Nanosized Silica Modified with Carboxylic Acid as Support for Controlled Release of Herbicides

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ABSTRACT: Hexagonal mesoporous silica modified with carboxylic acid (SiAc) has been obtained by reaction between chloroacetic acid and 3-aminopropyltrimethoxysilane, which was immobilized on porous material by a sol−gel process in the presence of an n-dodecylamine template. SiAc was characterized by TG, FT-IR, ^{29}Si NMR, ^{13}C NMR, SEM, surface charge density, surface area and porous diameter, which proved that the carboxylic group was chemically bonded to an inorganic structure, and the material presented a nanometric structure with spheres <50 nm and porous diameter of 10 nm. Herbicides 2,4-D and picloram were anchored on SiAc porous gel to produce the materials named SiD and SiPi, respectively. The controlled release of picloram from the SiAc was less than that of 2,4-D. After 26 days of releasing, 4.43×10^{-5} mol L^{-1} of picloram was delivered by SiPi, and 5.0×10^{-5} L^{-1} was released from the SiD in 30 days.

KEYWORDS: silica, mesoporous, controlled release

■ INTRODUCTION

Population growth has as a consequence the necessity of increasing food production.[1−3] On the other hand, food shortages lead not only to malnutrition and starvation but also to social, political and economical instability due to many countries have agriculture as the main or one of their major economical sources.[1−3] The presence of weeds decreases crop production. Thus, a viable alternative way to overcome the foreseeable crisis in agriculture is to increase the crop yield per acre.[1−3] With the use of excessive doses of herbicides, the greatest herbicide losses take place shortly after their application.[4−6] On the other hand, the excessive use of herbicides causes many environmental risks to several ecosystems.[7,8] In this way, in order to minimize these losses, controlled release formulations of herbicides have been developed. These formulations present many advantages, due to controlled release systems that can generate a slower release of herbicides in crops and, consequently, decrease herbicide contamination of the environment. Many materials have been applied to be a support matrix of controlled release formulations such as polysaccharides, cyclodextrins, natural polymers, lamellar silicates and modified mesoporous silicas.[8−14] These herbicides anchored on surfaces were denominated greener herbicides by David Bradley.[15]

In this direction, the present investigation reports the synthesis and characterization of mesoporous silica modified with carboxylic acid and its application as a support of controlled release of the typical herbicides 2,4-D and picloram.

■ EXPERIMENTAL SECTION

Chemicals. All chemicals were of reagent grade, and deionized water was used in the experiments. Silica gel (Merck), sodium hydroxide (Sinth) and hydrochloric acid (Vetec) were employed in all preparations.

Synthesis of Pendant Group. 4.36 mL of aminopropyltrimethoxysilane and 2.53 g of chloroacetic acid were solubilized in 40 mL of methanol with 6.97 mL of triethylamine as deprotonating agent. The reaction was carried out at 50 °C during 24 h. The final product was filtered in a drybox system and washed with xylol and ethanol, and then dried under vacuum at 50 °C.

Modified HMS Support. The catalyst was prepared by stirring 13.9 g of n-dodecylamine in water/ethanol (150 mL; 3:1 v/v) for 30 min until an opalescent solution was obtained as a consequence of micelle formation. Previously synthesized TEOS (27.88 mL) and pendant material were added to this micellar suspension in sequence. This suspension was stirred for 48 h at room temperature, resulting in a precipitate, which was filtered. The n-dodecylamine inside the pores of the synthesized compound was extracted with ethanol in a Soxhlet apparatus for 72 h, producing the final material, SiAc.

Anchoring of Herbicides in HMS. 0.5 g of SiAc and 0.1 g of herbicide (2,4-D or picloram) were suspended in 30 mL of methanol. Herbicides anchoring was carried out in a hydrothermal system at 75 °C at 24 h. The controlled release material was dried at room temperature and named SiD and SiPi for HMS containing 2,4-D and picloram, respectively.

Characterization. Thermogravimetric curves were obtained from approximately 10 mg of samples in a thermogravimetric analyzer model TA-2960 in a dynamic atmosphere using dry nitrogen flux, with a heating rate of 10 °C min^{-1} at room temperature up to 1000 °C.

Nitrogen adsorption−desorption data were measured in a Quantachrome Nova 2200 analyzer, at 77 K. Surface area was calculated by the Brunauer−Emmett−Teller (BET) method.

Powder X-ray diffraction patterns were measured in a Rigaku model D/Max-2A/C diffractometer using CuKα radiation.

Infrared spectra of all samples were performed using KBr pellets in the 4000−400 cm^{-1} region with a resolution of 4 cm^{-1}, by accumulating 32 scans using an MB-100 Bomem FTIR spectrophotometer.

^{29}Si nuclear magnetic resonance spectra of the solid samples were obtained in a Varian Mercury Plus 300 spectrometer at room temperature. For each run, approximately one gram of modified silica was compacted into a 7 mm silicon nitrite rotor. The measurements were obtained at a frequency of 59.61 MHz, for carbon and silicon,

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Table 1. Thermogravimetric Data for SiAc

$\Delta m/\%$	$\Delta T/°C$	thermal phenomenon
2.33	25.0−101.5	H_2O volatilization
1.56	101.5−241.3	decomposition of acid pendant group
14.45	241.5−690.2	silanol group condensation

respectively, with a magic-angle spinning speed of 3 kHz. In order to increase the signal-to-noise ratio of the solid-state spectra, the CP/MAS technique was used. ^{29}Si CP/MAS spectra were obtained with pulse repetitions of 1 s and contact time of 1 ms.

Scanning electron microscopy (SEM) was performed in a Zeiss EVO50 microscope. Samples were coated with carbon using a metalizer Baltec SCD 50. Apparatus was operated at 20 KeV.

Surface charge density of SiAc as a function of pH was calculated by applying eq 1 using K_1 and K_2 values obtained from simultaneous potentiometric and conductometric titrations.[16,17] These titrations were carried out with a 50.0 mL aqueous suspension of SiAc 40.0 g/L. First, SiAc was fully deprotonated by addition of 0.4 mL of NaOH 1.0 mol/L. This sample was titrated with HNO_3 0.1 mol/L. The potentiometric readings were done using a pHmeter pHtek PHS-3B, and the conductivity was measured in an Adamo conductometer.

Controlled Release Studies. Controlled release assays were carried out in triplicate by using static system at pH = 5 containing 20.0 mg of SiD, SiPi or SiPi suspended in 500 mL of water. The aliquots were obtained in time range during 24 h. Herbicide concentrations were followed in a UV−vis spectrophotometer Cary 50.

■ RESULTS AND DISCUSSION

Synthesis of Hexagonal Mesoporous Silica as Support for Herbicide Controlled Release System. The development of the organic pendant group immobilization on inorganic surface is closely related to the advancement of the synthetic chemistry involved. The key features associated with this subject can cause expansion or insertion of the main organic chain precursor silylating agent, by exploring the presence of reactive centers on it.[18,19]

The employed precursor aminopropyltrimethoxysilane was available to react with chloroacetic acid according to eq 1 to produce the new pendant group (PAc). This new acid silane was used with the aim to modify the hexagonal mesoporous silica.
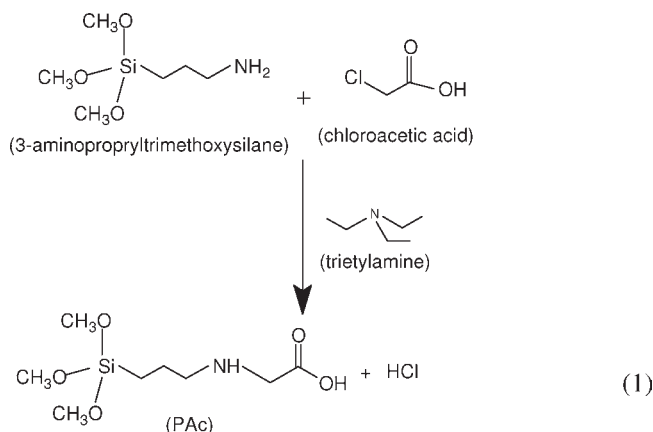
In order to obtain modified hexagonal mesoporous silica, the presence of n-dodecylamine, a molecule that contains a polar head and a long nonpolar hydrocarbon tail, allows the generation of a convenient experimental micellar condition in water. This
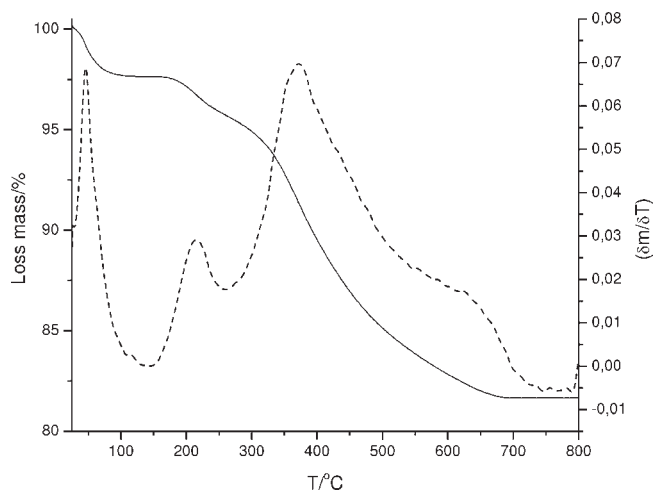
Figure 1. Thermogravimetric curve of SiAc.

micellar arrangement favors the tetraethoxysilane (TEOS) compound in the process of hydrolyzing. Thus, the silylating agent PAc and TEOS polymerization resulted in an organized arrangement around a micellar structure, forming an inorganic polymeric backbone. With such organization, the amine groups of the n-dodecylamine molecules are directed to the available silanol groups and the corresponding pendant groups are maintained around the micelles. These structured silanol−surfactant interactions can be explained by the electrostatic and hydrogen bond formation processes. Thus, both silylating agents can yield inorganic−organic mesoporous hybrids after polymerization, starting from TEOS molecules around the micelle previously formed by n-dodecylamine in water.[18−20] After this synthesis, template was removed by ethanol reflux, forming the modified mesoporous hexagonal silica named SiAc, according to eq 2.
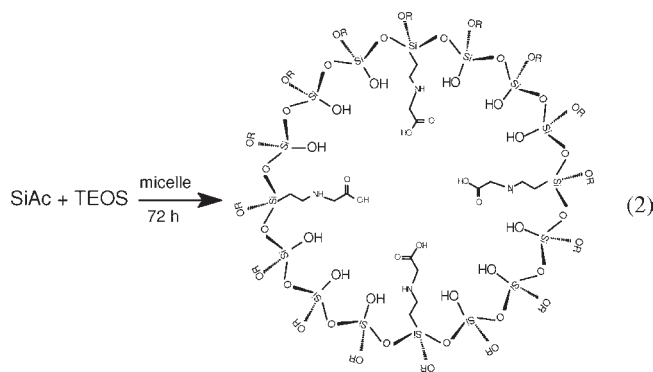
Characterization. The organic pendant group content of PAc was determined by TG analysis using residual data (Figure 1). TG curve also shows that the SiAc material presents three distinct loss mass steps. The first one, which occurred between 25 and 101.5 °C, was assigned to water volatilization. The next stage, between 101.5 and 241.3 °C, was related to the loss of organic pendant acid group. And the last step, between 241.3 and 690.2 °C, was assigned to silanol condensation in siloxane groups. The amount of acid organic pendant group per gram of silica was obtained by TG and elemental analysis, which was 1.34 mmol per gram of silica. All TG data are listed in Table 1.
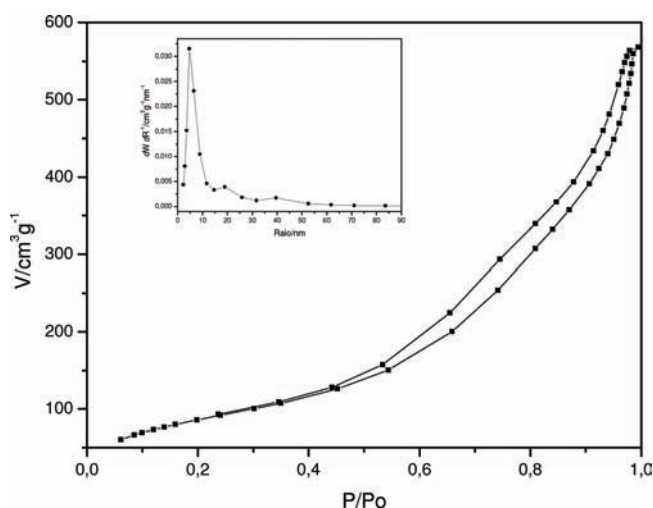
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Figure 2. N_2 adsorption−desorption isotherms for SiAc. Relative pressure is P/P_o where P is the equilibrium pressure of the adsorbate and P_o is the saturation pressure of the adsorbate at the temperature of the adsorbent. Inset: The corresponding BJH pore size distribution curves (dW/dR) for the normalized adsorbate volume with respect to the pore diameter.
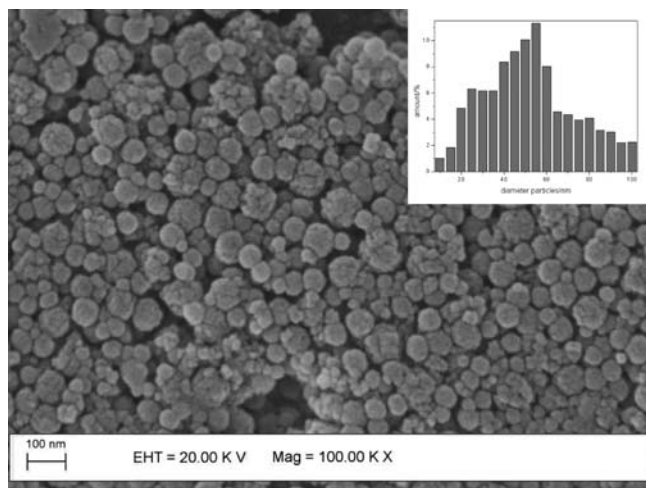

Figure 3. SEM image of SiAc. Inset: The corresponding distribution of particle size.

SiAc nitrogen adsorption−desorption isotherms are shown in Figure 2, which reveals that the adsorption−desorption process is not reversible, once it is a result of hysteresis loops caused by capillary condensation.[21−23]

The isotherm is reversible up to a relative pressure of about 0.45. Irreversibility is observed between 0.44 and 0.98, whereas the condensation in primary mesopores takes place slightly above the latter pressure limit, but the adsorption and desorption branches are not parallel to each other, resulting in the hysteresis loop.[19,20] By applying the BJH method, the pore size distribution was calculated from the N_2 adsorption−desorption isotherms, resulting in a pore diameter of 10.17 ± 0.91 nm. The surface area was calculated by the BET method, and a value of 824.7 ± 40 m^2/g was found.

SiAc SEM image was obtained in order to know the morphology of catalyst particles. Figure 3 shows that the SiAc particles
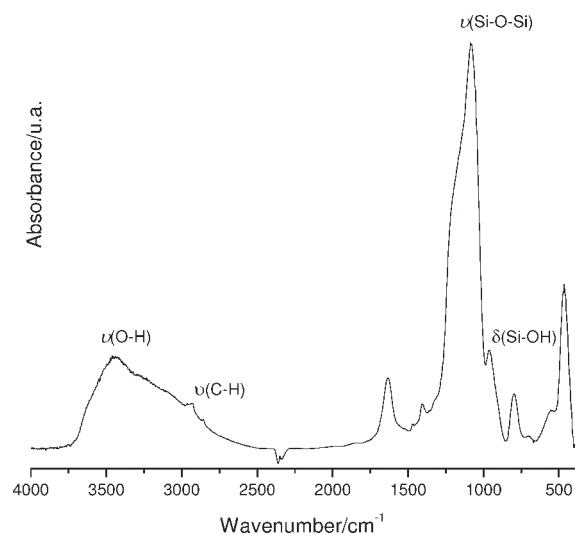

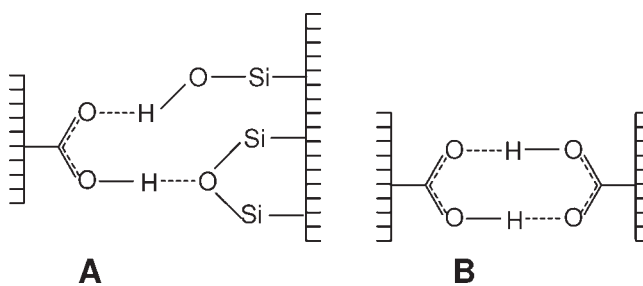**Figure 4.** Infrared spectrum of SiAc.

Figure 5. Proposed scheme of the carboxylic acid bonded with silanol and siloxane groups of silica (A) and carboxylic acid dymers (B).

presented a heterogeneous dispersion with particle diameter less than 50 nm. Indeed, these characterization data show that the SiAc presented a nanometric scale.

The SiAc material was characterized by the FTIR spectrum (Figure 4), as follows: (i) a large broad band between 3400 and 3200 cm^{-1} assigned to the presence of the O−H stretching frequency of silanol groups and also to the remaining adsorbed water; (ii) a band at 2950 cm^{-1} assigned to carbon sp^3 of the organic pendant group attached to the surface; (iii) an intense band at 1100 cm^{-1} related to the $n(Si−O−Si)$ siloxane stretching; (iv) a band at 900 cm^{-1} assigned to the Si−OH stretching frequency of silanol groups.[24−26]

This spectrum also showed two peaks at 1634 and 1404 cm^{-1}, which were assigned to asymmetric and symmetric stretching of carboxylate, respectively. These peaks suggest that the carboxylic acid must be bonded to silanol, siloxane and other carboxylic acid by hydrogen bonds as illustrated in Figure 5.

The ^{29}Si NMR spectrum presented five well-formed peaks at −47 ppm and four characteristic peaks at −62, −86, −97, and −106 ppm (Figure 6). The first two peaks are assigned to the silicon atom of the silylating agent bonded to one OH group, thus forming the $RSi(OSi)(OH)_2$ structure, usually named the T^2 signal. In the same way, the peak at 62 ppm is assigned to $RSi(OSi)_3$, named the T^4 signal. Both signals confirm that the organic groups were covalently bonded onto the silica surface. The other two peaks are related to the silica surface and assigned to $Si(OSi)_2(OH)_2$ (Q^2 signal), at −87 ppm; $Si(OSi)_3OH$ at −97
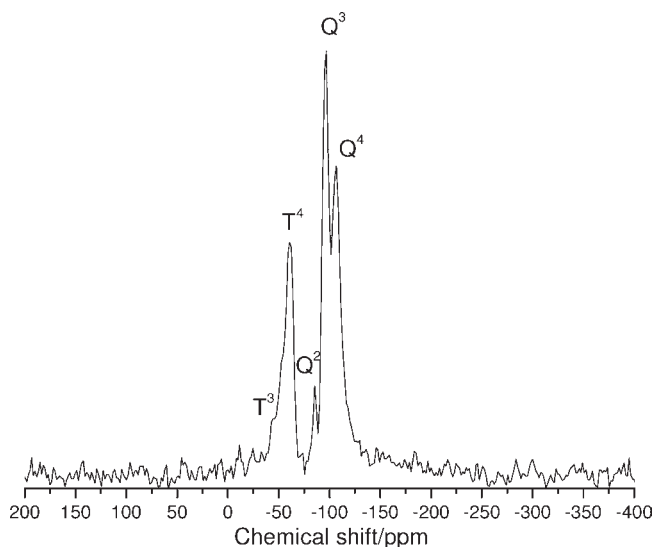
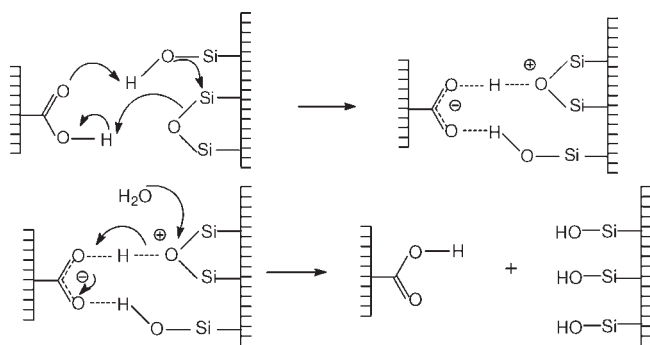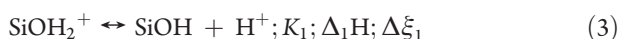**Figure 6.** ^{29}Si NMR solid state spectrum of SiAc material.

Figure 7. Proposed acid attack to siloxane forming silanol groups.

ppm (Q^3 signal) and Si(OSi)$_4$ at -106 ppm (Q^4 signal). The Q^2 peak needs to be highlighted, due to its not being a common peak, and its presence corroborates with carboxylic acid attack to silanol and siloxane groups forming Si(OSi)$_2$(OH)$_2$ species and carboxylate groups as presented in Figure 7.[27] The Si environment is schematically presented in Figure 8.

^{13}C NMR spectrum (Figure 9) presents five peaks attributed to the organic molecule attached on the silica surface, according to the carbons labeled from 1 to 5. Indeed, the peaks observed in the FTIR spectrum, ^{29}Si and ^{13}C NMR spectra confirm the covalent immobilization of chloroacetic acid onto the silica gel surface. ^{29}Si RMN shows T^4 and T^3, related to bonds Si$-$O$-$C, which confirms the covalent immobilization of the organic pendant group on silica feature.

The suspension of oxides in aqueous solution must form distinct surface charge sites as a result of two steps of protonation of the surface groups by hydration of the oxide surface leading to three distinct surface sites according to eqs 3 and 4.[28]

$$SiOH_2{}^+ \leftrightarrow SiOH + H^+; K_1; \Delta_1 H; \Delta \xi_1 \tag{3}$$

$$SiOH \leftrightarrow SiO^- + H^+; K_2; \Delta_2 H; \Delta \xi_2 \tag{4}$$

The surface of this material is dependent on pH values, which can present an acidified surface (SiOH$_2{}^+$) in strong acidic medium, amphoteric surface sites (SiOH) in intermediate media, and
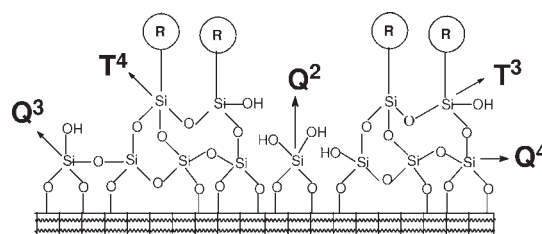

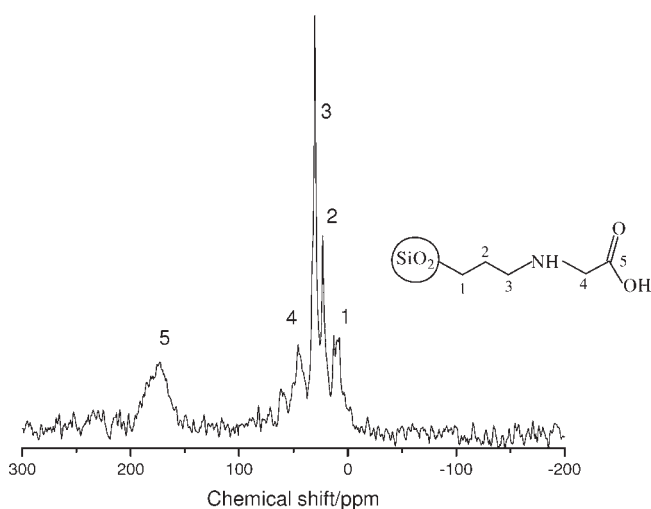**Figure 8.** Scheme of the chemical silicon environment distribution.

Figure 9. ^{13}C NMR solid state spectrum of SiAc material.

basic surface sites (SiO$^-$) in strong basic medium. The equilibrium constants K_1 and K_2 can be experimentally determined by the application of the Henderson$-$Hasselbach equation in the simultaneous potentiometric and conductometric titration data, as shown in Figure 10A. From equilibrium constants, the surface charge density of SiAC as a function of pH values can be calculated by using eq 5.[16,17]

$$\sigma_0 = \frac{F}{A} \left(\frac{10^{-2pH} - K_1 K_2}{10^{-2pH} + K_1 \times 10^{-pH} + K_1 K_2} \right) N_T \tag{5}$$

where F is the Faraday constant, A is the total surface area, N_T is the total number of moles of surface sites, and K_1 and K_2 correspond to the acid equilibrium constants.

Figure 10B was plotted by applying eq 5. This figure shows three distinct regions. The first region is assigned to the protonated surface corresponding to the SiOH$_2{}^+$ acid sites up to pH 4.10. SiAc presented amphoteric surface sites region (SiOH) between pH 4.1 and 6.3. Above pH 6.3, the deprotonated surface sites (SiO$^-$) can be observed. The point of zero charge (pzc) was observed at pH 5.15. These studies show that between pH 4.10 and 6.30 must be the best region to attach pesticides into SiAc.

Controlled Release Assays. Figure 11 shows that the SiD presented the maximum release of 5.0×10^{-5} mol L^{-1} of 2,4-D, which corresponds to 18.97% of total anchored 2,4-D amount on SiD nanocomposite after 7 days, maintaining the same delivery up to 30 days. The remnant herbicide amount (2.14×10^{-4} mol L^{-1}) can be delivered. Moreover, the SiAc support presented the ability to hold up the release of 2,4-D.

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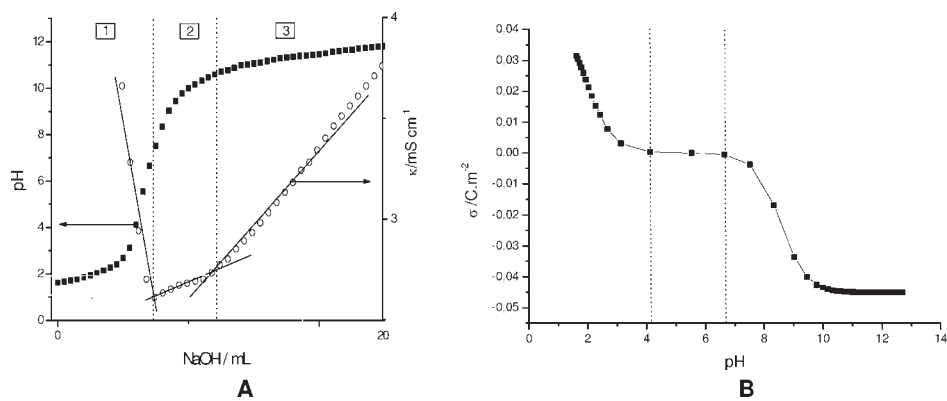dx.doi.org/10.1021/jf202509g |*J. Agric. Food Chem.* 2011, 59, 8847–8852

Figure 10. Simultaneous conductometric and potentiometric titration curves of the suspensions of SiAc (A) and density surface charge as a function of pH (B).
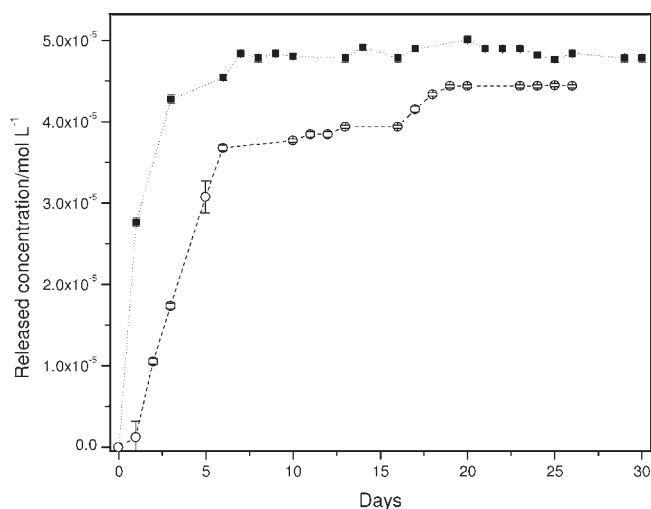

Figure 11. Controlled release of the 2,4-D (■) and picloram (○) from SiAc support.

The SiPi material presented the maximum delivery of 4.43×10^{-5} mol L^{-1} of picloram, which corresponds to 17.31% of total immobilized picloram amount in SiPi after 20 days, maintaining the same delivery up to 30 days. The remnant amount of picloram (2.12×10^{-4} mol L^{-1}) can be released.

Literature reports the controlled release of 2,4-D and picloram anchored on Mg/Al lamellar hydroxides. In these studies, the maximum of the release occurred in 8 days, delivering 9.05×10^{-5} mol L^{-1} of 2,4-D (18.1% of supported amount anchored on composite), and maximum of the delivery of the picloram was 7.45×10^{-5} mol L^{-1} after 8 days (0.15% of supported amount anchored on support). These data corroborate with the obtained controlled release data in this work.

The anchoring of pesticides on silica surfaces has been explored in order to increase the effectiveness, decreasing leaching losses and microbial degradation.

The mobility of pesticides in soil can occur because of leaching, surface runoff and volatilization. Conventional pesticides can be easily transported in soil; the mobility of pesticides anchored on a silica surface must decrease, due to the ability of clay to be aggregated with silica, reducing the pesticide mobility.

Moreover, previous studies showed that the anchoring of picloram and 2,4-D on silica gel decreased their toxicity.[29−32]

Thus, the anchoring of the new silylating agent using a sol−gel process driven by *n*-dodecylamine was viable, and occurred with success, producing a controlled nanostructured mesoporous material. Its characterization (FTIR, ^{29}Si NMR, ^{13}C NMR) proved that the carboxylic groups were covalently bonded on an inorganic framework in carboxylate form. The herbicides 2,4-D and picloram were anchored onto porous SiAc, and these pesticides were control released from inorganic matrix. The formulation of controlled release systems of herbicides is taking into account environmentally-friendly chemistry, resulting in the production of green herbicides.

Indeed, the obtained results corroborate with the philosophy of Green Chemistry once it is required to use a lower amount of applied pesticide in crops, due to controlled delivery systems result in a decrease of toxic products in the environment (third principle of Green Chemistry).

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