Simultaneous Removal of PAHs and Metal Contaminants from Water using Magnetic Nanoparticle Adsorbents

Yuxiong Huang[†], Aaron N. Fulton[‡], and Arturo A. Keller^{†}*

[†] Bren School of Environmental Science and Management, University of California at

Santa Barbara, CA, USA 93106

[‡] Department of Molecular, Cellular, and Developmental Biology, University of California,

Santa Barbara, CA, USA 93106

**Corresponding author.* Tel: +1 805 893 7548; fax: +1 805 893 7612. Email address:

keller@bren.ucsb.edu

1 **Abstract**

2 Many industrial wastewaters are contaminated with both heavy metal ions and organic
3 compounds, posing a major threat to public health and the environment. In this study,
4 magnetic nanoparticle adsorbents, namely Mag-PCMA-T, which contain a maghemite
5 core and a silica mesoporous layer that permanently confines surfactant micelles within
6 the mesopores, were synthesized to achieve simultaneous removal of polycyclic aromatic
7 hydrocarbons (PAHs) (1 mg/L) and metal contaminants (1 mg/L). The individual removal
8 efficiency of Cd^{2+} and acenaphthene using Mag-PCMA-T was evaluated under a range of
9 initial ion concentrations and adsorbent dosages, as well as the competitive adsorption
10 with Cd^{2+} and acenaphthene simultaneously present. The isotherms and kinetics of Cd^{2+}
11 and acenaphthene sorption onto Mag-PCMA-T were determined. Mag-PCMA-T
12 removed > 85% of the acenaphthene in less than 30 min, with relatively high sorption
13 capacity (up to 1060 mg/kg). Mag-PCMA-T also exhibited high sorption capacity for Cd-
14 $^{2+}$ (up to 2250 mg/kg). The simultaneous sorption performance was stable across a wide
15 pH range (4-9) as well as in the presence of competitive metal ions (Ca^{2+} and Mg^{2+}) or
16 natural organic matters. The Mag-PCMA-T can be regenerated and reused, providing a
17 sustainable, fast, convenient, and efficient approach for water treatment.

18

Keywords

Nanoparticle; Magnetic separation; PAHs; Metal Contaminants; Simultaneous removal.

1. Introduction

Persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAHs) and potentially toxic metal ions (Hübner et al., 2010) such as cadmium (Cd), pose a significant threat to public health and the environment due to their high toxicity and long persistence (Huang and Keller, 2015; Su et al., 2014; Su et al., 2016; Su et al., 2015; Vela et al., 2012). Numerous sites are contaminated by both PAHs and heavy metals, including e-wasting processing sites (Luo et al., 2011), manufactured gas plant sites (Thavamani et al., 2012), and river sediments (Feng et al., 2012), which require simultaneous remediation of PAHs and heavy metals. However, most recent studies have focused on the decontamination of PAHs (Chen et al., 2015; Lee et al., 2015) or heavy metals (Huang et al., 2014; Sargin et al., 2015) individually. Recently, more attention has been directed to the simultaneous removal of both heavy metals and organic contaminants from aquatic systems (Hung et al., 2016; Lalhmunsiamma et al., 2016; Liu et al., 2016; Luo et al., 2016; Ma et al., 2016a; Ma et al., 2016b; Zhang et al., 2016).

Surfactants can enhance the removal efficiency of hydrophobic organic compounds (HOCs) (Wang and Keller, 2008c) including PAHs and pesticides (Clark and Keller,

2012b) via micelles, which offer a good hydrophobic environment into which HOCs can partition (Wang and Keller, 2008a). Surfactants can also be used for metal contaminant remediation via complexation reactions and electronic interaction (Mulligan et al., 1999). Song et al. (2008) investigated simultaneous removal of phenanthrene and Cd from contaminated soils by a plant-derived biosurfactant, and demonstrated that phenanthrene was desorbed from soils by the partitioning of phenanthrene into surfactant micelles while Cd was removed via forming complexes with the external carboxyl groups of the micelle. However, one major drawback of directly applying surfactant for aquatic systems and soil remediation is the non-specific binding of the surfactants to clays and the organic matter naturally present (Wang and Keller, 2008b), which would cause the displacement and subsequent loss of the surfactant molecules during treatment (Hanna et al., 2002).

Thus, we developed magnetic permanently confined micelle arrays (Mag-PCMA) with a maghemite core and a silica porous layer that permanently confines surfactant micelles within the mesopores, which would reduce surfactant loss during use (Wang and Keller, 2008c). Featured as magnetic nanoparticle adsorbents, Mag-PCMA can be separated from solution by applying an external magnetic field and regenerated and reused (Adeleye et al., 2016). Based on the high removal performance Mag-PCMA for the remediation of HOCs (Wang and Keller, 2008c), pesticides (Clark and Keller, 2012b), natural organic matter (Wang et al., 2011), oxyanions (Clark and Keller, 2012a) and emerging organic

contaminants (Huang et al., 2016; Huang and Keller, 2013) in our previous studies, we propose using Mag-PCMAAs coupled with a nonionic surfactant, Triton X-100, for the simultaneous removal of PAHs and metal contaminants. In this study, acenaphthene and cadmium were selected to represent PAHs and metal contaminants, respectively, to study their sorption isotherms and kinetics onto Mag-PCMAAs in aqueous solution. In addition to characterizing their individual sorption, the simultaneous removal of acenaphthene and cadmium was investigated. Furthermore, the influence of pH, water hardness (Ca^{2+} , Mg^{2+}), and natural organic matter (NOM) on the performance of acenaphthene and cadmium sorption by the synthesized adsorbent was evaluated.

2. Experimental

2.1. Chemicals

Maghemite (iron (III) oxide) nanoparticles (30 nm in diameter) were purchased from Alfa Aesar (USA). Tetramethyl ammonium hydroxide (TMAOH) (25 wt % in water), Triton X-100, ammonia (28%), methanol, tetraethyl orthosilicate (TEOS), were purchased from Sigma-Aldrich (USA). Acenaphthene (99% pure) was purchased from Acros Organics (Geel, Belgium). Cadmium chloride anhydrous, calcium chloride dehydrate, and magnesium chloride were purchased from Fisher Scientific (USA). Standard Suwannee River NOM was obtained from the International Humic Substances Society (IHSS, USA). NOM stock solution (100 mg/L) was prepared by mixing a known amount of NOM with

deionized water (DI water) for 24 h. The pH of the stock solutions was then adjusted to 8 with 0.1 M and 0.01 M NaOH and HCl. All chemicals were used as received, without further purification. All solutions were prepared with deionized water (18 M Ω -cm) from a Barnstead NANOpure Diamond Water Purification System (USA).

2.2. Synthesis of Mag-PCMA

The core-shell structured Mag-PCMA were synthesized through a solvothermal reaction, which is a cooperative assembly of silica oligomers and surfactants onto the maghemite nanoparticles, as illustrated in Figure 1. Maghemite nanoparticles (0.1 g) were dispersed in 40 mL of TMAOH solution under constant mixing overnight as pre-treatment to activate the surface, which would help to generate a negative charge on the maghemite particles surface resulting in better binding of silicate and surfactant. The TMAOH-treated maghemite nanoparticles were washed thoroughly with ethanol. Then 1.5 mL of Triton X-100, nonionic surfactant was added to maghemite redispersed in water and ethanol in a volumetric ratio of 1:6 under constant stirring. Five mL of 28% ammonium hydroxide was added for base-catalyzed sol-gel hydrolysis along with 1 mL of TEOS to bind the surfactant onto the magnetic iron core. The mixture was stirred for 2 h at room temperature (22–25 °C). This method was adapted from the synthesis of Mag-PCMA reported in a previous study (Huang and Keller, 2013). To distinguish it from Mag-PCMA synthesized with other surfactants, this material is denominated Mag-PCMA-T, for Triton X-100.

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

2.3. Characterization of Mag-PCMA

Transmission electron microscopy (TEM) images were obtained using a JEOL 1230 Transmission Electron Microscope operated at 80 kV. Thermogravity measurements were used to investigate the amount of surfactant confined on magnetic particle adsorbents; thermogravimetric analyses (TGA) were carried out on a Mettler Toledo TGA/sDTA851e apparatus under an air flow of 100 mL/min with a heating rate of 5 °C/min. Magnetization measurements were performed on a Quantum Design MPMS 5XL superconducting quantum interference device (SQUID) Magnetometer. The zeta potential was measured using a Malvern Zetasizer (Nano-ZS; Malvern Instruments, Southborough, MA) with pH ranging from 4 to 10.

2.4. Batch sorption of PAHs and metal ions

For the individual isothermal experiments 5.0 mg of Mag-PCMA-T particles were mixed with 20 mL of acenaphthene (1 mg/L) or cadmium (Cd^{2+}) solution (1 mg/L) in 20 mL glass vials or 50 mL conical tubes, respectively, and the pH was adjusted to the desired condition

(range from 4 to 10) by using 0.1 M NaOH and 0.01 M HCl. Then, these tubes or vials were placed in an end-over-end shaker on a Dayton-6Z412A Parallel Shaft (USA) roller mixer with a speed of 70 rpm at room temperature for 24 h to ensure sufficient equilibration time. The variation in pH before and after the experiments is indicated in Table S1. Adsorption kinetics studies were carried out at the same conditions as individual isothermal experiments but for a set amount of time, varying from 1 min to 24 h, with pH=7. After this mixing, the Mag-PCMA-T particles were separated from the mixture with an Eclipse magnet. All experiments were conducted at ambient temperature (22–25 °C).

The concentration of adsorbent was varied from 0.25 to 1.25 g/L to study the individual adsorption isotherms of acenaphthene, NOM, or Cd^{2+} onto Mag-PCMA-T at pH 7. Additionally, solutions with varying initial concentrations of acenaphthene, NOM, or Cd^{2+} , which ranged from 0.5 mg/L to 50 mg/L were treated with the same procedure as above at pH 7 and 5.0 mg Mag-PCMA-T.

Simultaneous sorption was conducted with various dosages of Mag-PCMA-T particles (1 mg to 25 mg) mixed with 20 mL of acenaphthene (1 mg/L) and Cd^{2+} (1 mg/L) solution with or without 20 mg/L NOM present. The influence of solution pH and ionic strength on the simultaneous removal was investigated by mixing 10 mg of Mag-PCMA-T particles with 20 mL of acenaphthene and Cd^{2+} solution (1 mg/L) under various solution pH

(ranging from 4 to 10) and concentration of Ca^{2+} or Mg^{2+} (ranging from 1 mg/L to 50 mg/L), respectively.

2.5. Regeneration and reuse of Mag-PCMA-T

To investigate the regeneration and reuse of Mag-PCMA-T, a mixed solution with 1 mg/L acenaphthene, 1 mg/L Cd^{2+} and 20 mg/L NOM were used with the same adsorption process, followed by separation of the Mag-PCMA-T from solution with the handheld magnet. The collected Mag-PCMA-T was first rinsed with methanol to extract sorbed acenaphthene and NOM. Then the Mag-PCMA-T was rinsed with 1% HCl to extract sorbed Cd^{2+} . The regenerated Mag-PCMA-T particles were then reused for subsequent acenaphthene sorption experiments. The sorption, extraction, and reuse processes were repeated for five times. Changes in sorption capacity was determined at every cycle.

2.6. Analysis

An Agilent 7900 inductively coupled plasma with mass spectroscopy (ICP-MS) was used to analyze the concentration of Cd^{2+} . A Shimadzu high performance liquid chromatograph (HPLC) system (SPD-M10AVP, Shimadzu, MD) equipped with an Ascentis C-18 column (250 × 4.6 mm, 10 μm) and a UV-Vis spectrometer (BioSpec 1601, Shimadzu, MD) was used for PAHs analysis.

Removal efficiency and sorption capacity of PAHs and metal ions was calculated as:

$$\text{Removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

$$148 \quad \text{Sorption capacity} = q_e = \frac{(C_0 - C_t) \cdot V}{m} \quad (2)$$

149 where C_0 and C_t are the initial and final concentrations of PAHs or metal ions (mg/L), m
 150 is the mass of Mag-PCMA-Ts (g), and V is the volume of solution (L).

151 The equilibrium adsorption of PAHs and metal ions was evaluated according to
 152 Langmuir and Freundlich isotherms by Eq. 3 and Eq. 4, respectively (Morel and Hering,
 153 1993):

$$154 \quad \frac{C_e}{q_e} = \frac{1}{K_L \cdot q_m} + \frac{C_e}{q_m} \quad (3)$$

$$155 \quad \log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

156 where C_e is solute concentration (mg/L) at equilibrium and q_e is amount adsorbed
 157 (mg/g), q_m is the maximum sorption capacity (mg/g). K_L (L/mg) and K_F (mg/g)/(L/mg)⁻ⁿ
 158 are the Langmuir and Freundlich sorption equilibrium constants, respectively.

159 Kinetics were analyzed using the pseudo-second order model by Eq. 5 (Coleman et al.,
 160 1956), since it has been shown to be appropriate for many sorption processes (Ho, 2006;
 161 Ho and McKay, 1999; Wu et al., 2009):

$$162 \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

163 where k_2 ($\frac{g}{mg \cdot h}$) are the equilibrium rate constant of kinetics.

All tests were performed in triplicate and analysis of variance (ANOVA) was used to test the significance of results. A $p < 0.05$ was considered to be statistically significant.

3. Results and discussion

3.1. Characterization of Mag-PCMA-T

The core/shell structure of a Mag-PCMA-T is shown in TEM images (Figure 2), and the shell layer (silica porous framework) is approximately 20 nm as determined by TEM. The size of particles varied from hundreds of nanometers to several micrometers due to aggregation via magnetic forces or crosslinking of the silica framework. The weight percentage of surfactant within the silica framework of Mag-PCMA-T was determined by the difference of initial and final mass of the sample in the TGA measurement and was approximately 7.45% of the total mass of Mag-PCMA-T. Magnetic characterization by SQUID magnetometer at 300 K showed that maghemite and Mag-PCMA-T have magnetization saturation values of 52.8 and 14.65 emu/g, respectively (Figure 2C), indicating a relatively high magnetization of Mag-PCMA-T particles even with a thick silica coating. The zeta potential in the initial pH range of 4 to 10 is presented in Figure 2D for a suspension of Mag-PCMA-T in DI water. In this pH range, the zeta potential of Mag-PCMA-T is negative (-30.11 to -41.65 mv), and decreases slightly as pH increases. Even though the surfactant, Triton X-100, is nonionic, due to the pretreatment by TMAOH in the synthesis the surface of maghemite particle was strongly negatively charged (Wang

et al., 2009). It suggests the formation of anionic negatively charged surface complexes on the Mag-PCMA-T particles.

Figure 2. TEM micrographs of Mag-PCMA-T (A) at 400,000 $\times$, scale bar=20 nm and (B) at 500,000 $\times$, scale bar=20 nm; (C) the magnetic hysteresis loops of Mag-PCMA-T and maghemite nanoparticles; (D) zeta potential of Mag-PCMA-T particles as a function of pH.

3.2. Sorption isotherms of PAHs, metal ions and NOM

Figure 3 presents the experimental results of the non-competitive sorption for Cd^{2+} , acenaphthene and NOM for the range of concentrations studied, as well as the fit of the Langmuir and Freundlich isotherm model (fitted parameter values are summarized in Table 1). The Langmuir model provided a slightly better fit for Cd^{2+} , while the Freundlich model fitted acenaphthene and NOM adsorption better, based on the correlation coefficients (R^2) in Table 1. This suggests a multilayer sorption process (Weber et al., 1991). Since Triton X-100 is a nonionic surfactant confined in micelles within the silica framework of Mag-PCMA-T, there are several potential remediation mechanisms for these three different categories of contaminants. Triton X-100 is a poly(ethylene oxide), and interactions are predominantly between the ethylene oxide groups and the chlorinated and nonchlorinated hydrophobic organic contaminants (Wang and Keller, 2008b; Wang and Keller, 2008c). Due to the hydrophobic cores, the surfactant micelles can enhance the apparent acenaphthene solubility (Rosen and Kunjappu, 2012), which would promote the hydrophobic interaction between acenaphthene and the confined micelles. The ethylene oxide chain on the Triton X-100 can form complexes with metal ions (Kikuchi et al., 1992), explaining the sorption of Cd^{2+} onto Mag-PCMA-Ts. In addition, since the surface of Mag-PCMA-Ts is negatively charged, there are also favorable electrostatic interactions with cationic ions such as Cd^{2+} . NOM consists of both hydrophobic and hydrophilic regions as well as polar groups, such

210 as carboxylic groups (Tan, 2014). The sorption mechanism of NOM onto Mag-PCMA-T
211 could be the hydrophobic interaction between the hydrophobic fraction of NOM and
212 micelles to enhance the apparent NOM's hydrophobic groups' solubility (Rosen and
213 Kunjappu, 2012) ; or/and the hydrogen bond between carboxylic groups on NOM and
214 poly (ethylene oxide) groups on surfactants (Wang et al., 2011).

Figure 3. Langmuir adsorption isotherms fit for (A) Cd²⁺; (B) acenaphthene; and (C) NOM onto Mag-PCMA-T at pH 7; and Freundlich adsorption isotherms fit for (D) Cd²⁺;

(E) acenaphthene; and (F) NOM onto Mag-PCMA-T at pH 7, symbols represent experimental data, and red line represents model prediction.

Table 1. Isotherm parameters for Cd^{2+} , acenaphthene and NOM sorption on Mag-PCMA-T

	Langmuir			Freundlich		
	q_m (mg/g)	K_L (L/mg)	R^2	K_F ((mg/g)/(L/mg) ⁻ⁿ)	1/n	R^2
Cd^{2+}	1.48	62.4	0.999	1.81	0.27	0.998
Acenaphthene	0.39	-10.3	0.997	48.0	1.64	0.999
NOM	4.19	0.13	0.908	0.24	1.10	0.991

3.3. Sorption kinetics of PAHs and metal contaminants

Time dependent removal of acenaphthene and Cd^{2+} (initial concentration = 1 mg/L) by Mag-PCMA-T (0.25 g/L) showed rapid adsorption of acenaphthene and Cd^{2+} ; around 95% of the maximum sorption capacities were obtained in the first 30 min, as shown in Figure 4A. The pseudo-second order (Figure 4B and C) kinetic model was used to investigate the adsorption rate of acenaphthene and Cd^{2+} onto Mag-PCMA-Ts, and the kinetic parameters were listed in Table 2. Mag-PCMA-T's fast sorption kinetics for both acenaphthene and Cd^{2+} is due to the relatively high portion of the confined surfactant micelles. It also indicates the silica framework did not show significant effect on the diffusion of PAHs and metal contaminants into the micelles.

Figure 4. (A) Sorption capacity of acenaphthene and Cd²⁺ versus time; and sorption kinetics fitted by pseudo-second order of (B) acenaphthene; (C) Cd²⁺ onto Mag-PCMA-T

in solution at pH 7, symbols represent experimental data, and red line represents model prediction.

Table 2. Kinetic parameters for Cd^{2+} and acenaphthene sorption on Mag-PCMA-T

	q_e (mg/g)	k_2 (g/h·mg)	R^2
Cd^{2+}	0.78	0.98	0.978
Acenaphthene	4.19	1.43	0.975

3.4. Simultaneous sorption of PAHs, metal contaminants and NOM

Based on the above studies, Mag-PCMA-T can remove POPs, metals and NOM from contaminated water. Thus, there is the potential for simultaneous remediation of these contaminants (POPs and metals) even in the presence of NOM, which usually would affect the adsorption behavior (Luo et al.). The simultaneous removal of acenaphthene and Cd^{2+} is presented in Figure 5. Compared to the individual sorption of acenaphthene or Cd^{2+} , the sorption capacities decreased, indicating some competitive sorption between acenaphthene and Cd^{2+} . It results from the fact that both acenaphthene and Cd^{2+} interact with the poly(ethylene oxide) groups on the surfactant micelles (Kikuchi et al., 1992; Wang and Keller, 2008b; Wang and Keller, 2008c), given that the number of the reactive sites is limited. Competitive sorption is also evidenced by the fact that as Mag-PCMA-T dosage increased, the differences in sorption capacity between individual and simultaneous sorption decreased. Noticeably, competitive sorption results in less impact

252 on the adsorption capacity of acenaphthene than on Cd^{2+} . This can be explained by the
 253 faster sorption kinetics on acenaphthene, based on the kinetic constant k_2 (Table 2),
 254 which allows acenaphthene to occupy the available active sites first. This result also
 255 agrees with the fact that the difference was less significant with higher Mag-PCMA-T
 256 dosage, since there are more available sites.

257
 258 Figure 5. Simultaneous sorption of Cd^{2+} and acenaphthene as a function of adsorbent
 259 dose with a fixed initial concentration of 1 mg/L Cd^{2+} and acenaphthene equally.

Individual sorption capacity of Cd^{2+} and acenaphthene under same conditions are presented for comparison.

Furthermore, as NOM constitutes a major fraction of the organic matter in water, the simultaneous sorption of Cd^{2+} and acenaphthene in the presence of NOM was also investigated, as shown in Figure 6. The sorption capacity of Mag-PCMA-T for acenaphthene decreased slightly in the presence of NOM. This is not surprising because NOM also competes for the limited ethylene oxide groups on the surfactant micelles. Also, the concentration of NOM (20 mg/L) was much higher than acenaphthene, which increases the driving force and results in higher sorption of NOM. On the other hand, the sorption capacity of Cd^{2+} increased in the presence of NOM, since a significant amount of polar groups (e.g. carboxylic groups) on NOM (Tan, 2014) can also complex Cd^{2+} (Otto et al., 2001). The differences were smaller when a higher amount of Mag-PCMA-T was added.

Figure 6. Simultaneous sorption of Cd^{2+} , acenaphthene and NOM as a function of adsorbent dose with a fixed initial concentration of 1 mg/L of Cd^{2+} and acenaphthene equally in the presence of 20 mg/L NOM.

3.5. Effect of pH on simultaneous removal

pH is an important factor in water chemistry, which may affect the speciation of solutes as well as the surface charge of adsorbents. In Figure 7, as pH increased, the simultaneous sorption of both Cd^{2+} and acenaphthene increased, with a particularly significant increase in Cd^{2+} sorption. As indicated in Figure 2D, the surface of

Mag-PCMA-T is increasingly more negatively charged as pH increases. Simulation of the aqueous speciation of cadmium, using Visual MINTEQ (Gustafsson, 2006) software, indicates that for pH from 3 to 10, cadmium in DI water at these concentrations is mostly present as Cd^{2+} , which is favorable for the electrostatic interactions with Mag-PCMA-T's negatively charged surface across this pH range. It suggests that the dominant mechanism of Cd^{2+} remediation by Mag-PCMA-T is electrostatic interaction. The slight increase in the removal on acenaphthene indicates that the major removal path for HOCs is via hydrophobic interactions between the confined surfactant micelles and HOCs (Edwards et al., 1991), and electronic forces has less impact. There could be a slight rearrangement of the surfactant micelles with increasing pH, leading to slightly more sorption capacity for HOCs on the hydrophobic surfaces of Triton-X. Since acenaphthene has a very high pK_a value (>15) (Montgomery, 2007), higher than the range of pH (4.0–10.0) considered in the current study, it is neutral within the pH range (Atkins and De Paula).

Figure 7. Simultaneous sorption of Cd²⁺ and acenaphthene as a function of pH.

3.6. Effect of water hardness on simultaneous removal

Water hardness is usually expressed as the total amount of Ca²⁺ and Mg²⁺ present in the water, which varies in different water matrices. As complexes between poly(ethylene oxide) groups on the surfactant micelles and metal ions are not specific, thus, Ca²⁺ and Mg²⁺ may also compete with simultaneous sorption of Cd²⁺ and acenaphthene (Kikuchi et al., 1992). Figure 8 shows the simultaneous removal performance of Cd²⁺ and acenaphthene using Mag-PCMA-T in the presence of different concentrations of Ca²⁺ or

304 Mg^{2+} . No significant difference was found on the sorption capacity of acenaphthene with
305 either Ca^{2+} or Mg^{2+} concentrations up to 50 mg/L. However, the sorption capacity of Cd^{2+}
306 sharply decreased when more Mg^{2+} was present, while no obvious change was observed
307 with Ca^{2+} presence. Previous studies indicate that alkaline earth metal ion and Ca^{2+}
308 complexes with Triton X-100 showed low formation constant (Kikuchi et al., 1992),
309 suggesting less competitive sorption would be observed between Cd^{2+} and Ca^{2+} .
310

311

Figure 8. Simultaneous sorption of Cd²⁺ and acenaphthene in the presence of (A) Ca²⁺ (from 1 mg/L to 50 mg/L) and (B) Mg²⁺ (from 1 mg/L to 50 mg/L) at pH 7.

3.7. Regeneration and reuse of Mag-PCMA-T

To demonstrate the regenerability and reusability of the Mag-PCMA-T, the recovery of acenaphthene and NOM sorbed onto the Mag-PCMA-T was investigated using methanol extraction while the adsorbed Cd²⁺ was extracted by dilute acid (1% HCl). The simultaneous removal performance of acenaphthene, NOM and Cd²⁺ mixed solution during five continuous cycles of regeneration and reuse are shown in Figure 9. No

significant losses of sorption capacity of all these three compounds was observed for the regenerated Mag-PCMA-T up to 5 cycles, indicating good reusability of Mag-PCMA-T.

Figure 9. Sorption of acenaphthene onto Mag-PCMA-T during five regeneration cycles.

4. Conclusions

Micelle array permanently confined magnetic nanoparticle adsorbents with nonionic surfactant were successfully synthesized with Triton X-100 (Mag-PCMA-T), and the novel adsorbents performed well to remove Cd^{2+} , acenaphthene and NOM, individually

and simultaneously. The isotherm study indicated that hydrophobic interactions played an important role in the sorption process of acenaphthene while a complexation reaction is the most likely dominant mechanism for Cd^{2+} sorption. The kinetic study showed that sorption of PAHs and metal contaminants by Mag-PCMA-T was rapid. Mag-PCMA-T can simultaneously remove Cd^{2+} and acenaphthene with or without NOM present. The simultaneous sorption of Cd^{2+} and acenaphthene by Mag-PCMA-Ts was not significantly affected by the change of water hardness and increased with an increase of pH. Moreover, the adsorbent exhibited excellent regeneration performance and can be used for simultaneous removal of Cd^{2+} , NOM and acenaphthene several times without significant loss of sorption capacity. We demonstrated that Mag-PCMA-T can provide a fast, effective and more sustainable approach for simultaneous decontamination of PAHs, metal ions and NOM.

ACKNOWLEDGEMENTS

This work made use of MRL Central Facilities supported by the MRSEC Program of the National Science Foundation under awards NO. DMR 1121053; a member of the NSF-funded Materials Research Facilities Network (www.mrfn.org). We thank the MRL Central Facilities for the use of their TGA and SQUID instruments as well as Amanda

347 Strom and Paige Roberts at the UCSB MRL for their help with these instruments. AAK

348 also appreciates Agilent Technologies for their Agilent Thought Leader Award.

349

350 **References:**

- 351 Adeleye AS, Conway JR, Garner K, Huang Y, Su Y, Keller AA. Engineered
 352 nanomaterials for water treatment and remediation: Costs, benefits, and
 353 applicability. *Chemical Engineering Journal* 2016; 286: 640-662.
- 354 Atkins P, De Paula J. *Physical chemistry*, 2002. Oxford University Press, ca; 57: 80.
- 355 Chen C-F, Binh NT, Chen C-W, Dong C-D. Removal of polycyclic aromatic
 356 hydrocarbons from sediments using sodium persulfate activated by temperature
 357 and nanoscale zero-valent iron. *Journal of the Air & Waste Management*
 358 *Association* 2015; 65: 375-383.
- 359 Clark KK, Keller AA. Adsorption of perchlorate and other oxyanions onto magnetic
 360 permanently confined micelle arrays (Mag-PCMA-T). *Water research* 2012a; 46:
 361 635-644.
- 362 Clark KK, Keller AA. Investigation of two magnetic permanently confined micelle array
 363 sorbents using nonionic and cationic surfactants for the removal of PAHs and
 364 pesticides from aqueous media. *Water, Air, & Soil Pollution* 2012b; 223:
 365 3647-3655.
- 366 Coleman NT, Mcclung AC, Moore DP. Formation Constants for Cu(II)-Peat Complexes.
 367 *Science* 1956; 123: 330-331.
- 368 Edwards DA, Luthy RG, Liu ZB. Solubilization of Polycyclic Aromatic-Hydrocarbons in
 369 Micellar Nonionic Surfactant Solutions. *Environmental Science & Technology*
 370 1991; 25: 127-133.
- 371 Feng SL, Mai BX, Wei GJ, Wang XM. Genotoxicity of the sediments collected from
 372 Pearl River in China and their polycyclic aromatic hydrocarbons (PAHs) and
 373 heavy metals. *Environmental Monitoring and Assessment* 2012; 184: 5651-5661.
- 374 Gustafsson JP. Visual minteq. Capturado em de 2006; 26.
- 375 Hanna K, Beurroies I, Denoyel R, Desplandier-Giscard D, Galarneau A, Di Renzo F.
 376 Sorption of hydrophobic molecules by organic/inorganic mesostructures. *Journal*
 377 *of Colloid and Interface Science* 2002; 252: 276-283.
- 378 Ho Y-S. Review of second-order models for adsorption systems. *Journal of hazardous*
 379 *materials* 2006; 136: 681-689.
- 380 Ho Y-S, McKay G. Pseudo-second order model for sorption processes. *Process*
 381 *biochemistry* 1999; 34: 451-465.
- 382 Huang Y, Fulton AN, Keller AA. Optimization of porous structure of superparamagnetic
 383 nanoparticle adsorbents for higher and faster removal of emerging organic
 384 contaminants and PAHs. *Environmental Science: Water Research & Technology*
 385 2016.

386 Huang Y, Keller AA. Magnetic Nanoparticle Adsorbents for Emerging Organic
 387 Contaminants. *ACS Sustainable Chemistry & Engineering* 2013; 1: 731-736.
 388 Huang Y, Keller AA. EDTA functionalized magnetic nanoparticle sorbents for cadmium
 389 and lead contaminated water treatment. *Water Research* 2015; 80: 159-168.
 390 Huang Y, Yang J-K, Keller AA. Removal of Arsenic and Phosphate from Aqueous
 391 Solution by Metal (Hydr-)oxide Coated Sand. *ACS Sustainable Chemistry &
 392 Engineering* 2014; 2: 1128-1138.
 393 Hübner R, Astin KB, Herbert RJ. 'Heavy metal'—time to move on from semantics to
 394 pragmatics? *Journal of Environmental Monitoring* 2010; 12: 1511-1514.
 395 Hung P-C, Chang S-H, Ou-Yang C-C, Chang M-B. Simultaneous removal of PCDD/Fs,
 396 pentachlorophenol and mercury from contaminated soil. *Chemosphere* 2016; 144:
 397 50-58.
 398 Kikuchi Y, Suzuki T, Sawada K. Liquid—liquid extraction of alkaline earth metal ions
 399 with a non-ionic surfactant having a poly (oxyethylene) chain (Triton X-100).
 400 *Analytica chimica acta* 1992; 264: 65-70.
 401 Lalhmunsiam, Tiwari D, Lee S-M. Surface-functionalized activated sericite for the
 402 simultaneous removal of cadmium and phenol from aqueous solutions:
 403 Mechanistic insights. *Chemical Engineering Journal* 2016; 283: 1414-1423.
 404 Lee H, Jang Y, Lee YM, Lee H, Kim G-H, Kim J-J. Enhanced removal of PAHs by
 405 *Peniophora incarnata* and ascertainment of its novel ligninolytic enzyme genes.
 406 *Journal of environmental management* 2015; 164: 10-18.
 407 Liu W, Sun W, Borthwick AGL, Wang T, Li F, Guan Y. Simultaneous removal of Cr(VI)
 408 and 4-chlorophenol through photocatalysis by a novel anatase/titanate nanosheet
 409 composite: Synergetic promotion effect and autosynchronous doping. *Journal of
 410 Hazardous Materials* 2016; 317: 385-393.
 411 Luo C, Liu C, Wang Y, Liu X, Li F, Zhang G, et al. Heavy metal contamination in soils
 412 and vegetables near an e-waste processing site, south China. *Journal of Hazardous
 413 Materials* 2011; 186: 481-490.
 414 Luo F, Chen Z, Megharaj M, Naidu R. Simultaneous removal of trichloroethylene and
 415 hexavalent chromium by green synthesized agarose-Fe nanoparticles hydrogel.
 416 *Chemical Engineering Journal* 2016; 294: 290-297.
 417 Luo M, Huang Y, Zhu M, Tang Y-n, Ren T, Ren J, et al. Properties of different natural
 418 organic matter influence the adsorption and aggregation behavior of TiO₂
 419 nanoparticles. *Journal of Saudi Chemical Society*.
 420 Ma L, Chen Q, Zhu J, Xi Y, He H, Zhu R, et al. Adsorption of phenol and Cu(II) onto
 421 cationic and zwitterionic surfactant modified montmorillonite in single and binary
 422 systems. *Chemical Engineering Journal* 2016a; 283: 880-888.

423 Ma L, Zhu J, Xi Y, Zhu R, He H, Liang X, et al. Adsorption of phenol, phosphate and
 424 Cd(II) by inorganic–organic montmorillonites: A comparative study of single and
 425 multiple solute. *Colloids and Surfaces A: Physicochemical and Engineering*
 426 *Aspects* 2016b; 497: 63-71.
 427 Montgomery JH. *Groundwater chemicals desk reference*: CRC Press, 2007.
 428 Morel FMM, Hering JG. *Principles and Applications of Aquatic Chemistry*: Wiley, 1993.
 429 Mulligan CN, Yong RN, Gibbs BF, James S, Bennett HPJ. Metal removal from
 430 contaminated soil and sediments by the biosurfactant surfactin. *Environmental*
 431 *Science & Technology* 1999; 33: 3812-3820.
 432 Otto WH, Burton SD, Carper WR, Larive CK. Examination of cadmium (II)
 433 complexation by the Suwannee River fulvic acid using ¹¹³Cd NMR relaxation
 434 measurements. *Environmental science & technology* 2001; 35: 4900-4904.
 435 Rosen MJ, Kunjappu JT. *Surfactants and interfacial phenomena*: John Wiley & Sons,
 436 2012.
 437 Sargin İ, Kaya M, Arslan G, Baran T, Ceter T. Preparation and characterisation of
 438 biodegradable pollen–chitosan microcapsules and its application in heavy metal
 439 removal. *Bioresource technology* 2015; 177: 1-7.
 440 Su Y, Adeleye AS, Huang Y, Sun X, Dai C, Zhou X, et al. Simultaneous removal of
 441 cadmium and nitrate in aqueous media by nanoscale zerovalent iron (nZVI) and
 442 Au doped nZVI particles. *Water Research* 2014; 63: 102-111.
 443 Su Y, Adeleye AS, Huang Y, Zhou X, Keller AA, Zhang Y. Direct Synthesis of Novel
 444 and Reactive Sulfide-modified Nano Iron through Nanoparticle Seeding for
 445 Improved Cadmium-Contaminated Water Treatment. *Scientific Reports* 2016; 6:
 446 24358.
 447 Su Y, Adeleye AS, Keller AA, Huang Y, Dai C, Zhou X, et al. Magnetic
 448 sulfide-modified nanoscale zerovalent iron (S-nZVI) for dissolved metal ion
 449 removal. *Water Research* 2015; 74: 47-57.
 450 Tan KH. *Humic matter in soil and the environment: principles and controversies*: CRC
 451 Press, 2014.
 452 Thavamani P, Megharaj M, Naidu R. Multivariate analysis of mixed contaminants (PAHs
 453 and heavy metals) at manufactured gas plant site soils. *Environmental Monitoring*
 454 *and Assessment* 2012; 184: 3875-3885.
 455 Vela N, Martinez-Menchon M, Navarro G, Perez-Lucas G, Navarro S. Removal of
 456 polycyclic aromatic hydrocarbons (PAHs) from groundwater by heterogeneous
 457 photocatalysis under natural sunlight. *Journal of Photochemistry and*
 458 *Photobiology a-Chemistry* 2012; 232: 32-40.

- Wang H, Keller AA, Clark KK. Natural organic matter removal by adsorption onto magnetic permanently confined micelle arrays. *Journal of hazardous materials* 2011; 194: 156-161.
- Wang P, Keller AA. Adsorption of hydrophobic organic compounds onto a hydrophobic carbonaceous geosorbent in the presence of surfactants. *Environmental Toxicology and Chemistry* 2008a; 27: 1237-1243.
- Wang P, Keller AA. Particle-size dependent sorption and desorption of pesticides within a water-soil-nonionic surfactant system. *Environmental Science & Technology* 2008b; 42: 3381-3387.
- Wang P, Keller AA. Partitioning of hydrophobic organic compounds within soil-water-surfactant systems. *Water Research* 2008c; 42: 2093-2101.
- Wang P, Shi QH, Shi YF, Clark KK, Stucky GD, Keller AA. Magnetic Permanently Confined Micelle Arrays for Treating Hydrophobic Organic Compound Contamination. *Journal of the American Chemical Society* 2009; 131: 182-188.
- Weber WJ, Mcginley PM, Katz LE. Sorption Phenomena in Subsurface Systems - Concepts, Models and Effects on Contaminant Fate and Transport. *Water Research* 1991; 25: 499-528.
- Wu F-C, Tseng R-L, Huang S-C, Juang R-S. Characteristics of pseudo-second-order kinetic model for liquid-phase adsorption: A mini-review. *Chemical Engineering Journal* 2009; 151: 1-9.
- Zhang J, Gong J-L, Zenga G-M, Ou X-M, Jiang Y, Chang Y-N, et al. Simultaneous removal of humic acid/fulvic acid and lead from landfill leachate using magnetic graphene oxide. *Applied Surface Science* 2016; 370: 335-350.

Graphical Abstract