

Magnetic Permanently Confined Micelle Arrays for Treating Hydrophobic Organic Compound Contamination

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Abstract: Magnetic permanently confined micelle arrays (Mag-PCMA) have been successfully synthesized as sorbents for hydrophobic organic compound (HOC) removal from contaminated media. The synthesis of Mag-PCMA involves coating a silica/surfactant mesostructured hybrid layer on the negatively charged Fe₃O₄ microparticles to create a core/shell structure. The surfactant, 3-(trimethoxysilyl)propyl-octadecyldimethyl-ammonium chloride (TPODAC), has a reactive endgroup -Si(OCH₃)₃ on its hydrophilic groups, which allows the surfactant micelles to permanently anchor on the silica framework through covalent bonding. This unique structural property avoids surfactant loss during application and allows for sorbent regeneration. The isotherms and kinetics of four representative HOCs (atrazine, diuron, naphthalene, and biphenyl) onto Mag-PCMA were determined, and the regeneration and reusability of Mag-PCMA for diuron removal was also investigated. As a proof of principle for application of Mag-PCMA for soil-washing, the use of Mag-PCMA for removal of diuron from a contaminated soil was also demonstrated. All of the results showed that Mag-PCMA are reusable sorbents for fast, convenient, and highly efficient removal of HOCs from contaminated media.

1. Introduction

Today, hydrophobic organic compounds (HOCs) such as hydrophobic pesticides, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs) are ubiquitous environmental contaminants, many of which have been identified as carcinogens.^{1–6} Due to their hydrophobicity, HOCs can be significantly bioaccumulated,¹ so the presence of the HOCs in drinking water, ambient water, industrial wastewater, soils, and sediments poses a major risk to humans and local ecosystems, especially to organisms who are at the top of food chain.^{1,4,6} Given their persistence and in many cases continued and increasing emissions, HOCs represent a very important environmental issue. In the past, various techniques have been developed to remove HOCs from contaminated media, such as chemical oxidation,^{7,8} membrane filtration,^{9,10} and adsorption

for contaminated water,¹¹ and bioremediation¹² and *ex situ* soil washing^{13,14} for contaminated soils and sediments. Among these treatment technologies, chemical oxidation and membrane filtration are usually not economically attractive due to their high operation costs while bioremediation is generally too time-consuming. Adsorption and *ex-situ* soil washing, on the other hand, have been favorable for HOC decontamination.

One of the most commonly used sorbents for HOCs is activated carbon, which has been widely used as a versatile sorbent for contaminated water.^{11,15} However, the small particle size, high regeneration temperatures, and decreasing sorption capacity influences their performance.^{15,16} For example, the small particle size useful for a high surface-to-volume ratio can generate high back pressure; regeneration of activated carbon is generally performed at high temperatures (up to 800 °C), which means relatively high energy costs. Also, activated carbon can adsorb some water molecules, which influences its adsorption capacity for HOCs in water.¹⁶ In the past few years, magnetic sorbents have emerged as a new generation of materials for environmental decontamination, especially for

- (1) Blais, J. M.; Schindler, D. W.; Muir, D. C. G.; Kimpe, L. E.; Donald, D. B.; Rosenberg, B. *Nature* **1998**, *395*, 585–588.
- (2) Hageman, K. J.; Simonich, S. L.; Campbell, D. H.; Wilson, G. R.; Landers, D. H. *Environ. Sci. Technol.* **2006**, *40*, 3174–3180.
- (3) Fernandez, A. E. *Environ. Sci. Technol.* **2000**, *34*, 1906–1913.
- (4) Harding, G. C.; Addison, R. F. Accumulation and effects of PCBs in marine invertebrates and vertebrates. In *PCBs and the Environment II*; Wood, J. S., Ed.; CRC Press: Boca Raton, FL, 1986.
- (5) Jonker, M. T. O.; van der Heijden, S. A.; Kreitinger, J. P.; Hawthorne, S. B. *Environ. Sci. Technol.* **2007**, *41*, 7472–7478.
- (6) Douben, P. E. T., Ed. *PAHs: An Ecotoxicological Perspective*; John Wiley and Sons: New York, 2003.
- (7) Ferrarese, E.; Andreotola, G.; Oprea, I. A. *J. Hazard. Mater.* **2008**, *152*, 128–139.
- (8) Lindsey, M. E.; Xu, G. X.; Lu, J.; Tarr, M. A. *Sci. Total Environ.* **2003**, *307*, 215–229.
- (9) Li, Q. L.; Snoeyink, V. L.; Campos, C. *Water Res.* **2003**, *37*, 4863–4872.

- (10) Kimura, K.; Amy, G.; Drewes, J.; Watanabe, Y. *J. Membr. Sci.* **2003**, *221*, 89–101.
- (11) Zhang, Y. P.; Zhou, J. L. *Water Res.* **2005**, *39*, 3991–4003.
- (12) Talley, J. W., Ed. *Bioremediation of Recalcitrant Compounds*; CRC Taylor and Francis: Boca Raton, FL, 2006.
- (13) Wang, P.; Keller, A. A. *Environ. Sci. Technol.* **2008**, *42*, 3381–3387.
- (14) Sanchez-Camazano, M.; Rodriguez-Cruz, S.; Sanchez-Martin, M. *Environ. Sci. Technol.* **2003**, *37*, 2759–2766.
- (15) Bandosz, T. J. *Activated Carbon Surfaces in Environmental Remediation*; Academic Press: New York, 2006.
- (16) Sun, Z. H.; Wang, L. F.; Liu, P. P.; Wang, S. C.; Sun, B.; Jiang, D. Z.; Xiao, F. S. *Adv. Mater.* **2006**, *18*, 1968–1971.

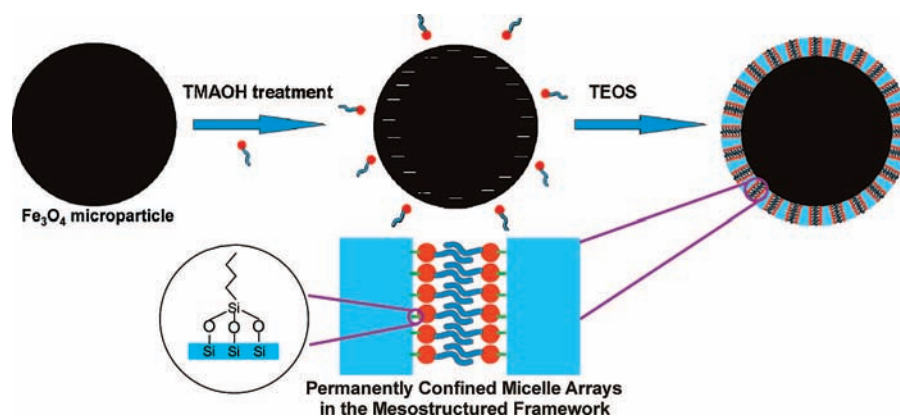


Figure 1. Schematic representation of Mag-PCMA synthesis (note: the core and shell are not drawn to scale).

arsenic¹⁷ and chromium,¹⁸ since magnetic separation is highly desirable. The magnetic separation in these cases simply involves applying an external magnetic field to extract the adsorbents, which can be generated by various sources (e.g., permanent magnets, alternating currents, etc.). Magnetic separation overcomes many of the issues present in filtration, centrifugation or gravitational separation, generally requiring less energy to achieve a given level of separation. To the best of our knowledge magnetic sorbents have not been reported for HOC decontamination.

Amphiphilic surfactant consists of a hydrophilic head and a hydrophobic tail. Above a critical aqueous concentration, the critical micelle concentration (CMC), surfactant monomers aggregate in aqueous solution to form micelles, which consist of a hydrophobic core and a hydrophilic shell.¹⁹ Owing to their hydrophobic cores, surfactant micelles have the capability of significantly enhancing the water solubility of HOCs,^{14,19,20} which has prompted the use of surfactants in conventional soil washing systems to enhance their treatment efficiency for HOC-contaminated soils and sediments *ex situ*.^{13,14} However, it has been found that surfactants, especially nonionic and cationic surfactants, can themselves strongly sorb onto soils and sediments which are usually negatively charged, resulting in a significant surfactant loss during the process.^{13,20,21} Adding to the problem, the sorbed surfactants serve as more effective sorbents for HOCs than the original soil and sediment phases.^{13,20–23} Therefore, instead of extracting the sorbed HOCs from soils and sediments, surfactant sorption onto the soils and sediments works undesirably against the remedial goal, causing even more HOCs to be accumulated in the soil and sediment as the amount of surfactant sorbed increases.^{13,20,21} As a result, a significantly greater amount of surfactant is needed to overcome the sorption of the HOCs onto the sorbed surfactant phase to achieve the treatment goals. Although the sorption of the surfactants onto the soil and sediment conforms to Langmuir behavior,¹³ reaching an asymptotic sorption capacity as the equilibrium aqueous surfactant concentration reaches its CMC, in many cases the cost of applying an extra amount of surfactant

to extract the sorbed HOCs out of the sorbed surfactant phase may be uneconomical. For example, a sorption capacity of around 30 g nonionic surfactant Triton X-100 per kg of soil was reported,¹³ and a total of around 80 g of Triton X-100 per kg of soil was required to begin extracting a hydrophobic pesticide, diuron, from the soil. Only beyond this point (80 g Triton X-100/kg soil) did the desorption of diuron out of the contaminated soils occur, indicating a significantly amount of surfactant required for decontamination.

For anionic surfactants, the loss *via* sorption onto soils and sediment may be low, but loss *via* complexation with divalent cations in soils (e.g., Ca²⁺, Mg²⁺) can be so significant that the use of anionic surfactants for remediating contaminated soils rich in divalent cations is typically ineffective.^{24,25} Furthermore, in the conventional surfactant-washing system, there is a need to separate fine soil or sediment particles that are laden with surfactants out of aqueous phase after soil washing, which usually is an energy-intensive process, involving centrifugation.^{26,27} In addition, recovering of the HOCs from or disposal of a large volume of aqueous solution with high surfactant micelle concentration is also a major concern.²⁷

In view of these challenges, a novel material has been developed with permanently confined surfactant micelles within a solid framework that can serve as an effective sorbent for HOCs from contaminated soil, sediments and water. In this paper, we report the synthesis and use of magnetic permanently confined micelle arrays (Mag-PCMA) consisting of solidified micelle arrays with a magnetite core, as shown in Figure 1, for HOC removal. Four representative HOCs (atrazine, diuron, naphthalene, and biphenyl) were chosen to study HOC sorption kinetics and isotherms onto Mag-PCMA from aqueous solution in the absence and presence of natural organic matter, as represented by humic acid (HA). In addition, as a proof of principle, the regenerability of Mag-PCMA and the reusability of Mag-PCMA for diuron removal were studied. Finally, the application of Mag-PCMA for HOC contaminated soil treatment was demonstrated. The results showed that Mag-PCMA are effective, regenerable, convenient sorbents for HOCs and thus a promising material for HOC decontamination.

(17) Yavuz, C. T.; et al. *Science* **2006**, *314*, 964–967.

(18) Hu, J.; Chen, G. H.; Lo, I. M. C. *Sep. Purif. Technol.* **2007**, *56*, 249–256.

(19) Rosen, M. J., Ed. *Surfactant and Interfacial Phenomena*; Wiley, New York, 1989.

(20) Wang, P.; Keller, A. A. *Water Res.* **2008**, *42*, 2093–2101.

(21) Wang, P.; Keller, A. A. *Water Res.* **2008**, *42*, 3781–3788.

(22) Boyd, S. A.; Lee, J. F.; Mortland, M. M. *Nature* **1988**, *333*, 345–347.

(23) Sheng, G.; Wang, X.; Wu, S.; Boyd, S. A. *J. Environ. Qual.* **1998**, *27*, 806–814.

(24) Jafvert, C. T.; Heath, J. K. *Environ. Sci. Technol.* **1991**, *25*, 1031–1039.

(25) Yang, K.; Zhu, L.; Xing, B. *Environ. Pollut.* **2007**, *145*, 571–576.

(26) Anderson, R.; Rasor, E.; Van Ryn, F. *J. Hazard. Mater.* **1999**, *66*, 89–98.

(27) Sheets, R. G.; Bergquist, B. A. *J. Hazard. Mater.* **1999**, *66*, 137–150.

2. Experimental Section

2.1. Chemicals. Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) was purchased from Supelco Inc. (Bellefonte, PA); diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) was purchased from ChemService Inc. (West Chestnut, PA); biphenyl and naphthalene were purchased from ACROS (Geel, Belgium); tetraethyl orthosilicate (TEOS), [3-(trimethoxysilyl)propyl]-octadecyldimethylammonium chloride (TPODAC) (72 wt.% in methanol), a cationic surfactant, and tetramethylammonium hydroxide (TMAOH) (25 wt.% in water) were purchased from Sigma-Aldrich (San Louis, MO). All these chemicals were used as received. The selected physicochemical properties of the HOCs and surfactant can be found in the Supporting Information. Humic acid (HA), a representative of natural organic matter, was purchased from Sigma-Aldrich.

2.2. Synthesis of Fe₃O₄ Microparticles. The core magnetite particles were prepared through a solvothermal reaction according to a previous report.²⁸ Briefly, 2.70 g of FeCl₃ · 6H₂O and 7.20 g of sodium acetate were dissolved in 160 mL of ethylene glycol. The obtained homogeneous solution was solvothermally heated at 200 °C for 8 h. The obtained black particles were washed with ethanol and water for 6 times, and then dried at 60 °C for 12 h.

2.3. Synthesis of Fe₃O₄@SiO₂-TPODAC Core/Shell Structured Particles. The core-shell structured Fe₃O₄@SiO₂-TPODAC particles were prepared by means of cooperative assembly of silica oligomers and TPODAC on the Fe₃O₄ microparticles. Briefly, 0.10 g of Fe₃O₄ microparticles were treated with 40 mL TMAOH solution overnight. The TMAOH-treated Fe₃O₄ microparticles were washed thoroughly with ethanol and then dispersed in a mixture of 60 mL ethanol and 10 mL deionized (DI) water. During mechanical stirring, 0.24 mL of TPODAC (72 wt.%) was added, followed by the addition of 1.0 mL of aqueous ammonia solution (25 wt.%) and 0.22 mL of TEOS. After stirring at room temperature for 6 h, the Fe₃O₄@SiO₂-TPODAC particles were washed with ethanol thoroughly, dried at 60 °C for 12 h, and stored in a capped bottle prior to use. In this paper, Fe₃O₄@SiO₂-TPODAC core/shell structured particles are described as Mag-PCMA to indicate both their structure and composition.

2.4. Material Characterization. Powder X-ray diffraction (XRD) patterns were collected on a Scintag PADX diffractometer with Ni-filtered Cu K α radiation (45 kV, 35 mA). Transmission electron microscopy (TEM) images were obtained using a JEOL 2010 microscope operated at 200 kV. Scanning electron microscopy (SEM) studies were performed on a FEI XL40 Sirion FEG microscope equipped with an Oxford EDX analysis system. Organic solvent extraction and thermogravimetry measurement were used to investigate the strength of bonding between the surfactant and the solid framework. Typically, 0.1 g of Mag-PCMA were treated with 50 mL of methanol by stirring for 4 h. Mag-PCMA were then collected and thermogravimetric (TG) analyses were carried out on a Mettler Toledo TGA/sDTA851e apparatus under an air flow of 100 mL/min with a heating rate of 10 °C/min.

2.5. Sorption Kinetics of HOCs onto Mag-PCMA from Contaminated Water. The HOC sorption kinetics onto Mag-PCMA were determined by batch experiments. Aliquots (50 mg) of Mag-PCMA were mixed in 10 mL glass tubes with 10.0 mL of an aqueous solution of each HOC. The initial HOC concentrations were 25.5 μmol/L for atrazine, 25.8 μmol/L for diuron, 46.9 μmol/L for naphthalene, and 39.0 μmol/L for biphenyl. The caps of the tubes were lined with PTFE. The tubes were shaken at 60 rpm at 22 ± 2 °C continuously. At the end of 5, 10, 20, 30, 45, 60, 90, 120, 180, 200, 360, 720, and 1440 min, one tube was taken out. A magnet was then used to separate the Mag-PCMA from the aqueous phase. Preliminary results showed that the sorption of HOCs onto the glass tubes was insignificant. 1.0 mL of the supernatant was taken for HOC analysis on a high performance liquid chromatography (HPLC). The amount of HOC sorbed was

calculated as the difference between the initial and final HOC mass in aqueous phase. In order to investigate the effect of the presence of HA on HOC sorption kinetics, diuron sorption kinetics were determined in the presence of 20 mg/L HA (organic carbon content), an environmental relevant HA concentration.²⁹ The initial diuron concentration was 34.3 μmol/L.

2.6. Sorption Isotherms of HOCs onto Mag-PCMA from Contaminated Water. The sorption isotherms of the HOCs onto Mag-PCMA were determined by the same procedure as the sorption kinetics determination except that the initial HOC concentration spanned over a large range and the equilibration time was 240 min (4 h) uniformly, which was determined to be more than enough for HOC sorption equilibrium to be reached. The highest initial HOC concentrations used for the sorption experiments were 125 μmol/L for atrazine, 137 μmol/L for diuron, 218 μmol/L for naphthalene, and 39 μmol/L for biphenyl, each of which is close to the water solubility of each HOC respectively. The pH of the suspensions was stable between 6~7 and did not show significant change before or after sorption. All measurements were carried out at room temperature (22 ± 2 °C).

The HOC sorption experiments were also conducted in the presence of 20 mg/L HA to investigate the effect of natural organic matter on HOC sorption onto Mag-PCMA. Only the highest initial HOC concentrations were used in these cases. The equilibrium aqueous HA concentration was measured on a total organic carbon analyzer (Shimadzu).

2.7. Regeneration and Reuse of Mag-PCMA. Diuron was chosen to study the recovery of the sorbed HOCs from Mag-PCMA and regeneration of Mag-PCMA. The same sorption experiment was conducted first, followed by separating the Mag-PCMA solid by magnetic separation. Diuron was then extracted with methanol from the collected Mag-PCMA. The diuron concentration in the extracted solution was determined by HPLC. Only the highest diuron initial concentration (137 μmol/L) was used in this case. The regenerated Mag-PCMA were then reused for subsequent diuron sorption experiments again. The sorption, extraction, and reuse processes were repeated for five times.

2.8. Application of Mag-PCMA for Soil Treatment. A soil was collected at Santa Barbara, California and the physicochemical properties of the soil can be found in the Supporting Information. The soil was contaminated with diuron in the laboratory. The contamination involved treating 2.0 g of the soil with 10 mL of 137 μmol/L diuron solution to reach sorption equilibrium, separating the solid phase *via* centrifugation, decanting and replacing the supernatant with DI water. The aqueous diuron concentration in the supernatant was determined and the amount of diuron sorbed onto the soil was calculated as the difference between the initial and final mass of diuron present in the aqueous phase. A total of 50 mg of Mag-PCMA were then added to the above-prepared contaminated-soil and water system and the whole mixture was mixed for 2 h to reach equilibrium, followed by magnetic separation of Mag-PCMA out of the soil-water system. The methanol extraction was then conducted with the separated Mag-PCMA, followed by determination of the diuron concentration in the methanol extraction solution. The Mag-PCMA were then reused for a second and a third time in the same soil-water system following the same procedure.

2.9. HPLC Analysis. A Shimadzu HPLC system was equipped with two LC-10AT VP pumps, a Sil-10AF autosampler, a DGU-14A degasser, and a SPD-M10AVP diode array detector. A Premier C18 5 μ reverse phase column was used with a length of 250 mm and an inner diameter of 4.6 mm. The HPLC analyses were carried out using an isocratic mode with a mobile phase constituted by 90% acetonitrile/10% deionized water. The analyses were performed at a constant flow rate of 1.0 mL/min. The UV detector monitored the absorbance at 222 nm for atrazine, 247 nm for diuron, 196 nm

(28) Deng, Y.; Qi, D.; Deng, C.; Zhang, X.; Zhao, D. *J. Am. Chem. Soc.* **2008**, *130*, 28–29.

(29) Tan, K. H. *Humic matter in soil and the environment*; Marcel Dekker, Inc.: New York, 2003.

for biphenyl, and 219 nm for naphthalene. An injection volume of 20 μL was used in all cases. Calibration was conducted daily and the R^2 was greater than 0.98 in all cases.

3. Results and Discussions

3.1. Mag-PCMA Synthesis and Characterization. The synthesis of Mag-PCMA consists of three steps, which are schematically presented in Figure 1. First, superparamagnetic Fe_3O_4 microparticles are prepared *via* a solvothermal method as described before.²⁸ As-prepared Fe_3O_4 microparticles have a mean diameter of ~ 200 nm based on the size measurement of 100 microparticles and are the aggregates of ~ 15 nm nanoparticles, leading to the superparamagnetic behavior of the particles.²⁸ Figure S1 in the Supporting Information shows the powder XRD pattern, SEM, and TEM micrographs of Fe_3O_4 microparticles.

Second, the as-prepared Fe_3O_4 microparticles were treated with TMAOH to make the particle surface negatively charged. TMAOH treatment reverses the surface charges of Fe_3O_4 particles from positive (ζ -potential = 18.0 mV at pH = 7) to strongly negative (ζ -potential = -46.3 mV at pH = 7), which is the critical step in the synthesis. The negatively charged Fe_3O_4 surface allows for coassembly of the cationic surfactant, TPODAC, and silica species on the particle surface and therefore direct deposition of the ordered mesostructured surfactant/silica hybrid layer in the later step, avoiding an intermediate nonporous silica coating on the Fe_3O_4 particles.^{28,30} The highly negatively charged Fe_3O_4 surface also minimizes particle aggregation during the mesostructured layer coating process because of electrostatic repulsion.

The third synthesis step involves coating a layer of silica/TPODAC mesostructured hybrid layer on the negatively charged Fe_3O_4 microparticles to create a core/shell structure (Figure 1). TPODAC, a commercially available quaternary ammonium type cationic surfactant, can act as a structure-directing agent in forming ordered mesostructured hybrid material *via* cooperative assembly with silica precursors under basic conditions, similar with other quaternary ammonium type cationic surfactant such as cetyltrimethylammonium bromide (CTAB).³¹ Cooperative assembly of surfactant and silica precursors solidifies micelle arrays in the mesostructured silica framework,³¹ leading to the confinement of large amounts of surfactant micelles in a small volume. The surfactant, TPODAC, has reactive endgroups $-\text{Si}(\text{OCH}_3)_3$ on its hydrophilic groups, which allows the surfactant micelles to permanently anchor on the silica framework through covalent bonding. Silica provides a solid framework to condense and support surfactant micelles in a high density manner. The framework is not limited to silica; other inorganic components are suitable as well, such as titanium oxide, but silica is an inexpensive material and its coassembly with surfactant molecules to create ordered mesostructured hybrids has been well-documented.³¹ The core/shell structure of a Mag-PCMA is shown in Figure 2. The ordered mesostructure of the shell is demonstrated by TEM micrograph (Figure 2A and B). The mesostructured layer is approximately 100 nm as determined by TEM (Figure 2A) and by SEM (Figure 2C). Owing to the magnetic Fe_3O_4 cores, the synthesized Mag-PCMA shows a fast response to an applied magnetic field (Figure 2D).

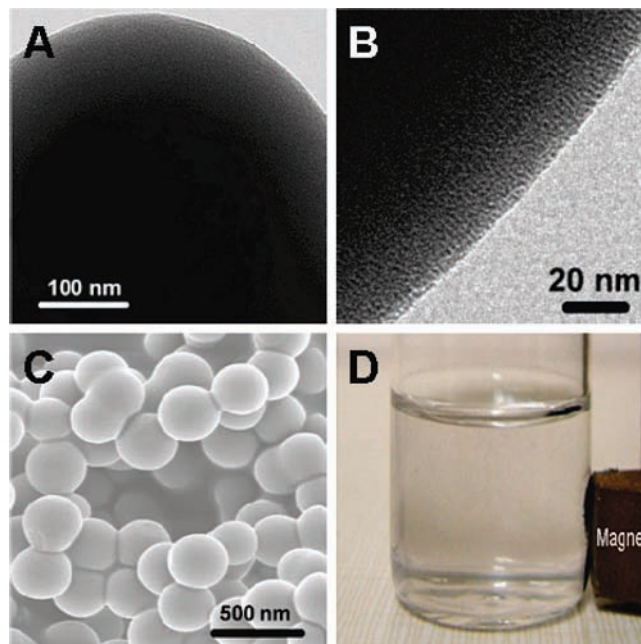


Figure 2. (A) TEM micrographs of Mag-PCMA; (B) mesostructure of Mag-PCMA; (C) SEM micrographs of Mag-PCMA; (D) magnetic separation of Mag-PCMA. Note: The surfactant was removed by calcination for better contrast in the TEM images.

Figure 3 presents the small angle XRD pattern and thermogravimetric (TG) curves of Mag-PCMA. One intense diffraction peak at a 2 theta value of 2.2° and a broad peak at $4\text{--}5^\circ$ can be found in its small-angle XRD pattern, indicating the formation of ordered mesostructure. As demonstrated in its TEM image (Figure 2B), although the mesostructure is not highly ordered, it shows uniform meso-scale structure due to the formation of micelles with similar diameter and uniform silica wall thickness. These results indicate that a silica confined micelles array layer was successfully coated on the magnetic core surface.

The TG curves of as-made Mag-PCMA (Figure 3B) show three weight loss steps at about 220, 310, and 600 $^\circ\text{C}$, as demonstrated in its derivative curve, which can be ascribed to the decomposition of quaternary ammonium group, the decomposition and carbonization of alkyl chain, and the burn off of carbon, respectively. The weight percentage of the surfactant confined within the ordered silica framework of Mag-PCMA can be determined by the difference of initial and final mass of the sample in TG curve in Figure 3 and was measured to be approximately 30% of the total mass of Mag-PCMA. The high fraction of micelles and ordered mesostructure lead to a large, connecting hydrophobic environment with high affinity toward HOCs. The TG curves of as-made and methanol-washed Mag-PCMA do not show any significant difference, indicating that essentially no surfactant was removed during methanol treatment and therefore that the surfactant is chemically confined in the silica framework. Thus, the unique structural configuration of the Mag-PCMA avoids surfactant loss during application and sorbent regeneration.

3.2. Sorption Isotherms and Kinetics of HOCs from Contaminated Water. The sorption of four environmentally representative HOCs (atrazine, diuron, naphthalene, biphenyl) onto Mag-PCMA was determined by the batch equilibration method. The sorption isotherm can usually be mathematically described

(30) Zhao, W.; Gu, J.; Zhang, L.; Chen, H.; Shi, J. *J. Am. Chem. Soc.* **2005**, *127*, 8916–8917.

(31) Monnier, A.; Schüth, F.; Huo, Q.; Kumar, D.; Margolese, D.; Maxwell, R. S.; Stucky, G. D.; Krishnamurty, M.; Petroff, P.; Firouzi, A.; Janicke, M.; Chmelka, B. F. *Science* **1993**, *261*, 1299–1303.

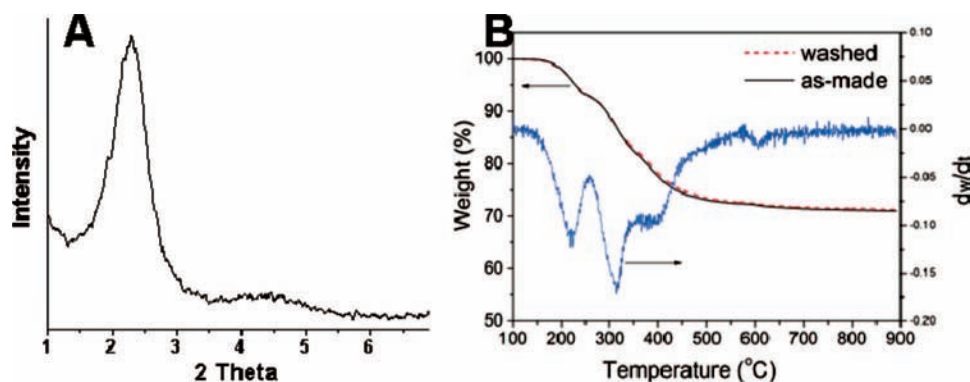


Figure 3. (A) Small-angle XRD patterns of Mag-PCMA and (B) thermogravimetric (TG) analyses of as-made and methanol-washed Mag-PCMA.

Table 1. Measured HOC Sorption Parameters by Mag-PCMA

HOC	solubility (mg/L)	K_{ow}	K_f	N	% removal ^a	% removal ^b
Atrazine	153	416	0.72	0.97	75%	76%
Diuron	180	660	2.23	0.90	91%	90%
Naphthalene	225	3235	4.32	0.97	95%	94%
Biphenyl	44	7079	19.65	0.99	99%	97%

Note: ^a Average percent HOC removal across all initial concentrations tested in the absence of HA. ^b Percent HOC removal at highest initial HOC concentrations in the presence HA (20 mg/L).

by either a linear, Freundlich, or Langmuir sorption model.³² In this study, the sorption data were best fitted by the Freundlich sorption model based on a sum of least-squares analysis. The Freundlich model has the following form:

$$C_s = K_f C_e^n \quad (1)$$

Where C_s is the sorbed HOC concentration ($\mu\text{mol/g}$), C_e is the equilibrium aqueous HOC concentration ($\mu\text{mol/L}$), and K_f ($\mu\text{mol/g}(\mu\text{mol/L})^{-n}$) and n (dimensionless) are constants at a given temperature. K_f is the HOC sorption capacity evaluated at $C_e = 1 \mu\text{mol/L}$.

Equation 1 can be linearized by a logarithmic transformation:

$$\log C_s = \log K_f + n \log C_e \quad (2)$$

Fitting eq 2 to the observed data for HOCs resulted in a linear relationship with R^2 greater than 0.97. Freundlich parameters for sorption (K_f and n) were calculated from the slope and intercept of the linear regression and are listed in Table 1. Figure 4a presents the measured HOC sorption isotherms along with the Freundlich fitted isotherms. Also presented in Table 1 are the octanol–water coefficients (K_{ow}) of the HOCs, a commonly used indicator for chemical hydrophobicity,^{32–34} and the removal percentage (%) of the HOCs. As can be seen, K_f is strongly correlated with K_{ow} , as expected from the hydrophobic interactions.

Not surprisingly, the % removal of HOCs is found to increase with hydrophobicity of the HOCs, as indicated by the increasing K_{ow} value. It is worth mentioning that under these conditions, the % removal of naphthalene is 95% and that of biphenyl is 99%. Essentially complete removal can be expected under the same conditions for HOCs more hydrophobic than biphenyl.

HA constitutes a major fraction of surface water organic matter and of soil organic matter and is the most abundant naturally occurring organic macromolecule on earth.²⁹ The structure of HA is usually described as assemblies of covalently linked aromatic and aliphatic residues, in which the aromatic fraction ranges from ca. 10–40%. On the other hand, HA is amphiphilic, containing a significant amount of polar groups (e.g., carboxylic groups).²⁹ Due to the ubiquitous presence of HA, in this study, the sorption of HA onto Mag-PCMA and the effect of HA on the HOC sorption onto Mag-PCMA were also investigated.

Our results show that the sorption of the HA onto Mag-PCMA was insignificantly (only 0.58 mg/g and less than 15% of the total was removed by Mag-PCMA). This is not surprising because the polar groups, such as carboxylic groups, associated with HA were repelled by the confined micelles and the HA sorption was limited to the external surface of the Mag-PCMA. Table 1 presents the percentage HOC removal by Mag-PCMA in the presence of 20 mg/L HA. As can be seen, the sorption of HA onto the Mag-PCMA had a minimal effect on HOC sorption, further suggesting that the sorption of HOCs and HA occur in different domains.

Figure 4b presents the measured HOC sorption kinetics. As can be seen, for all HOCs, more than 87% sorption occurred in the first 5 min, 96% sorption occurred in the first 10 min, and 99% sorption occurred within the first 45 min. Comparing with activated carbon, whose contaminant sorption equilibrium usually occurs after a few hours equilibration due to its significant microporosity,^{11,15} Mag-PCMA have very fast HOC sorption kinetics due to the large amount of surfactant micelles accessible to the HOCs in solution. Also, it suggests that the mesostructured silica is not the limiting factor for HOC diffusion into the confined surfactant micelles. Diuron sorption kinetics in the presence of HA showed that the presence of HA had no significant effect on HOC sorption kinetics, suggesting the sorption of natural organic matter would not block the entry of HOCs into the micelles confined within the mesopores.

3.3. Regeneration and Reuse of Mag-PCMA. One key feature of this approach is the ability to regenerate and reuse the Mag-PCMA, using solvents to extract the HOCs without affecting the stability of the Mag-PCMA. TG analysis has previously shown that the solvent extraction did not remove any significant amount of the confined micelles from the mesostructured silica framework.

To further demonstrate the regenerability and reusability of the Mag-PCMA, the recovery of diuron sorbed onto the Mag-PCMA was investigated by methanol extraction. The diuron percentages removal and percentages recovery during five

(32) Schwarzenbach R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*, 2nd ed.; Wiley: New York, 2003.

(33) Chiou, C. T.; Porter, P. E.; Schmedding, D. W. *Environ. Sci. Technol.* **1983**, *17*, 227–231.

(34) Karickhoff, S. W.; Brown, D. S.; Scott, T. A. *Water Res.* **1979**, *13*, 241–248.

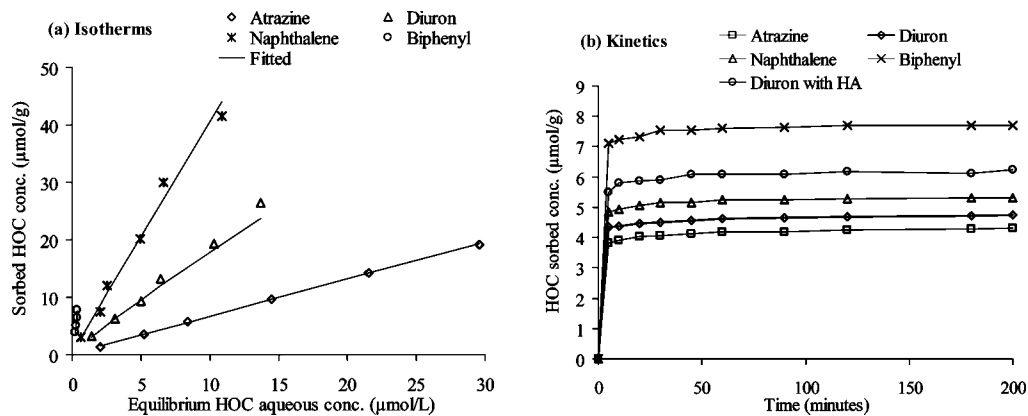


Figure 4. (a) HOC sorption isotherms and (b) HOC sorption kinetics onto Mag-PCMA.

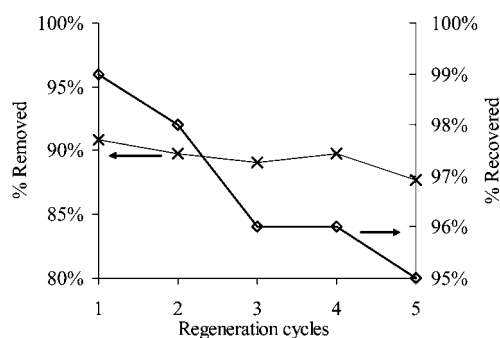


Figure 5. Sorption and recovery of diuron onto Mag-PCMA during five regeneration cycles. Note: % removed refers to the percent diuron removal out of the original diuron solution of 34 mg/L while % diuron recovered refers to the percent diuron recovery out of the total amount of diuron sorbed by Mag-PCMA in each case.

continuous cycles of regeneration and reuse are shown in Figure 5. It was found that nearly all of the sorbed HOCs (>95%) could be recovered, indicating easy regeneration of Mag-PCMA (Figure 5). No significant loss of HOC sorption capacity was observed on the regenerated Mag-PCMA, which is superior to activated carbon, whose regeneration involves high temperatures that affects carbon properties and leads to a reduction of its sorption capacity.^{16,18}

On the basis of these results and fast HOC sorption kinetics as demonstrated earlier, continuous Mag-PCMA-based flow-through or fluidized bed systems can be designed for contaminated sediment or water treatment with high HOC removal efficiency.

3.4. Application of Mag-PCMA for Soil Treatment. The representative physicochemical properties of the soil can be found in the Supporting Information. The soil was first contaminated with diuron and the amount of diuron sorbed was determined to be 61 mg/kg. The sorption of HOCs onto the soil has been identified to be mainly on soil organic matter phase *via* hydrophobic interaction.^{13,32–35}

Figure 6 presents the accumulative recovery of the diuron originally sorbed with the soil by Mag-PCMA through three treatment cycles. As can be seen, 75% of the total amount of the soil-sorbed diuron was recovered by the end of the first cycle, 86% at the end of the second cycle, and 90% at the end of third cycle. This simple test demonstrated that the Mag-PCMA can be used for soil-washing application and the regeneration and reuse of Mag-PCMA for soil application are promising.

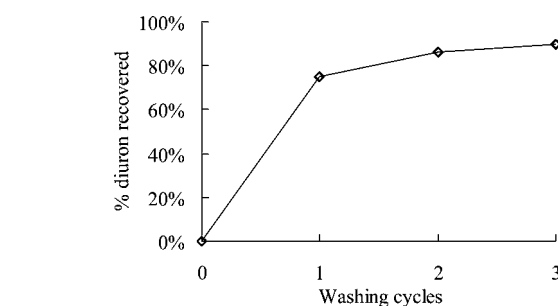


Figure 6. Cumulative % diuron recovered by Mag-PCMA from diuron contaminated soil through three cycles.

Soil organic matter is a loosely packed hydrophobic medium containing an abundance of polar functional groups^{29,36} while the confined TPODAC micelles are a well-ordered, rigid structure, with the hydrophobic chains of TPODAC constituting a very hydrophobic medium.³⁶ Thus, the affinity of HOCs toward confined surfactant micelles is expected to be much higher than toward soil organic matter. For this reason, the presence of Mag-PCMA tends to extract the originally soil-sorbed HOC out of the soil organic matter phase and into the confined micelle phase using the aqueous solution as an intermediate.

4. Conclusions

To address the challenges associated with remediating HOC contaminated media, Mag-PCMA have been successfully synthesized and evaluated. The synthesis of Mag-PCMA involves coating a silica/surfactant mesostructured hybrid layer on the negatively charged Fe₃O₄ microparticles to create a core/shell structure. The surfactant, TPODAC, has reactive endgroup -Si(OCH₃)₃ on its hydrophilic groups, which allows the surfactant micelles to permanently anchor on the silica framework through covalent bonding. Cooperative assembly of surfactant with silica precursors solidifies micelle arrays in the mesostructured silica framework, leading to the confinement of large amounts of surfactant micelles in a small volume.

The results of removal of HOCs from contaminated media showed that Mag-PCMA represent a significant improvement in HOC decontamination, in that (1) Mag-PCMA eliminate surfactant loss during application and thus allow for sorbent regeneration and reuse, significantly increasing treatment ef-

(35) Chiou, C. T.; Peters, L. J.; Freed, V. H. *Science* **1979**, *206*, 831–832.

(36) Sheng, G. Y.; Xu, S. H.; Boyd, S. A. *Environ. Sci. Technol.* **1996**, *30*, 1553–1557.

iciency and reducing operation cost; (2) the superparamagnetic Fe_3O_4 core allows rapid separation of Mag-PCMA after HOC sorption; (3) the residual solvent-HOC solution represents a very small fraction of the initial contaminated mass and volume. Therefore, Mag-PCMA are reusable sorbents for the fast, convenient, and highly efficient removal of HOCs from contaminated media.

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Supporting Information Available: Properties of HOCs, TPODAC, and soil sample, XRD pattern, TEM and SEM micrographs of Fe_3O_4 microparticles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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