# Magnetic Nanoparticle Adsorbents for Emerging Organic Contaminants

Yuxiong Huang and Arturo A. Keller*

Bren School of Environmental Science and Management, University of California, Santa Barbara, California 93106, United States

ABSTRACT: The recognition that pharmaceuticals, personal care product chemicals, and endocrine disruptors can cause deleterious effects has led to search new approaches for removing them from contaminated waters. The emergence of tailored nanomaterials, with magnetic properties and high adsorption capacity for a wide range of compounds, provides a new tool to deal with these complex emerging organic contaminants (EOCs). Magnetic permanently confined micelle arrays (Mag-PCMAs) synthesized with cationic surfactants can provide several sorption mechanisms for the multifunctional EOCs. The sorption onto Mag-PCMAs of seven EOCs and two more conventional contaminants was studied. The results indicate high sorption capacity for many of the EOCs. However, because of the complex nature of these EOCs, it is not possible to predict their adsorption based on a single physicochemical characteristic such as K_{ow} or pK_a. Sorption kinetics are relatively fast, within the typical range for water treatment processes. The low energy required for the synthesis of Mag-PCMAs, relatively low cost (~$4/kg), ease of recovery with a magnetic field, and regenerability make them a much more sustainable option than more traditional approaches for removing EOCs, such as high energy granular activated carbon adsorption or advanced oxidation processes.

KEYWORDS: *Mag-PCMAs, Regeneration, Pharmaceuticals, Octanol−water partitioning, pK_a*
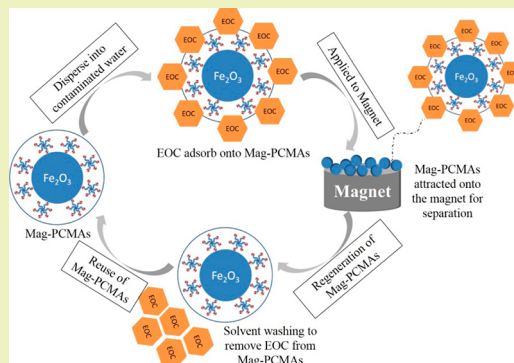
INTRODUCTION

Recent attention has been directed at chemicals that are historically unregulated or not commonly regulated as contaminants but have the potential to enter the environment and cause known or suspected adverse ecological and human health effects, such as pharmaceuticals, personal care products, surfactants, various industrial additives, and endocrine disruptors, including hormones.[1−3] These chemicals are collectively defined as emerging organic contaminants (EOCs) (http://toxics.usgs.gov/regional/emc). The presence of these synthetic chemicals in the wastewater or surface water may contaminate ecosystems and surface and drinking water supplies. Recent studies have shown that EOCs may have biological effects and even potential ecotoxicological impacts on invertebrates (such as daphnids), fish, algae, mussels, and also human embryonic cells.[4−10] To date, most of the studies have focused on the occurrence and/or fate of EOCs in surface waters[11−15] and/or wastewater.[1,16−19] However, there are few studies on approaches to remove EOCs from aqueous media. Therefore, the development of technologies to remove legacy and emerging organic contaminants from water is of great importance.

In recent years, magnetic particles have received a lot of attention as powerful adsorbents because their inherent superparamagnetic properties make them desirable for magnetic field assisted separations.[20−23] For instance, magnetic iron oxides (Fe_2O_3 and Fe_3O_4) have been reported as potential adsorbents for the removal of pollutants from aqueous media.[24−27]

The surface characteristics of the sorbents are very important to the effectiveness of the adsorption process. Because sorption of organic chemicals can be enhanced by coating of surfactants onto the sorbent, in a previous study we synthesized magnetic permanently confined micelle arrays (Mag-PCMAs) with a magnetite core and a silica porous layer that permanently confines surfactant micelles within the mesopores.[28] The magnetic core allows for rapid separation of the Mag-PCMAs from solution by applying a magnetic field. Mag-PCMAs have been applied to the removal of very hydrophobic compounds,[28] natural organic matter,[29] and oxyanions.[30]

The objective of this study is to determine the effectiveness of Mag-PCMAs to remove EOCs from water. For comparison, two legacy contaminants (e.g., ethylbenzene, 2-chlorophenol) were also evaluated. The microenvironment of the interactions between the mesoporous layers of the Mag-PCMAs and the multiple binding sites on EOCs make it a significant study for sorbents in complex chemical environments, such as water treatment. Mag-PCMAs have low energy requirements in their synthesis, use, and regeneration, compared to other adsorbents such as granular activated carbon (GAC), resulting in a much more sustainable material.

MATERIALS AND METHODS

Chemicals. Tetramethyl ammonium hydroxide (TMAOH) (25 wt % in water), 3-(trimethoxysily)propyl-octadecyldimethyl-ammonium

chloride (TPODAC) (72 wt % in methanol), ammonia (28%), methanol, tetraethyl orthosilicate (TEOS), atenolol, gemfibrozil, sulfamethoxazole, D-gluconic acid sodium salt, and succinic acid disodium salt were purchased from Sigma-Aldrich (St. Louis, MO, U.S.A.). Methyl orange and l-3-(3,4-dihydroxyphenyl)alanine (L-DOPA) were purchased from Acros Organics (Geel, Beligum). Ethylbenzene and 2-chlorophenol were purchased from Fisher Scientific (Pittsburgh, PA, U.S.A.). Maghemite iron(III) oxide nanoparticles (30 nm in diameter) were purchased from Alfa Aesar (Ward Hill, MA, U.S.A.). All chemicals were used as received, without further purification. Relevant physico-chemical properties for the contaminants are presented in Table 1.

Table 1. Properties of Compounds for Sorption Studies

compound	molecular mass (g/mol)	$\log_{10}$ octanol−water partition coefficient ($\log_{10} K_{ow}$)	pK_a
2-chlorophenol	128.560	2.17	8.29
atenolol	266.336	0.16	9.6
D-gluconic	218.139	−6.00	3.7
ethylbenzene	106.170	3.11	−
gemfibrozil	250.333	4.77	4.75
L-DOPA	197.190	0.28	8.7
methyl orange	327.330	0.68	3.47
succinic acid	118.090	−0.59	4.2
sulfamethoxazole	253.279	0.89	5.7

Synthesis of Mag-PCMAs. The synthesis procedure for Mag-PCMAs was improved compared to the previous study to improve yield and reduce the use of ethanol.[28] The core−shell structured Mag-PCMAs were synthesized through a solvothermal reaction, which is cooperative assembly of silica oligomers and TPODAC on the Fe$_2$O$_3$ nanoparticles. This three-step preparation of Mag-PCMAs is illustrated in Figure 1. Maghemite iron(III) oxide nanoparticles were dispersed in
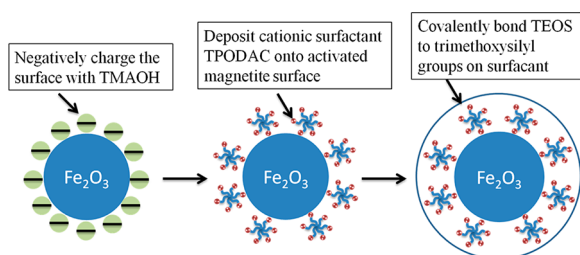

Figure 1. Mag-PCMA synthesis is done with stepwise reagent addition. Silica is interspersed between the surfactant and magnetite covalently securing the micelles to the iron core and leaving void space for contaminant sorption.

40 mL of TMAOH solution (25% by weight) under constant mixing overnight to activate the surface. Then 0.5 mL of TPODAC, a cationic surfactant, was added to the maghemite suspension under constant stirring. Next, 5 mL of 28% ammonium hydroxide were added for base catalyzed sol−gel hydrolysis of TEOS (1.1 mL) to cross-link the surfactant onto the magnetic iron core. The three steps are done at room temperature (22 °C).

Scanning Electronic Microscopy. Scanning electronic micros-copy (SEM) imaging was performed under vacuum on an FEI XL40 FEG digital scanning microscope using an accelerating voltage of 5.00 kV.

Batch Sorption of Emerging Organic Contaminants. Adsorption kinetics were determined by batch experiments. A total of 2.0 mg of Mag-PCMAs was mixed with 20 mL of a given organic contaminant in 20 mL vials. The initial concentration of contaminant was 100 mg/L in all cases. All experiments were conducted at pH 7.0. These vials were shaken in an end-over-end shaker on Dayton-6Z412A Parallel Shaft roller mixer with a speed of 70 rpm at room temperature. The concentration of the sample was measured at the end of 5, 15, 30,

60, 90, 120, and 180 min. Then the Mag-PCMAs particles with adsorbed contaminants were separated from the mixture with an Eclipse Magnetics N821permanent hand-held magnet (50 mm ×50 mm ×12.5 mm; 243.8 g; pull force: 40.1 N)

To develop adsorption isotherms, solutions with varying initial concentrations were treated with the same procedure as above at room temperature. The equilibration time was 24 h uniformly, which was determined to be sufficient to reach the adsorption equilibrium. Preliminary experiments indicated that more than 99% of adsorption occurred within the first 120 min. The contaminant concentrations ranged from 10 to 3000 mg/L, and the Mag-PCMAs concentration were 100 mg/L.

The solid-phase concentrations were determined by mass balance, according to eq 1

$$q_e = \frac{V \times (C_0 - C_e)}{M} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentration of EOC in the liquid phase (mg/L), respectively; q_e is the equilibrium concentration of contaminants adsorbed on the unit mass of Mag-PCMAs (mg/g); V is the volume of solution, and M is the mass of dry Mag-PCMAs (g).

Analysis by UV-Spectrophotometry and HPLC. Two instru-ments were used: a high performance liquid chromatography HPLC system (SPD-M10AVP, Shimadzu, MD) or a UV−vis spectrometer (BIOSPEC-1601, Shimadzu, MD). Each instrument was used to determine the final concentration of organic contaminants after adsorption occurred. HPLC was used for the analysis of L-DOPA. The HPLC system was equipped with two LC-10AT VP pumps, a Sil-10AF autosampler, DGU-14A degasser, and SPD-M10AVP diode-array detector. A TSKgel ODS-120A column (length, 250 mm; inner diameter, 4.6 mm) was used. The HPLC analyses were carried out with a mobile phase comprised of 30% methanol/70% water. The analyses were performed at a constant flow rate of 1.0 mL/min. The ultraviolet detector monitored the absorbance at 261 nm for L-DOPA. The UV−vis spectrometer was used to monitor the concentration of organics in water at the absorption maximum for each compound: methyl orange at 400 nm, ethylbenzene at 261 nm, 2-chlorophenol at
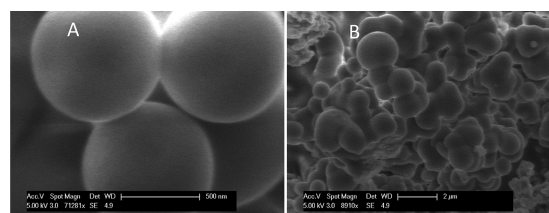

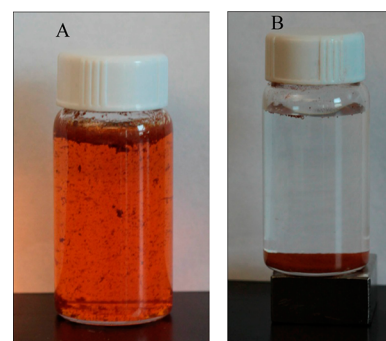**Figure 2.** SEM of (A) Mag-PCMA at 71281X and (B) Mag-PCMA at 8910X.

Figure 3. (A) Mag-PCMA particles are introduced into a vial containing contaminated water. (B) A permanent magnet is placed at the bottom of the vial to attract the magnetic particles, demonstrating the rapid removal of Mag-PCMAs from the suspension within seconds of applying a magnetic field.
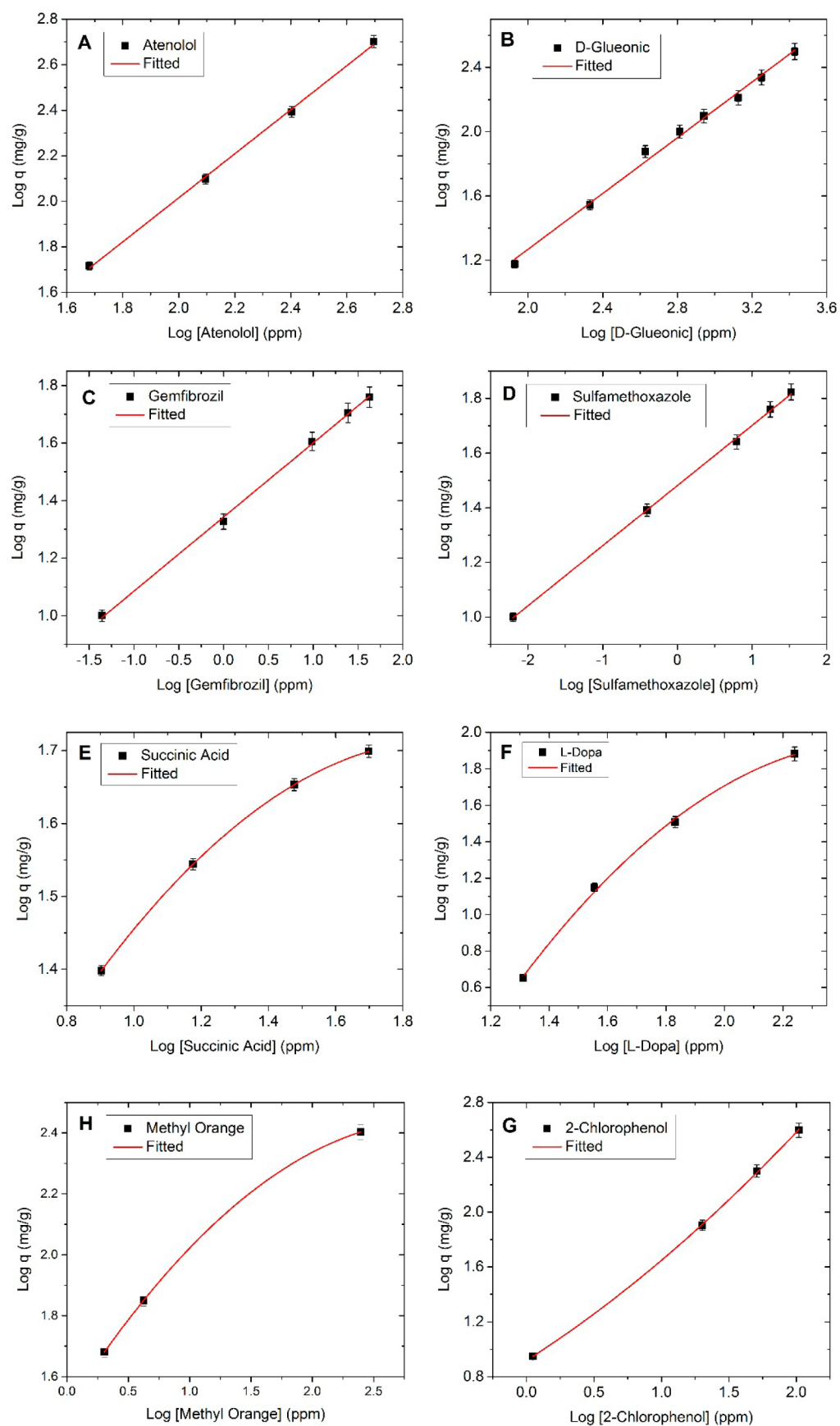
Figure 4. Noncompetitive sorption onto Mag-PCMAs across a concentration range for (A) atenolol, (B) D-gluconic, (C) gemfibrozil, (D) sulfamethoxazole, (E) succinic acid, (F) L-DOPA, (G) methyl orange, (H) 2-chlorophenol, and (I) ethylbenzene. The solid lines represent model fits based on the best model for each compound.

Table 2. Fitted Parameter Values for Each Compound in Non-Competitive Sorption

compounds		n	95% LCL for n	95% UCL for n	log K_f	95% LCL for log K_f	95% UCL for log K_f	K_f	R^2
					Freundlich Model				
D-gluconic		0.867	0.867	0.867	−0.467	−0.467	−0.467	0.34	0.999
atenolol		0.967	0.967	0.967	0.080	0.080	0.080	1.20	0.999
gemfibrozil		0.257	0.257	0.257	1.34	1.34	1.34	21.8	0.999
sulfamethoxazole		0.219	0.211	0.226	1.48	1.47	1.49	30.3	0.999
					Exponential Model				
L-DOPA	n	4.622	−2.72	11.9	−3.81	−9.85	2.24	1.55×10^{-4}	0.997
	n_2	−0.931	−3.08	1.21					
succinic acid	n	1.16	1.15	1.17	0.596	0.589	0.604	3.945	1
	n_2	−0.299	−0.304	−0.295					
2-chlorophenol	n	0.628	0.628	0.628	0.917	0.917	0.917	8.260	1
	n_2	0.102	0.102	0.102					
ethylbenzene	n	0.173	0.0685	0.277	0.966	0.945	0.988	9.256	0.999
	n_2	0.272	0.204	0.339					
methyl orange	n	0.627	0.627	0.627	1.50	1.50	1.50	31.550	1
	n_2	−0.104	−0.104	−0.104					

272.93 nm, atenolol at 274 nm, succinic acid at 218 nm, D-glueonic at 208 nm, sulfamethoxazole at 268 nm, and gemfibrozil at 275 nm. Calibration curves were performed daily with a regression (R^2 value) of 0.99 or greater.

RESULTS AND DISCUSSION

Mag-PCMA Characterization. SEM images show the hydrated particles are 600 nm to 1 um in size (Figure 2). Figure 3 presents the separation of Mag-PCMAs from the suspension using a simple magnet. The dispersed Mag-PCMAs can be separated within a few seconds from the suspension, with a very high recovery of the Mag-PCMAs. The energy requirements for the separation of the magnetic particles is minimal, particularly if a permanent magnet is used.

Noncompetitive Sorption Studies. Figure 4 presents the experimental results for the noncompetitive sorption for each compound for the range of concentration studies, as well as the fit of a Freundlich isotherm, linearized by taking the logarithm of both sides of the equation[31]

$$\log q = \log K_f + n \log C_e \tag{2}$$

where q is the amount of contaminant adsorbed at equilibrium (mg/g); C_e is the equilibrium concentration of contaminant in solution (mg/L); K_f is the Freundlich adsorption constant ($\text{mg}^{1-n}\,\text{g}^{-1}\,\text{L}^n$); and n is a measure of adsorption intensity (dimensionless). The Freundlich parameters K_f and n were determined from the intercept and slope of eq 2. Table 2 summarizes the fitted values from all compounds. The Freundlich isotherm was used because it provided a better fit than linear or Langmuir models. Additionally, 2-chlorophenol, ethylbenzene, succinic acid, and L-DOPA were fitted using a nonlinear exponential model[32] to provide a better fit

$$\log q = n \log C_e + n_2 (\log C_e)^2 + \log K_f \tag{3}$$

On the basis of the equilibrium sorption concentrations, q, at a given C_e Mag-PCMAs exhibited the highest sorption capacity for L-DOPA and the lowest for D-gluconic acid. While for more conventional non-ionic and contaminants such as petroleum hydrocarbons and chlorinated solvents, there is a strong correlation between removal efficiency and the octanol–water partitioning coefficient (K_{ow}),[28] and for anionic compounds removal efficiency can be predicted by their Gibbs free energy of adsorption.[30] The EOC present multiple characteristics that

control their affinity for the cationic TPODAC surfactant. In general the amount sorbed decreases with increasing K_{ow} (Figure 5), with L-DOPA and D-gluconic acid representing
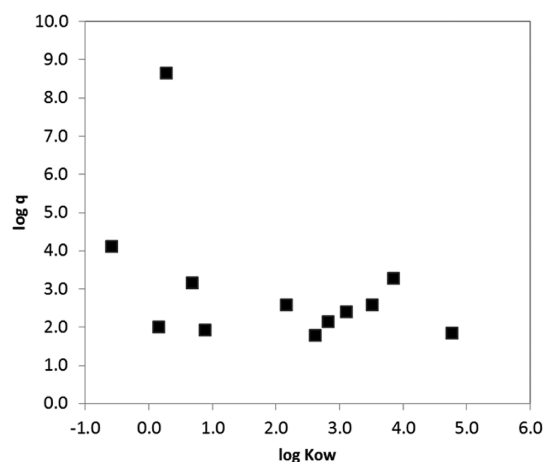

Figure 5. Sorption onto Mag-PCMAs for various compounds as a function of log K_{ow}. D-gluconic acid is not included because it represents a major outlier with a log K_{ow} of −6.0.

major outliers. The large number of −OH groups on both of these compounds results in very different behavior than the other compounds studied. The trend is much less conclusive than for a sequence of hydrophobic organic contaminants where in fact adsorption increases with hydrophobicity. For ionizable compounds, their adsorption onto Mag-PCMAs generally increases with pK_a (Figure 6), although the behavior is not easily predictable based on this physicochemical characteristic alone. Further work will be done with a broader range of compounds to elucidate more clearly the relationships.

For non-ionic compounds, removal was strongly correlated with the K_{ow} of the compounds, a common indicator of hydrophobicity (Figure 6). In general, removal rate was found to decrease with hydrophobicity, except for ethylbenzene. Repeated adsorption experiments for ethylbenzene resulted in similar results, indicating that some additional adsorption mechanism must be involved for this compound.

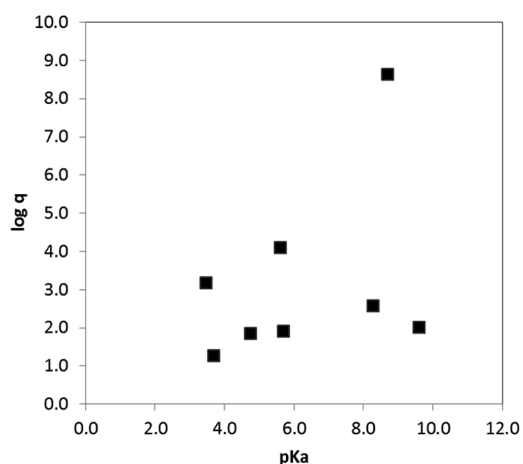**Adsorption Kinetics for Methyl Orange.** Methyl orange was used to evaluate the adsorption kinetics onto Mag-PCMA,

Figure 6. Sorption onto Mag-PCMAs for various compounds as a function of pK_a. All ionizable compounds are considered.

given the high sorption capacity for this compound. Sorption occurred rapidly, even for an initial concentration of 100 mg/L. Within the first 60 min, almost all of the methyl orange was adsorbed, with minimal additional sorption after 2 h (Figure 7A).
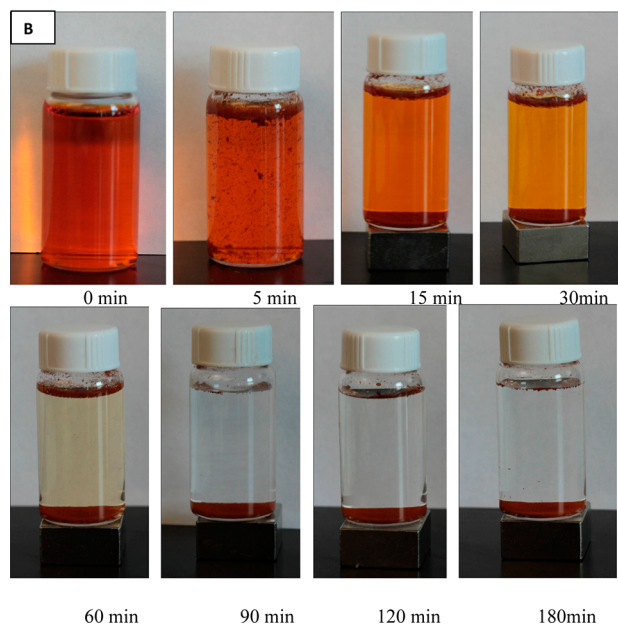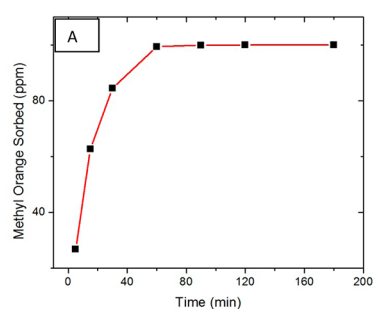

Figure 7. (A) Methyl orange equilibration kinetics. (B) Sorption time sequence.

Figure 7B shows the evident color change in the mixture solution with the passage of time indicating the concentration of methyl orange decreased quickly. Note that the image was made after concentrating the Mag-PCMAs at the bottom of the vial using a permanent magnet.

■ CONCLUSIONS

Mag-PCMAs with a core−shell structure are fast, convenient, and efficient sorbents for removing rather soluble organic contaminants from water. This study has extended the application of Mag-PCMAs from removing very hydrophobic compounds, natural organic matter, and oxyanions to consider emerging organic compounds, including pharmaceuticals and personal care compounds. The most likely mechanisms of adsorption of organic contaminants onto Mag-PCMAs are hydrophobic interactions, hydrogen bonding, and electrostatic interactions. Because all of these mechanisms are at play for these mixed functionality compounds, it is not easy to predict the adsorption capacity simply on the basis of one physicochemical property (e.g., K_{ow} or pK_a). Further work will be done with a broader range of compounds to elucidate more clearly the relationships.

The synthesis procedure for Mag-PCMAs is simple and requires low energy and relatively low cost (∼$4/kg), and the Mag-PCMAs with adsorbed organic contaminants can be easily removed from water via magnetic separation. This can be compared to carbon nanotubes (CNTs) that have been considered as adsorbents, with a cost of $500−1000/kg. This is in part because manufacturing CNTs requires high pressure and temperature, i.e., considerable energy. Granular activated carbon (GAC) is less than $1/kg, but synthesis of GAC requires heating the carbon source several hundreds of degrees to activate the carbonaceous surface. Increasing the input energy can shorten the time needed for equilibrium. The regeneration of Mag-PCMAs, presented in previous studies,[28,30] can be done at room temperature using ethanol or methanol to desorb the low K_{ow} compounds or by changing pH for the ionic compounds. The Mag-PCMAs perform well with a wide range of different organic contaminants with different solubility and pK_a. It is expected that the Mag-PCMAs will have potentially wide application in the removal of emerging organic contaminants from water.

■ AUTHOR INFORMATION

Corresponding Author
*Tel: +1 805 893 7548. Fax: +1 805 893 7612. E-mail: keller@bren.ucsb.edu.

Notes
The authors declare the following competing financial interest(s): The corresponding author has a minor interest (less than 1%) in a start-up company that has taken the synthesis process to a pre-commercial level and is building prototype treatment systems for the industry.

■ REFERENCES

(1) Kuster, M.; de Alda, M. J.; Hernando, M. D.; Petrovic, M.; Martin-Alonso, J.; Barcelo, D. Analysis and occurrence of pharmaceuticals, estrogens, progestogens and polar pesticides in sewage treatment plant effluents, river water and drinking water in the Llobregat river basin (Barcelona, Spain). *J. Hydrol.* **2008**, *358*, 112−123.
(2) Bolong, N.; Ismail, A. F.; Salim, M. R.; Matsuura, T. A review of the effects of emerging contaminants in wastewater and options for their removal. *Desalination* **2009**, *239*, 229−246.
(3) Murray, K. E.; Thomas, S. M.; Bodour, A. A. Prioritizing research for trace pollutants and emerging contaminants in the freshwater environment. *Environ. Pollut.* **2010**, *158*, 3462−3471.
(4) Hoeger, B.; Kollner, B.; Dietrich, D. R.; Hitzfeld, B. Water-borne diclofenac affects kidney and gill integrity and selected immune

parameters in brown trout (*Salmo trutta f. fario*). *Aquat. Toxicol.* **2005**, *75*, 53–64.

(5) Pomati, F.; Castiglioni, S.; Zuccato, E.; Fanelli, R.; Vigetti, D.; Rossetti, C.; Calamari, D. Effects of a complex mixture of therapeutic drugs at environmental levels on human embryonic cells. *Environ. Sci. Technol.* **2006**, *40*, 2442–2447.

(6) Kim, Y.; Choi, K.; Jung, J. Y.; Park, S.; Kim, P. G.; Park, J. Aquatic toxicity of acetaminophen, carbamazepine, cimetidine, diltiazem and six major sulfonamides, and their potential ecological risks in Korea. *Environ. Int.* **2007**, *33*, 370–375.

(7) Kolok, A. S.; Snow, D. D.; Kohno, S.; Sellin, M. K.; Guillette, L. J. Occurrence and biological effect of exogenous steroids in the Elkhorn River, Nebraska, USA. *Sci. Total Environ.* **2007**, *388*, 104–115.

(8) Lyssimachou, A.; Arukwe, A. Alteration of brain and interrenal StAR protein, P450scc, and Cyp11 beta mRNA levels in Atlantic salmon after nominal waterborne exposure to the synthetic pharmaceutical estrogen ethynylestradiol. *J. Toxicol. Environ. Health, Part A* **2007**, *70*, 606–613.

(9) Lai, H. T.; Hou, J. H.; Su, C. I.; Chen, C. L. Effects of chloramphenicol, florfenicol, and thiamphenicol on growth of algae *Chlorella pyrenoidosa, Isochrysis galbana*, and *Tetraselmis chui*. *Ecotoxicol. Environ. Saf.* **2009**, *72*, 329–334.

(10) Carlsson, C.; Johansson, A. K.; Alvan, G.; Bergman, K.; Kuhler, T. Are pharmaceuticals potent environmental pollutants? Part I: Environmental risk assessments of selected active pharmaceutical ingredients. *Sci. Total Environ.* **2006**, *364*, 67–87.

(11) Hao, C. Y.; Lissemore, L.; Nguyen, B.; Kleywegt, S.; Yang, P.; Solomon, K. Determination of pharmaceuticals in environmental waters by liquid chromatography/electrospray ionization/tandem mass spectrometry. *Anal Bioanal. Chem.* **2006**, *384*, 505–513.

(12) Lin, A. Y. C.; Plumlee, M. H.; Reinhard, M. Natural attenuation of pharmaceuticals and alkylphenol polyethoxylate metabolites during river transport: Photochemical and biological transformation. *Environ. Toxicol. Chem.* **2006**, *25*, 1458–1464.

(13) Xu, W. H.; Zhang, G.; Zou, S. C.; Li, X. D.; Liu, Y. C. Determination of selected antibiotics in the Victoria Harbour and the Pearl River, South China using high-performance liquid chromatography-electrospray ionization tandem mass spectrometry. *Environ. Pollut.* **2007**, *145*, 672–679.

(14) Pedrouzo, M.; Reverte, S.; Borrull, F.; Pocurull, E.; Marce, R. M. Pharmaceutical determination in surface and wastewaters using high-performance liquid chromatography-(electrospray)-mass spectrometry. *J. Sep. Sci.* **2007**, *30*, 297–303.

(15) Zhang, S. Y.; Zhang, Q. A.; Darisaw, S.; Ehie, O.; Wang, G. D. Simultaneous quantification of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and pharmaceuticals and personal care products (PPCPs) in Mississippi river water, in New Orleans, Louisiana, USA. *Chemosphere* **2007**, *66*, 1057–1069.

(16) Santos, J. L.; Aparicio, I.; Callejon, M.; Alonso, E. Occurrence of pharmaceutically active compounds during 1-year period in wastewaters from four wastewater treatment plants in Seville (Spain). *J. Hazard. Mater.* **2009**, *164*, 1509–1516.

(17) Nakada, N.; Kiri, K.; Shinohara, H.; Harada, A.; Kuroda, K.; Takizawa, S.; Takada, H. Evaluation of pharmaceuticals and personal care products as water-soluble molecular markers of sewage. *Environ. Sci. Technol.* **2008**, *42*, 6347–6353.

(18) Stulten, D.; Zuhlke, S.; Lamshoft, M.; Spiteller, M. Occurrence of diclofenac and selected metabolites in sewage effluents. *Sci. Total Environ.* **2008**, *405*, 310–316.

(19) Chang, H.; Hu, J. Y.; Wang, L. Z.; Shao, B. Occurrence of sulfonamide antibiotics in sewage treatment plants. *Chin. Sci. Bull.* **2008**, *53*, 514–520.

(20) Latham, A. H.; Williams, M. E. Controlling transport and chemical functionality of magnetic nanoparticles. *Acc. Chem. Res.* **2008**, *41*, 411–420.

(21) Toprak, M. S.; McKenna, B. J.; Mikhaylova, M.; Waite, J. H.; Stucky, G. D. Spontaneous assembly of magnetic microspheres. *Adv. Mater.* **2007**, *19*, 1362–+.

(22) Ambashta, R. D.; Sillanpaa, M. Water purification using magnetic assistance: A review. *J. Hazard. Mater.* **2010**, *180*, 38–49.

(23) Yavuz, C. T.; Mayo, J. T.; Yu, W. W.; Prakash, A.; Falkner, J. C.; Yean, S.; Cong, L. L.; Shipley, H. J.; Kan, A.; Tomson, M.; Natelson, D.; Colvin, V. L. Low-field magnetic separation of monodisperse Fe_3O_4 nanocrystals. *Science* **2006**, *314*, 964–967.

(24) Shannon, M. A.; Bohn, P. W.; Elimelech, M.; Georgiadis, J. G.; Marinas, B. J.; Mayes, A. M. Science and technology for water purification in the coming decades. *Nature* **2008**, *452*, 301–310.

(25) Ai, Z. H.; Cheng, Y.; Zhang, L. Z.; Qiu, J. R. Efficient removal of Cr(VI) from aqueous solution with $Fe@Fe_2O_3$ core-shell nanowires. *Environ. Sci. Technol.* **2008**, *42*, 6955–6960.

(26) Tuutijarvi, T.; Lu, J.; Sillanpaa, M.; Chen, G. As(V) adsorption on maghemite nanoparticles. *J. Hazard. Mater.* **2009**, *166*, 1415–1420.

(27) Yantasee, W.; Warner, C. L.; Sangvanich, T.; Addleman, R. S.; Carter, T. G.; Wiacek, R. J.; Fryxell, G. E.; Timchalk, C.; Warner, M. G. Removal of heavy metals from aqueous systems with thiol functionalized superparamagnetic nanoparticles. *Environ. Sci. Technol.* **2007**, *41*, 5114–5119.

(28) Wang, P.; Shi, Q. H.; Shi, Y. F.; Clark, K. K.; Stucky, G. D.; Keller, A. A. Magnetic permanently confined micelle arrays for treating hydrophobic organic compound contamination. *J. Am. Chem. Soc.* **2009**, *131*, 182–188.

(29) Wang, H. T.; Keller, A. A.; Clark, K. K. Natural organic matter removal by adsorption onto magnetic permanently confined micelle arrays. *J. Hazard. Mater.* **2011**, *194*, 156–161.

(30) Clark, K. K.; Keller, A. A. Adsorption of perchlorate and other oxyanions onto magnetic permanently confined micelle arrays (Mag-PCMAs). *Water Res.* **2012**, *46*, 635–644.

(31) Lee, C. M. Environmental organic chemistry, 2nd edition (Schwarzenbach, Rene P.; Gschwend, Philip M.; Imboden, Dieter M.). *J. Chem. Educ.* **2003**, *80*, 1143.

(32) Langmuir, D. *Aqueous Environmental Geochemistry*; Prentice Hall: Upper Saddle River, NJ, 1997.