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Research Article

Synthesis and Characterization of TiO_2 Modified with Polystyrene and Poly(3-chloro-2-hydroxypropyl Methacrylate) as Adsorbents for the Solid Phase Extraction of Organophosphorus Pesticides

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Novel hybrid TiO_2 particles were developed and assessed as an adsorbent for solid phase extraction (SPE) of organophosphorus pesticides (fensulfothion, parathion methyl, coumaphos, and diazinon) from spiked water. The sol-gel method was used to synthesize TiO_2 particles, which were coated with free-radical polystyrene (PS) and poly(3-chloro-2-hydroxypropyl methacrylate) (PClHPMA) polymers. Particle structures were determined via Fourier transform infrared spectroscopy to confirm that the polymers were successfully anchored to the TiO_2 particles. Thermogravimetric analysis was conducted to determine organic and inorganic matter in TiO_2-PS and TiO_2-PClHPMA particles showing results of 20 : 80 wt/wt% and 23 : 77 wt/wt%, respectively. SEM-EDS and X-ray diffraction test were conducted to determine the morphology and semielemental composition of the particles showing amorphous characteristics. By observing the contact angle, particles coated with PClHPMA were determined to be more hydrophilic than TiO_2-PS particles. The pore size distributions obtained from the N_2 adsorption-desorption isotherms were 0.150 and 0.168 cm^3g^{-1}. The specific surface area (BET) was 239.9 m^2g^{-1} for TiO_2-PS and 225.7 m^2g^{-1} for TiO_2-PClHPMA. The synthesized particles showed relatively high yields of adsorption in SPE. The pesticide recoveries obtained by high performance liquid chromatography ranged from 6 to 26% for TiO_2-PClHPMA and 44 to 92% for TiO_2-PS.

1. Introduction

Solid phase extraction (SPE) is a simple and versatile extraction technique. It is an alternative to liquid-liquid extractions, and it permits the preconcentration of the sample with minimal risk of loss or contamination, retaining the desired component in a solid phase while the unwanted components of the matrix are eluted with a suitable solvent [1]. SPE provides options for the development of new analytical protocols and has been utilized in food products (eggs, honey, milk, fish, and oranges) [2, 3] as well as different water samples (tap water, surface water, mineral water, wastewater, groundwater, and run-off water) [4]. Various analytes, such as dichlorodiphenyltrichloroethane (DDT) [5], heavy metals [6], polycyclic aromatic hydrocarbons (PAHs) [7], and pesticides [4, 8–14], have been extracted from different types of samples. Different techniques have been utilized to determine organophosphorus pesticides (OPPs), such as gas chromatography with flame photometric detector (GC–FPD) [9, 12], gas chromatography with flame ionization detector (GC–FID) [10], and high performance liquid chromatography with UV detector (HPLC-UV) [11, 13].

Typically, the sorbents used for SPE have been materials based on nonderivatized silica (silica gel, sand, and florisil) as well as silica bonded to organic functional groups such as the octyl ($-C_8$), octadecyl ($-C_{18}$), cyanopropyl [$-(CH_2)_3CN$], aminopropyl [$-(CH_2)_3NH_2$], and phenyl propyl groups; silica bonded to $-C_8$ or $-C_{18}$ is the most used sorbent. Other reports have demonstrated the application of novel materials in SPE, such as carbon fibers [15], aluminum [16], polymeric materials [9, 12, 17], graphitized carbon black [18], and titanium dioxide (TiO_2) [19].

Titanium dioxide (TiO_2) is one of the most important inorganic materials due to its potential applications in photocatalysis, its ability for photoelectric conversion in solar cells, and its optical and adsorption properties. The surface of TiO_2 particles is particularly attractive for its application in SPE because it can act as a Lewis acid (Ti^+) or a Bronsted-Lowry acid (Ti-OH) and interact with a variety of both organic and inorganic compounds [20]. Therefore, the following compounds based on TiO_2 have been used as adsorbents in SPE: TiO_2 particles have been used to preconcentrate organic compounds and metals [21–24], TiO_2 nanotubes were applied for the extraction of DDT and its metabolites [25], SiO_2-TiO_2 particles were tested for their adsorption of carcinogenic metals [26] and nitrogen compounds [27], TiO_2 was modified with dithizone for mercury adsorption [28], TiO_2 nanotubes coated with cetyltrimethylammonium bromide were applied in the solid phase microextraction (μSPE) of a preconcentration of PAHs [29], and TiO_2 particles coated with polyacrylonitrile were utilized as ion exchangers for metal extraction [30]. However, the synthesis of a TiO_2 hybrid material modified with polystyrene (or poly(3-chloro-2-hydroxypropyl methacrylate)) and its application as a sorbent in SPE for the extraction of organophosphorus pesticides have not been reported.

The particles of metal oxides such as TiO_2 can be used as sorbents without surface modification due to the presence of different types of titanol groups (Ti-OH). However, to increase their applicability and to modify their retention properties, the surface of such materials can be altered with immobilized organic phases to promote the interactions between the solid surface and organic molecules, such as van der Waals interactions, electrostatic attraction, donor-acceptor interactions, and chemisorption [31]. Various organic compounds can be incorporated within the gel network via chemical bonds by the copolymerization of organic and inorganic precursors, for sol-gel processing.

Typically, the reagents tetraethylorthosilicate and alkoxysilanes (or tetramethyl orthosilicate) are used as precursors in sol-gel synthesis. The polycondensation of alkoxysilanes is carried out at room temperature and can be described by three reactions: (i) hydrolysis, (ii) silanol condensation, and (iii) silanol-alcohol condensation. Sol-gel synthesis allows one to obtain materials with different physicochemical properties, such as surface area, particle shape and size, porosity, and degree of functionalization, which are associated with the possibility of obtaining binary oxides and inorganic phases [27]. With respect to SPE, the morphological and mechanical properties and, importantly, the chemical behavior of the inorganic sorbent play a significant role in facilitating the immobilization of organic groups on the particle [32].

The aim of this work was the synthesis and characterization of two novel hybrid sorbents based on TiO_2. The TiO_2 particles were synthesized through a sol-gel process followed by a free radical polymerization with polystyrene (PS) or poly(3-chloro-2-hydroxypropyl methacrylate) (PClHPMA). Both hybrid materials were analyzed by surface and structural characterization techniques. Additionally, the hybrid particles were used to pack cartridges to evaluate their potential application as sorbents for the solid phase extraction of four organophosphorus pesticides (OPPs) from spiked water. The optimization of the SPE extraction is beyond the scope of this paper.

2. Materials and Methods

2.1. Materials. The reagents for hybrid polymer preparation: vinyltrimethoxysilane (VTMOS), titanium isopropoxide (IPT), benzoyl peroxide (BPO), 2,2-azobisisobutyronitrile (AIBN), styrene (S), and 3-chloro-2-hydroxypropyl methacrylate (ClHPMA) and OPPs fensulfothion (FST), parathion methyl (MP), diazinon (DZN), and coumaphos (CMF), were obtained from Sigma-Aldrich (Saint Louis, MO, USA). Hydrochloric acid (HCl), tetrahydrofuran (THF), toluene, acetone, ethanol, methanol, ammonium hydroxide (NH_4OH), and acetonitrile (ACN) were purchased from J. T. Baker (Phillipsburg, NJ, USA). All reagents were used as received without further purification.

2.2. Synthesis. The sol-gel method reported by several authors was adapted for the synthesis of hybrid materials [33, 34].

The first step (Figure 1(a)) was the synthesis of TiO_2 particles functionalized with vinyl groups (TiO_2-VTMOS). Thirty-one milliliters of HCl was mixed with 40 mL of ethanol in a baker. Following this, 115 mL of titanium isopropoxide (IPT) and 14.5 mL of vinyltrimethoxysilane (VTMOS) were slowly added to the baker and stirred for 15 min. Then, a solution of 30 mL of H_2O, 104 mL of NH_4OH, and 47 mL of ethanol was added dropwise to the baker. The solution was allowed to stand for 24 hours to obtain a white precipitate, which was filtered and then washed three times with acetone and ethanol. Finally, the product was dried in an oven at 70°C for 24 hours.

The second step (Figure 1(b)) was the coating of the TiO_2-VTMOS particles with a monomer through free radical polymerization. In the case of polystyrene (PS), 10 g of TiO_2-VTMOS, 11.2 mL of S, 0.10 g of benzoyl peroxide (BPO), and 30 mL of toluene were placed in a 3-necked flask. Then, nitrogen gas was supplied to the flask for 10 min to create an inert atmosphere and the mixture was refluxed with constant stirring for 24 hours. The obtained particles (TiO_2-PS) were subjected to Soxhlet extraction for 24 hours using toluene as a solvent, and the particles were finally dried in an oven at 100°C for 24 hours.

The above procedure was also used to obtain particles of TiO_2 coated with 3-chloro-2-hydroxypropyl methacrylate (TiO_2-PClHPMA). In this case, 8.6 mL of monomer was used instead of 11.2 mL.

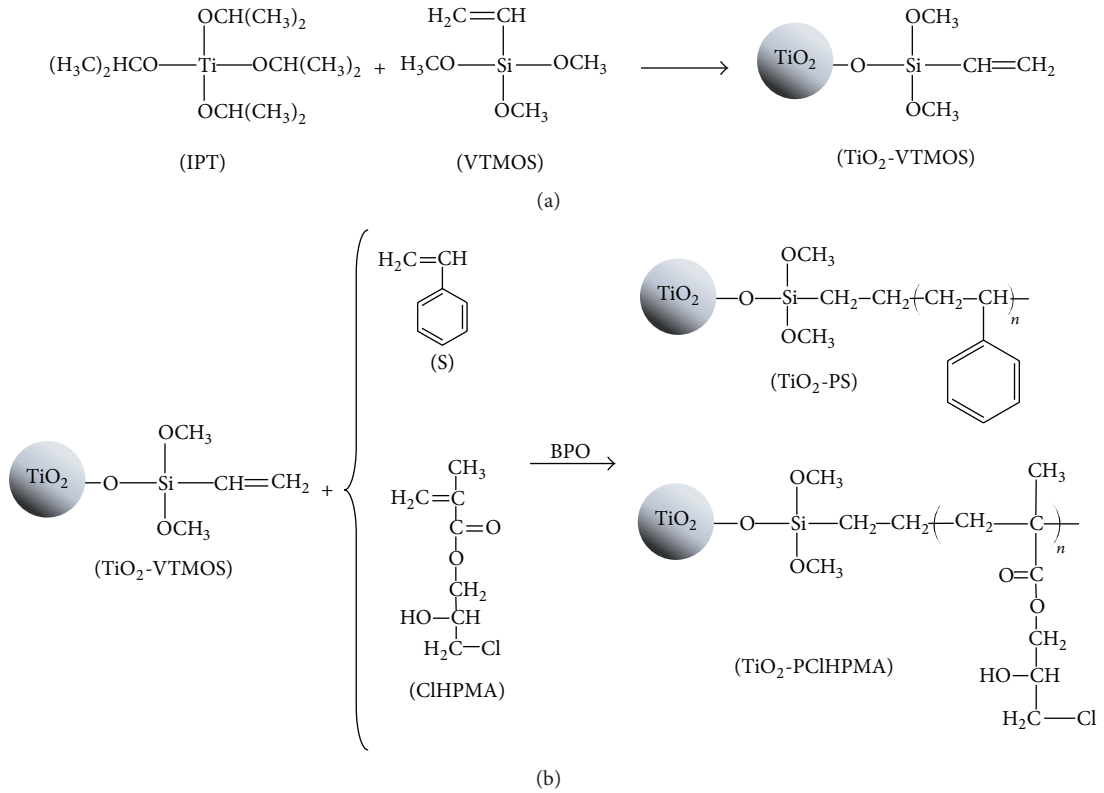


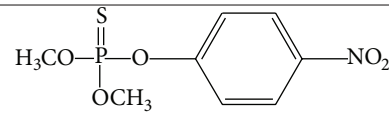
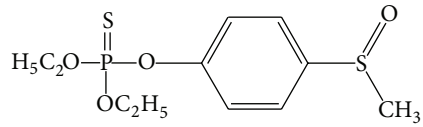
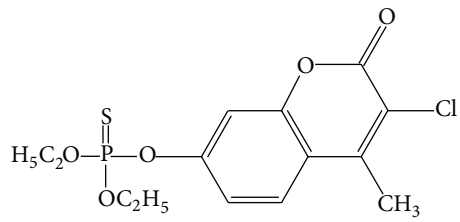
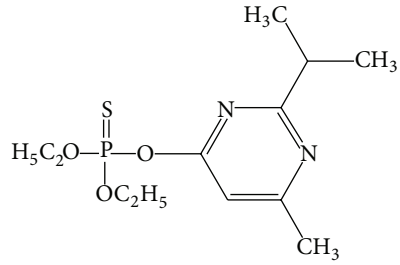
Figure 1: Schematic representation of hybrid particles preparation: (a) preparation and functionalization of TiO_2 particles and (b) free radical polymerization of PS or PClHPMA on the surface of the TiO_2 particles.

2.3. Characterization. Field emission scanning electron microscopy (FE-SEM) was performed using a JEOL JSM-6510LV coupled to an Oxford energy-dispersive X-ray spectrometer (EDS). Samples were fixed on a support with a copper film and sputter-coated with gold in a Denton Desk IV sputtering chamber. The FTIR spectra were obtained using a Fourier transform infrared spectrophotometer (Thermo-Nicolet 380 FTIR) on KBr pellets in the wavenumber range of 4000–400 cm^{-1}. Thermogravimetric analysis (TGA) was performed to study the thermal decomposition behavior of the particles, using a TA Instruments SDT Q 600, with a heating rate of 10°C/min from 30°C to 800°C under a N_2 atmosphere. To determine the crystallinity of the adsorbent, a diffractometer Bruker D8 Advance with Bragg-Brentano geometry, CuKa radiation, and Lynxeye detector were used. The contact angle was studied with a Nikon FM10 reflex camera to determine the hydrophobicity of the particles, and the images were processed with the free software ImageJ. The nitrogen adsorption-desorption isotherms of the particles were determined by a Quantachrome Instruments NOVA 2200e surface area and pore size analyzer. Prior to the experiments, the samples were degassed at 200°C in a vacuum for 16 hours. The volume of adsorbed N_2 was normalized to a standard temperature and pressure. The specific surface area of the hybrid materials was determined using the Brunauer-Emmett-Teller (BET) multipoint method, and the specific total pore volume was obtained using the Density Functional Theory (DFT) method.

2.4. Spiked Water (Sample). To prepare the sample, 50 mL of distilled water was spiked by adding 300 μL of each of the standard solutions (1000 mg L^{-1}) of fensulfothion (FST), parathion methyl (MP), coumaphos (CMF), and diazinon (DZN) to obtain a final concentration of 6 mg·L^{-1}. The chemical structures and the logarithm of the octanol-water partition coefficient ($\log K_{ow}$) of the evaluated organophosphorus pesticides (OPPs) are presented in Table 1.

2.5. SPE Extraction. To perform the SPE, preliminary tests were conducted with different conditioning of the particles and under elution by different solvents (hexane and methanol). The conditions that resulted in the best adsorption and elution of analytes are described below. SPE cartridges were prepared by placing four circles of Whatman Grade 42 filter paper with an internal diameter of 10 mm (10 mm i.d.) at the bottom of a polypropylene column (65 mm × 10 mm i.d.) and then packing in 100 mg of synthesized particles that had recently been washed with ethanol and acetone and then dried. Then, 3 mL of the sample (water spiked with 6 mg L^{-1} of OPPs) was passed through the cartridge and recollected in a test tube to quantify the pesticides that remained in the spiked water. The tubes were centrifuged at 13,000 rpm (10 min) and filtered (syringe filter 0.20 μm). The pesticides adsorbed onto the hybrid particles were eluted with 1 mL of methanol, which was passed dropwise through the cartridge. Methanol was collected and

Table 1: Chemical structures and log K_{ow} of the organophosphorus pesticides evaluated.

Compound	Structure	log K_{ow}
Fensulfothion (FST)		2.23
Parathion methyl (MP)		3.0
Coumaphos (CMF)		4.13
Diazinon (DZN)		3.3

centrifuged at 13,000 rpm (10 min). After that, methanol was filtered (syringe filter 0.20 μm), and the eluted analytes were quantified by HPLC. This process was performed in triplicate with each material, as illustrated in Figure 2.

2.6. Liquid Chromatography. The final OPP concentrations in spiked water (or methanol) were obtained by introducing 20 μL into the injection port of a liquid chromatograph (Model 1100, Agilent Technologies, Santa Clara, CA, USA) with a diode array detector (G1315B), degasser (G1379A), and quaternary pump (G1311A). The elution was isocratic, and the mobile phase was an acetonitrile/H_2O (70 : 30, v/v) mixture with a flow rate of 1 mL/min. A reversed phase column (Kinetex C18, 150 × 4.6 mm, 5 μm of particle size) was used to separate the pesticides. The wavelengths used to quantify the OPPs were 230 nm (FST), 254 (DZN), 270 (MP), and 315 nm (CMF).

2.7. Adsorption and Recovery Evaluation. Two sets of standard solutions were prepared. To obtain the adsorption percentage of the OPPs, one set (0.05, 0.10, 0.30, 0.50, 2.0, 3.5, 5.0, and 6.0 mg L^{-1}) was prepared by dilution of the pesticide stock solution (6 mg L^{-1}) with an appropriate volume of distilled water. Another set (0.5, 2.0. 4.0. 6.0. 8.0, and 10.0 mg L^{-1}) was prepared by dilution of the pesticide stock solution (20 mg L^{-1}) with a water/methanol (1 : 1, v/v) mixture to recover the pesticides.

3. Results and Discussion

3.1. Characterization of the TiO_2-PS and TiO_2-PClHPMA Particles. SEM-EDS was applied to determine the morphology and semielemental composition of the particles. Figure 3 shows the SEM micrographs and compositional analyses of (a) the TiO_2-PS particles and (b) the TiO_2-PClHPMA particles. As seen in Figures 3(a) and 3(b), the particles are composed of several microparticles with irregular morphologies, and they show a nonuniform particle size distribution and agglomerated nature. Using the semielemental analysis of the studied particles, the following empirical formulas were obtained: $Ti_{4.6}SiO_{20.6}C_{18.8}$ for TiO_2-PS and $Ti_{4.8}SiO_{22.3}C_{37.7}Cl_{4.9}$ for TiO_2-PClHPMA. These show that both Ti and Si contents remain practically constant but the O and C contents vary in the particles. In this case, the variation of carbon and oxygen depends on the amount of monomer needed to achieve binding to the surface of the particles to form oligomers or polymers, as will be seen in the TGA analysis.

The functionalization of the solid was determined by FTIR. The infrared spectra of (a) TiO_2-VTMOS, (b) PS, (c) TiO_2-PS, (d) PClHPMA, and (e) TiO_2-PClHPMA particles are shown in Figure 4. In the TiO_2-VTMOS spectrum, the bands at 526 and 768 cm^{-1}, associated with amorphous TiO_2, are due to the vibration of the Ti–O bond in the tetrahedral TiO_4 [35], and the band at 850 cm^{-1} is attributed to the Si–O–Ti vibration [36, 37]. The spike at 1401 cm^{-1} is attributed to the vibration of the Si–C bond [38]. Another spike at 1610 cm^{-1} is

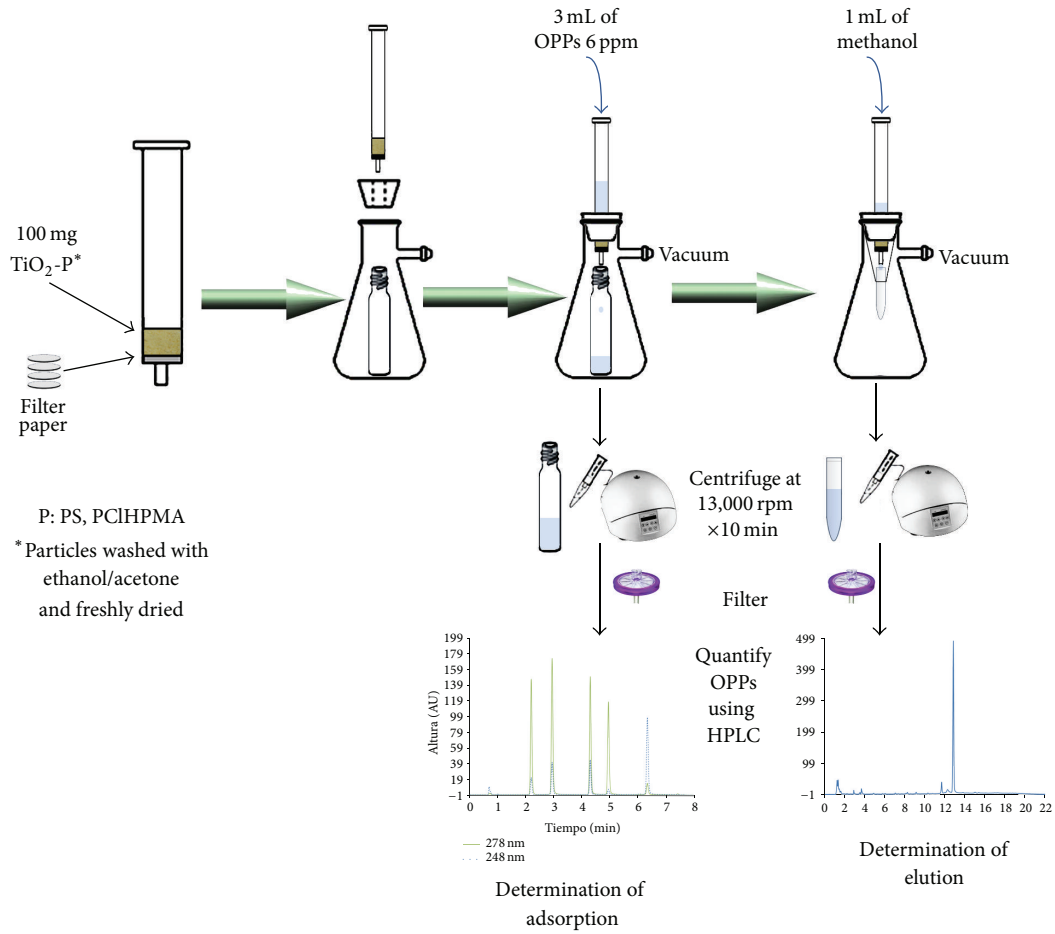


Figure 2: Process of SPE extraction and quantification of OPPs.

ascribed to the vibration of the vinyl groups of the coupling agent [39], suggesting that VTMOS was successfully bonded onto the surface of titanium dioxide. Lastly, a characteristic band appeared approximately between 3000 and 3500 cm^{-1} because of adsorbed water on the adsorbent, which is due to the strong Lewis acid properties of (Ti^{4+}) in TiO_2 [35].

In the PS spectrum (Figure 4(b)), the bands identified at 3026 and 2849 cm^{-1} correspond to the aromatic and aliphatic C–H stretch, respectively. The signals at 1601 and 1493 cm^{-1} are related to C=C aromatic stretching. At 758 cm^{-1}, there is a C–H deformation vibration due to the hydrogen of benzene. The signal at 700 cm^{-1} corresponds to the deformation vibration of the aromatic ring. Signals corresponding to the C–H stretching vibrations of the aromatic ring were observed between 3000 and 3100 cm^{-1} [40].

In the spectrum for TiO_2-PS (Figure 4(c)), signals were observed at 700 and 758 cm^{-1} in addition to the TiO_2-VTMOS signals already described above; these are attributed to the styrene molecule and suggest that the PS remained anchored to the TiO_2 particles.

Figure 4(d) shows the spectrum for PClHPMA. The characteristic bands of an ester are present at 1730 and 1448 cm^{-1}; the first relates to –C=O stretching (free carbonyl group) and the second to $–O–CH_3$ stretching [41]. The two bands at 1273 and 860 cm^{-1} are ascribed to C–O stretching and C–O–C stretching, respectively [39]. In addition, a strong broad band was observed at approximately 2995 cm^{-1} due to the stretching vibration modes of CH_3 and CH_2, indicating a high hydrogen content in the CH_x of PClHPMA. The signals at approximately 1450 and 1380 cm^{-1} correspond to the in-phase and out-of-phase bending vibrations of CH_3 [41]. The band at 740 cm^{-1} is related to the C–Cl stretching vibration and a broad band was observed at approximately 3400 cm^{-1} due to the hydroxyl group.

Several of the signals described above were observed in the spectrum for TiO_2-PClHPMA (Figure 4(e)). For example, the characteristic signals of an ester (1730 and 1448 cm^{-1}) were observed, as well as the signals present in the spectrum for TiO_2-VTMOS, suggesting that the PClHPMA was anchored to the TiO_2 particles.

Thermogravimetric analysis was employed to determine the ratio between the organic and inorganic parts of the particles. The thermogram (TG) and the derivative of the thermogram (DTG) are shown in Figure 5. For both thermograms, the weight loss occurs in three stages. The TG and DTG curves exhibit an initial weight loss of 16.44 wt% for TiO_2-PS and 16.10 wt% for TiO_2-PClHPMA at 200°C, which is due to the presence of humidity and the excess of solvents

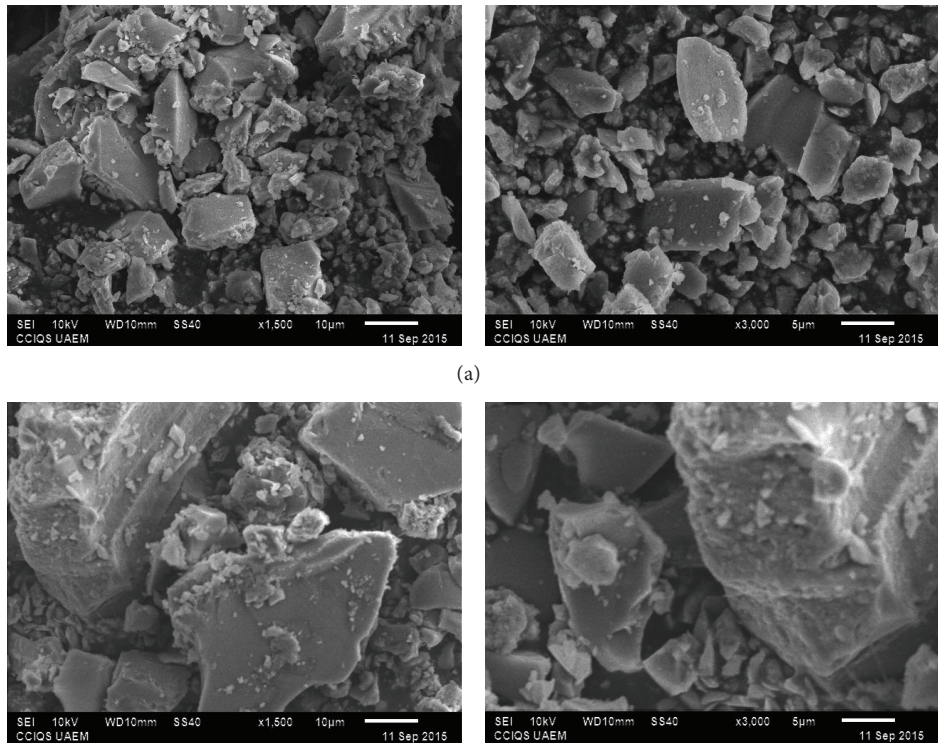


Figure 3: SEM images of (a) TiO_2-PS and (b) TiO_2-PClHPMA.

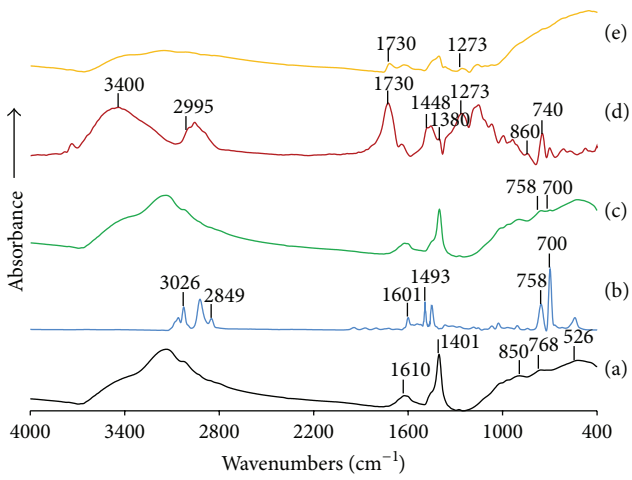


Figure 4: FTIR spectra of (a) TiO_2-VTMOS; (b) PS; (c) TiO_2-PS; (d) PClHPMA; and (e) TiO_2-PClHPMA.

in the particles. The second stage presents a weight loss of 9.65 wt% between 200 and 321°C for TiO_2-PS and a loss of 12.17 wt% between 200 and 359°C for TiO_2-PClHPMA; these weight losses may be due to the decomposition of short-strand oligomers present on the surface of the hybrid particles. The third stage presents a loss of 6.81 wt% between 321 and 470°C for TiO_2-S and a loss of 7.18 wt% between 359 and 500°C for TiO_2-PClHPMA; this last phase is ascribed to the decomposition of the polymers [42, 43]. As seen in Figure 5, the decomposition temperature of PClHPMA (383.83°C) is higher than that of PS (352.85°C), which indicates that the polymer PClHPMA has a higher thermal stability than PS.

These results suggest that the particles are composed of an organic/inorganic ratio of 20 : 80 wt/wt% for TiO_2-PS and 23 : 77 wt/wt% for TiO_2-PClHPMA, considering that only the organic part of the polymer was lost at 500°C and the TiO_2 particles do not exhibit any significant weight loss up to 700°C.

Figure 6 shows the X-ray diffraction (XRD) patterns of (a) TiO_2-PS and (b) TiO_2-PClHPMA, collected at $2\theta = 10\sim80°$. The XRD patterns show diffuse halos of glassy materials, and there are not distinguishable sharp diffraction peaks of any crystalline phase. This observation indicates that both types of hybrid particles are amorphous.

To study the hydrophobicity or hydrophilicity of the particles, the contact angles of TiO_2-PS and TiO_2-PClHPMA were determined; these angles were 61.68° ± 1.66° and 45.20° ± 0.49°, respectively. It was observed that the particles coated with PClHPMA were more hydrophilic due to the hydroxyl group in its structure and the particles coated with PS were more hydrophobic due to the nonpolar structure of PS.

The pore size distribution was obtained from the N_2 adsorption-desorption isotherms by using the DFT method. The nitrogen adsorption-desorption isotherm is shown in Figure 7. According to the IUPAC classification, the isotherms of TiO_2-PS and TiO_2-PClHPMA are type IV isotherms. A type IV isotherm is indicative of a material

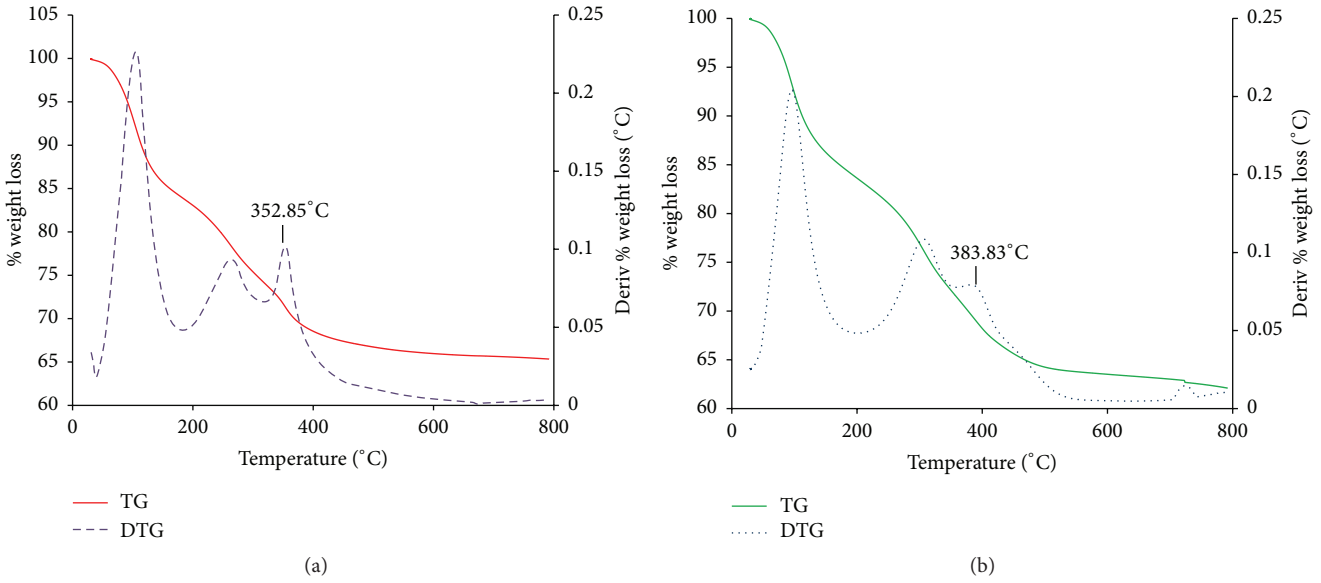


Figure 5: TG and DTG curves of (a) TiO_2-PS and (b) TiO_2-PClHPMA.

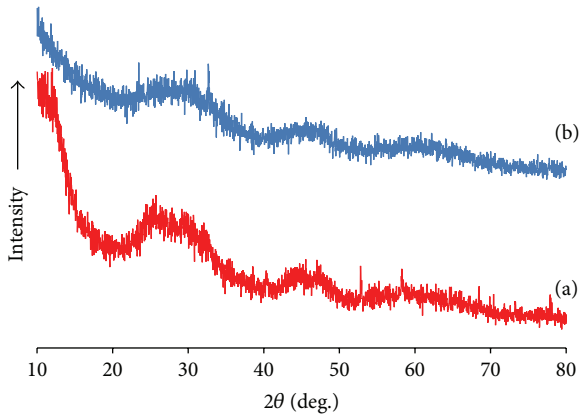


Figure 6: The XRD patterns of (a) TiO_2-PS and (b) TiO_2-PClHPMA.

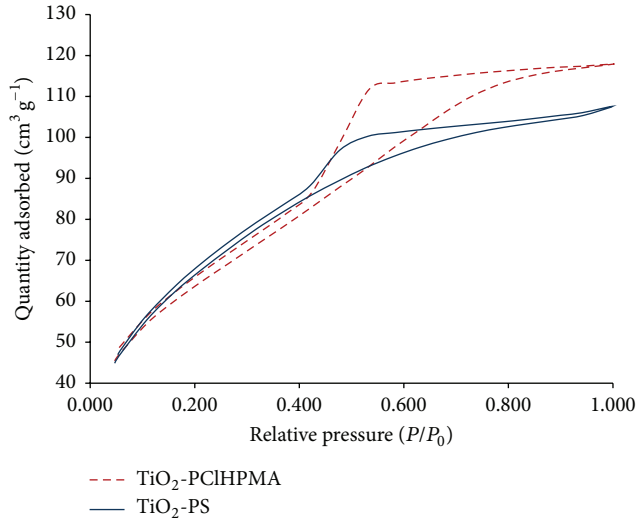


Figure 7: N_2 adsorption-desorption isotherm of the TiO_2-PS and TiO_2-PClHPMA.

with micropores (≤2 nm) and mesopores (2–50 nm) [44]. The specific total pore volume (DFT method) was 0.150 and 0.168 $cm^3\ g^{-1}$, and the specific surface area (BET) was 239.9 and 225.7 $m^2\ g^{-1}$ for TiO_2-PS and TiO_2-PClHPMA, respectively. According to the literature, sorbents with surface area greater than 100 $m^2\ g^{-1}$ are suitable for SPE [45].

In summation, the characterization results suggest that the particles are coated by polymers and that they can be used as adsorbents in solid phase extraction.

3.2. SPE Extraction. The SPE cartridges were packed with 100 mg of particles to facilitate the flow of liquid and four times the volume occupied by the particles in the SPE cartridge was set as the volume of water sample allowed to pass through it.

To create a sorbent environment compatible with the aqueous sample, the sorption capacity of the particles was evaluated after conditioning with MeOH or ACN. An additional experiment was run without conditioning for comparison. In general, recoveries and adsorption without conditioning were higher than those after conditioning because the strong interactions between MeOH (or ACN) and the inorganic and organic part of the sorbent do not allow the adsorption of the analytes onto the particles (Figure 8 as typical example).

To elute the analyte from the sorbent, MeOH and hexane were evaluated because of the difference in their polarities. MeOH showed higher recoveries of analytes because the strength of hexane was not enough to elute the compounds (Figure 8).

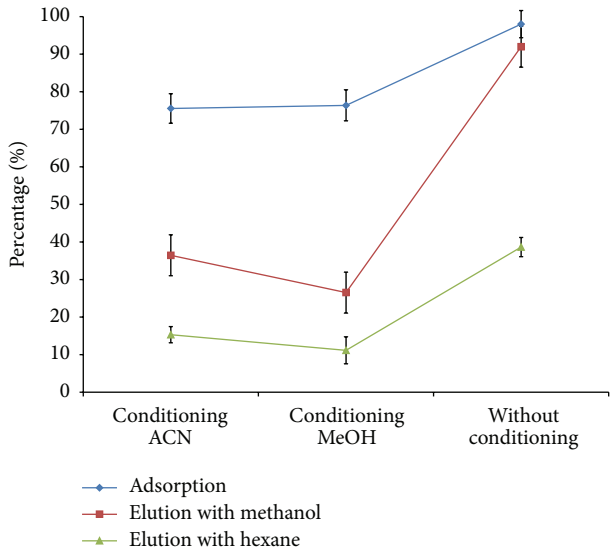


Figure 8: Effect of conditioning and solvent elution of methyl parathion from the SPE cartridge packed with TiO_2-PS particles.

Table 2: Average adsorption (%) ($n = 3$) of the OPPs onto the hybrid particles synthesized.

Pesticide	Adsorption (%) ± RSD (%)	
	TiO_2-PClHPMA	TiO_2-PS
Fensulfothion	21.16 ± 8.28	94.27 ± 2.01
Parathion methyl	33.31 ± 6.75	98.11 ± 0.97
Coumaphos	50.03 ± 4.84	99.77 ± 0.16
Diazinon	49.73 ± 3.86	99.29 ± 0.38

Table 3: Recoveries (%) for OPPs ($n = 3$) with hybrid particles.

Pesticide	Recovery (%) ± RSD (%)	
	TiO_2-PClHPMA	TiO_2-PS
Fensulfothion	5.60 ± 1.04	91.77 ± 7.55
Parathion methyl	14.74 ± 2.88	91.87 ± 2.69
Coumaphos	26.37 ± 5.05	43.73 ± 3.85
Diazinon	22.19 ± 2.92	72.68 ± 1.20

Quantification of the OPPs was performed by HPLC; the retention times were 1.91, 2.52, 3.87, and 4.10 min for FST, MP, CMF, and DZN, respectively. The slope and intercept values and their standard deviations were determined using least squares linear regression analysis; the calibration curves with methanol (or water) had R^2 values > 0.99.

The adsorption percentages for the studied OPPs are presented in Table 2. The two particles exhibit the same behavior for the adsorption of the pesticides (CMF > DZN > MP > FST), which agrees with the values of $\log K_{ow}$ (4.1, 3.3, 3.0, and 2.2, resp.). The TiO_2-PS particles showed much higher adsorption of pesticides (between 94 and 99%) compared to the TiO_2-PClHPMA particles, which had the smallest percent of adsorption (between 21 and 50%). This behavior is related with the affinity of relatively nonpolar analytes towards the relatively hydrophobic phenyl groups in TiO_2-PS. This is because the retention mechanism of the analytes is principally based on the π-π interactions between the aromatic groups of the adsorbent (TiO_2-PS) and the π electrons of the analytes [9].

Ballesteros and Parrado [10] performed SPE extractions of parathion methyl, diazinon, and six other organophosphate pesticides (1.0 ng L^{-1}) in 10 mL of different water samples; they used 100 mg of commercial adsorbent (RP-C_{18}) and obtained percentages of adsorption greater than 97%, which were similar to those obtained with our TiO_2-PS particles.

The adsorption times of the synthesized particles in our work were less than 1 minute. With these times, an adsorption percentage between 94.3 and 99.8% was achieved. A mass/time relation of 18 μg min^{-1} was obtained for TiO_2-PS. This value is greater than that obtained by Li and coworkers [11] (0.25 μg min^{-1}) who used 100 mg of magnetic titanium oxide (Fe_3O_4@TiO_2) modified with cetyl trimethyl ammonium bromide (CTBA) as an adsorbent for magnetic solid phase extraction (MSPE) of three organophosphorus pesticides (chlorpyrifos, dimethoate, and trichlorfon 10 ng mL^{-1}) from 500 mL samples of water. They reported that the pesticide adsorption was complete after 20 minutes of contact.

As shown in Table 3, the pesticide recoveries achieved with the TiO_2-PS particles (between 43 and 91%) were much higher than the pesticide recoveries achieved with the TiO_2-PClHPMA particles (between 5 and 26%). The low recoveries of TiO_2-PClHPMA are because these particles exhibit lower adsorption and showed high polarity in comparison with TiO_2-PS.

The CMF showed the lowest recovery with the TiO_2-PS particles (43%) because they have a high affinity for CMF due to their π-π interactions with the aromatic rings (Figure 1(b)). These interactions cause retention of the pesticide on the particle surface and do not allow its elution with methanol. With the TiO_2-PClHPMA particles, the CMF had the highest recovery among the four pesticides. This is because the interaction of CMF with the hydrophilic adsorbent is weaker than its interaction with other pesticides. On the other hand, the relatively hydrophilic pesticides (fensulfothion and parathion methyl) showed a low recovery because of their affinity towards the TiO_2-PClHPMA particles. This result agrees with the recoveries obtained with the TiO_2-PS adsorbent, in which fensulfothion and parathion methyl have the highest recoveries because of the relatively high hydrophobicity of the material.

In Table 4, the recovery percentages obtained in this work with the TiO_2-PS particles are compared with those reported by different authors when they extracted OPPs from different water samples by SPE. As shown in the table, the MP and the DZN presented similar recoveries as those obtained with other adsorbents; the recovery percentage of the CMF in the TiO_2-PS particles was only similar to the graphitized carbon black. None of the authors evaluated the recovery of FST.

Table 4: Comparison of the reported methods on the separation and determination of OPPs in water samples in solid phase extraction.

Adsorbent material	Adsorbent mass (mg)	Sample volume (mL)	Eluent	Pesticides concentration (% recovery)	Reference
TiO_2-S	100	3	Methanol	FST = 6 mg L^{-1} (92%) MP = 6 mg L^{-1} (92%) CMF = 6 mg L^{-1} (44%) DZN = 6 mg L^{-1} (73%)	This method
Styrene-divinylbenzene (XAD-2) XAD-2-Teflon XAD-2-Acrylate (XAD-7)	2000	2500	Acetone	MP = 144 ng L^{-1} (60–75%) CMF = 636 ng L^{-1} (100%) DZN = 144 ng L^{-1} (>91%)	[12]
C_{18}	100	10	Ethyl acetate	MP = 1.0 ng L^{-1} (>93%) DZN = 1.0 ng L^{-1} (>94%)	[10]
Carbon nanotubes	50	200	Acetonitrile	DZN = 10 g L^{-1} (94–97%)	[13]
Polystyrene-divinylbenzene	200	1000	Dichloromethane	MP = 90 ng L^{-1} (54–90%) CMF = 398 ng L^{-1} (74–95%) DZN = 90 ng L^{-1} (62–90%)	[9]
Graphitized carbon black	500	1000	Dichloromethane	MP = 90 ng L^{-1} (60–98%) CMF = 398 ng L^{-1} (45–69%) DZN = 90 ng L^{-1} (68–98%)	[9]

4. Conclusions

The sol-gel method was used to synthesize TiO_2 particles, which were coated with polystyrene (PS) and poly(3-chloro-2-hydroxypropyl methacrylate) (PClHPMA) via free radical polymerization. The particles presented suitable characteristics for use as an adsorbent in SPE. They exhibited a rough surface with a specific total pore volume of 0.150 and 0.168 $cm^3\ g^{-1}$ and a specific surface area of 239.9 and 225.7 $m^2\ g^{-1}$ for TiO_2-PS and TiO_2-PClHPMA, respectively. The synthesized particles showed good performance for the SPE extraction of organophosphorus pesticides (fensulfothion, parathion methyl, coumaphos, and diazinon each with a concentration of 6 mg L^{-1}) present in spiked water samples. The TiO_2-PClHPMA particles presented lower adsorption percentages and PPO recoveries compared to the TiO_2-PS particles. Acceptable PPO recoveries were achieved with TiO_2-PS particles FST (91.77 ± 7.55), MP (91.87 ± 2.69), and DZN (72.68 ± 1.20), while a low recovery was obtained for CMF (43.73 ± 3.85). These recoveries are similar to those reported by other authors with different adsorbents (polystyrene-divinylbenzene, graphitized carbon black, and C_{18}). Therefore, the TiO_2-PS and TiO_2-PClHPMA particles have the potential to be applied to extract organophosphorous pesticides from other liquid samples by SPE. We are running additional experiments in our laboratory to evaluate the extraction of other analytes (polyaromatic hydrocarbons and antibiotics, among others) by SPE with both particles.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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