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Synthesis and Characterization of Functionalized Silica-Nanoparticles and their Applications for the Removal of Pesticides from Aqueous Solution

Khalid A. Al-Saad, Ahmed A. Ramadan, Md F Rakib, Abdullah A. Abul Baker

Qatar University, QA

Email: kalsaad@qu.edu.qa

1. Abstract

Silica nanoparticles functionalized with three different active functional groups (C-8, cyano-propyl, and methacrylate (MA)) were synthesized, characterized and applied for the removal of ten carbamate pesticides from aqueous solution. Two methods were used for the synthesis of functionalized silica (grafting and sol-gel method). SEM, FTIR, and HCN were used for the characterization of the particles, while LC-MS/MS was used for the quantitative analysis of carbamate pesticides in the non-treated and treated aqueous solutions. The characterization results indicated the formation of uniformed, spherical and mono-dispersed particles when the cyano and MA particles were prepared by the Sol-gel. Also, results indicated that all of the synthesized particles were enhances for the removal of carbamate pesticides, and MA prepared by the Sol-gel methods had the highest % removal for most of the carbamate pesticides tested.

2. Introduction

Active functional groups such as C8 and cyano-propyl have good recovery and can selectively react with carbamate pesticides [1]. Also, previous works [2] have shown that methyl methacrylate have some selectivity and high efficiency to bind with carbamate pesticides. Yet, investigations are still needed to improve the selectivity and efficiency of solid phase extraction via surface modifications. Successful identification of the host functional groups that will selectively react with the guest (contaminant or analyte) will be highly important for the purpose extraction and quantification of the specific analyte. Also, the success to immobilize host molecules that react specifically with pollutants in aqueous solution will allow the remediation of water. The objective of this work is to prepare modified

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silica-nanoparticles by immobilizing reactive functional groups as hosts on the surface of these particles and to characterize and apply these particles for the removal of pesticides from contaminated water.

3. Experimental

3.1. Material

All the reagents and chemicals used in this study were obtained commercially from Sigma-Aldrich company. The chemicals used were methanol LC-MS grade, octyl-triethoxysilane, 3-cyanopropyltrimethylsilane, trimethylsilyl-methacrylate, silicon dioxide nanoparticles, xylene, hexane, ammonium hydroxide, 3-methacryloxypropyl trimethoxysilane, tetraethoxysilane, ethanol, and carbamate standard (46856-U). Using these chemicals, five particles were synthesized: 1. silica grafted with cyano-group; 2. silica grafted with methacrylate particles; 3. silica grafted with C8; 4. cyano-particles synthesized by Sol-gel method; and 5. propyl methacrylate particles synthesized by sol-gel method.

3.2. Preparation of particles

The particles were prepared following previously developed methods by other scientists [3,4].

3.2.1. Preparation of cyano grafted particles Prior to preparation, the silicon oxide (SiO_2) was activated by heating overnight. 5.0 g of the activated SiO_2 was mixed with 0.347 mL of 3-cyanopropyltrimethyl-silane, and 100 mL of xylene. The mixture was placed in sonicator for one hour, and then was heated overnight. After that, the mixture was centrifuged for ten minutes with 5000 rpm. The particles were finally washed with methanol for three times.

3.2.2. Preparation of methacrylate grafted particles 5.0 g of the activated SiO_2 was mixed with 0.237 mL of trimethyl-silyl methacrylate, and 100 mL of xylene. The mixture was placed in sonicator for one hour, and then was heated overnight. After that, the mixture was centrifuged for ten minutes with 5000 rpm. The particles were finally washed with methanol for three times.

3.2.3. Preparation of C-8 grafted particles 5.0 g of the activated SiO_2 was mixed with 0.414 mL of octyltriethoxysilane, and 100 mL of xylene. The mixture was placed in sonicator for one hour, and then was heated overnight. After that, the mixture was centrifuged for ten minutes at 5000 rpm. The particles were finally washed with methanol for three times.

3.2.4. Preparation of cyano and methacrylate particles by Sol-gel-method 40 mL of ethanol was transferred into a flask, and both 1.0 mL of ultrapure water, and 25 mL of NH_4OH were added to the ethanol. The mixture solution was then stirred for 14 minutes at 4000 rpm. After that, 1.0 ml tetraethyl-orthosilicate diluted in 4.0 ml of ethanol was added to the solution. Finally, the mixture solution above was divided equally into two different bottles. In one of the bottles, 0.578 mL of 3-cyanopropyltrimethyl-silane was added in order to prepare the SolGel-Cyano particles and in the other bottle 0.444 ml of trimethyl-silylmethyl methacrylate was added in order to prepare SolGel-MA particles.

3.3. Instrumentation

The synthesized nanoparticles were characterized by an FEI Quanta 200, USA scanning electron microscope at an accelerating voltage of 3 kV was used for these analyses. Fourier-transform infrared spectroscopic measurements of the samples were obtained in the range from 400 to 4000 cm^{-1} using a Perkin Elmer Spectrum 400 FTIR with an ATR detector at a resolution of 4 cm^{-1} . The elemental analysis were carried out by using CHN analyzer. Then, the synthesized particles examined for their ability to remove pesticides from water. The pesticides were separated and analyzed by LC-MS/MS (Agilent,1290).

3.4. Pesticide treatments and analysis

Six 15-mL tubes were prepared. 1.0 mL of carbamate in acetone was added into each tube and kept to dry overnight in order to avoid the presence of acetone, which is expected to compete with the particles in extracting the pesticides. Then 2.0 mL of deionized water was added into each tube. One of the tube was kept as control (not treated), while

the carbamate solutions in the other five tubes were treated with the five synthesized nanoparticles. 0.25 g of the five different nanoparticles were added to the five tubes. The tubes were vortexed for 1 minute, and left to settle for 10 minutes, and then were centrifuged for two minutes at 4500 rpm. The solutions in each tube were transferred into new tubes and analyzed by LC-MS/MS.

4. Results and Discussions

4.1. Characterization results

The nanoparticles were synthesized and characterized by SEM, FTIR, TGA, and EDX. The results of SEM indicated the formation of relatively small (nano-size) particles (Fig 1 a-e). Both the cyano and MA particles that were prepared by sol-gel method appeared to be uniformly and homogeneously spherical (Fig 1 d,e), unlike the other particles, which were prepared by the grafting method. According to the CHN analysis results (Table 1), the amount of C, H, and N elements were relatively high in the particles prepared by Sol-gel methods compared to those prepared by the grafting methods, with highest percentage found in the MMA particles prepared by the sol-gel methods. According to the FTIR results (Fig 2 and Fig 3), different patterns were observed for the different synthesized particles and there was indication of OH present in the MMA particles that was prepared by sol-gel method, The different structures of the synthesized particles were clearly in the fingerprint region of the FTIR spectra.

4.2. Pesticide treatments and analysis results

The carbamate pesticides were fully separated as observed in the chromatogram in Fig 4. Retention times of the pesticides belonging to the chromatogram are shown in Table 2. Also, the table shows the areas of the peaks belonging to the pesticides in the chromatogram before and after treatments with the five synthesized particles. It is clearly observed that the concentration of pesticides significantly went down after treatment with the particles. For most pesticides, the MA particles prepared by the Sol-gel methods showed the highest removal of pesticides.

5. Conclusion

Both cyano and MA particles prepared by the Sol-gel appeared to more uniformed, spherical and monodispersed under the scanning electron microscope and gave higher relative amounts of C, H, and N elements. MA particles prepared by the Sol-gel was the most efficient in removing the pesticides, although all synthetically prepared nanoparticles showed promising result in removing the pesticides. More investigation is required to determine the proper dose of these particles and to examine the effect of pH, temperatures, contact times, as well as the concentration of pesticides. Also, more investigations are needed to determine the efficiency of these particles to remediate solutions contaminated with other pesticides such organophosphorous and chlorinated pesticides.

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