%$
SiAPTS	7.0	320–770
SiHA1	10.0	260–540
	31.9	740–950
SiHA2	10.8	260–540
	28.0	740–950
HA	85.5	240–790

Both immobilization methods presented similar thermal stability and degree of HA anchored onto the silica surface. Thus, this new modified inorganic support can be potentially used in adsorption processes, with the advantage of high thermal stability. The synthetic procedure did not require organic solvent, that is a fundamental principle established by green chemistry [23]. Potential applications are to remove toxic cations and organic contaminants from water solution, due to the fact that SiHA is insoluble in water and presents a large range of active basic centers.

Conclusions

HA immobilization onto silica gel previously modified with a 3-aminopropyl-trimetoxysilane occurred with success with both methods applied. Both procedures yielded similar surfaces in relation to the degree of anchoring and thermal stability. A great advantage of such immobilization onto silica gel is that the attached HA maintains its properties, presenting higher thermal stability when compared with the free compound, without being attacked by solvents.

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