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Authors

Huang, Yuxiong
Fulton, Aaron N
Keller, Arturo A

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Simultaneous removal of PAHs and metal contaminants from water using magnetic nanoparticle adsorbents

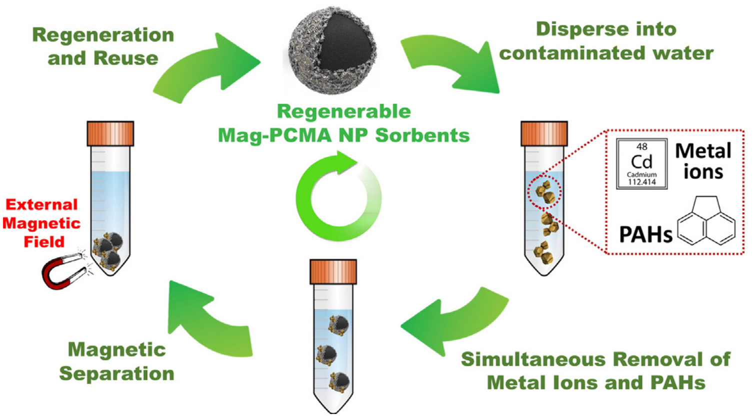
Yuxiong Huang [a], Aaron N. Fulton [b], Arturo A. Keller [a,*]

[a] Bren School of Environmental Science and Management, University of California, Santa Barbara, CA 93106, USA
[b] Department of Molecular, Cellular, and Developmental Biology, University of California, Santa Barbara, CA 93106, USA

HIGHLIGHT

- Fast magnetic nanosorbents for simultaneous removal of PAHs and metals
- Stable remediation performance across wide pH range (4–9)
- High water hardness resistance across wide range of Ca^{2+} or Mg^{2+} concentration
- Low energy use for regeneration of adsorbent and able to reuse multiple times

GRAPHICAL ABSTRACT



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ABSTRACT

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

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* Corresponding author.
E-mail address: keller@bren.ucsb.edu (A.A. Keller).

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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; Sargın 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; Lalhmunsiama and Lee, 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-PCMAs) 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-PCMAs 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-PCMAs 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-PCMAs 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-PCMAs 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 dihydrate, 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 MΩ-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 Fig. 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 milliliters 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-PCMAs 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.

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

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

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 were 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:

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

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

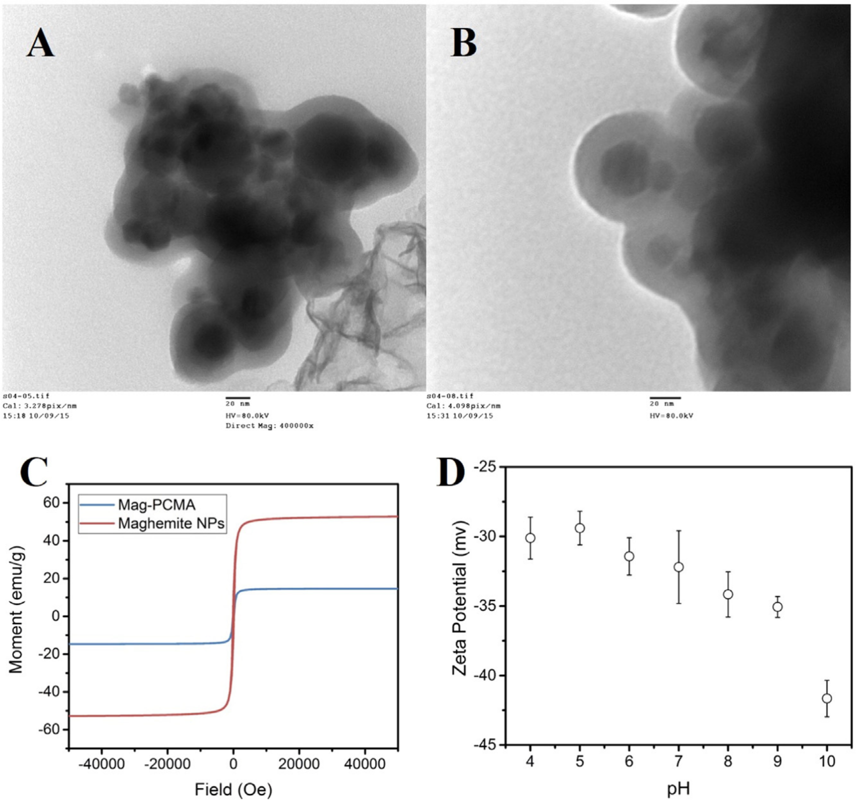

Fig. 2. TEM micrographs of Mag-PCMA-T (A) at 400,000×, scale bar = 20 nm and (B) at 500,000×, scale bar = 20 nm; (C) the magnetic hysteresis loops of Mag-PCMA-T and maghemite nanoparticles; (D) zeta potential of Mag-PCMA-T particles as a function of pH.

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

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

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot q_m} + \frac{C_e}{q_m} \tag{3}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

where C_e is solute concentration (mg/L) at equilibrium and q_e is amount adsorbed (mg/g), q_m is the maximum sorption capacity (mg/g). K_L (L/mg) and K_F $(\mathrm{mg/g})/(\mathrm{L/mg})^{-n}$ are the Langmuir and Freundlich sorption equilibrium constants, respectively.

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

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \tag{5}$$

where k_2 $\left(\frac{g}{mg \cdot h}\right)$ 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 (Fig. 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

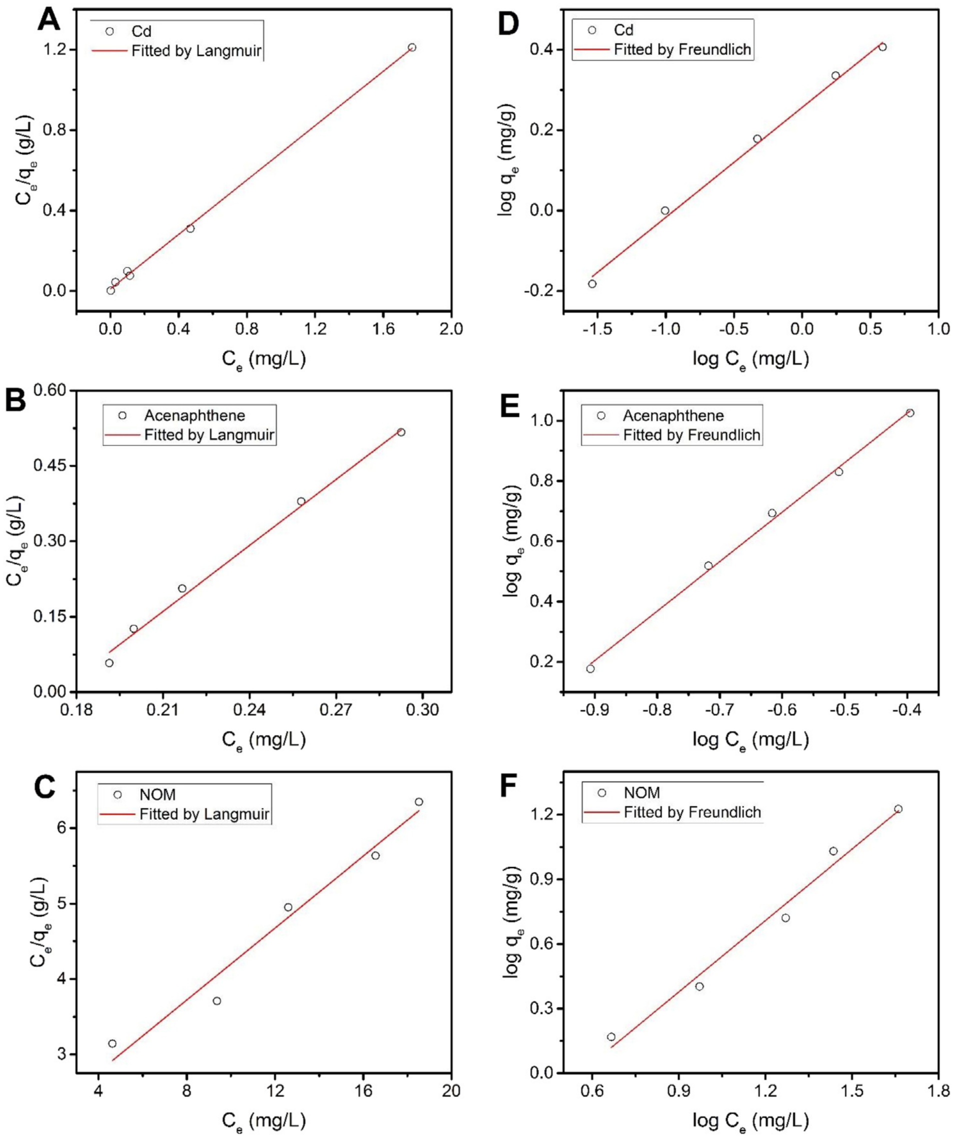

Fig. 3. Langmuir adsorption isotherms fit for (A) Cd^{2+}; (B) acenaphthene; and (C) NOM onto Mag-PCMA-T at pH 7; and Freundlich adsorption isotherms fit for (D) Cd^{2+}; (E) acenaphthene; and (F) NOM onto Mag-PCMA-T at pH 7, symbols represent experimental data, and red line represents model prediction. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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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

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 (Fig. 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 Fig. 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.

3.2. Sorption isotherms of PAHs, metal ions and NOM

Fig. 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 as carboxylic groups (Tan, 2014). The sorption mechanism of NOM onto Mag-PCMA-T could be the hydrophobic interaction between the hydrophobic fraction of NOM and micelles to enhance the apparent NOM's hydrophobic groups' solubility (Rosen and Kunjappu,

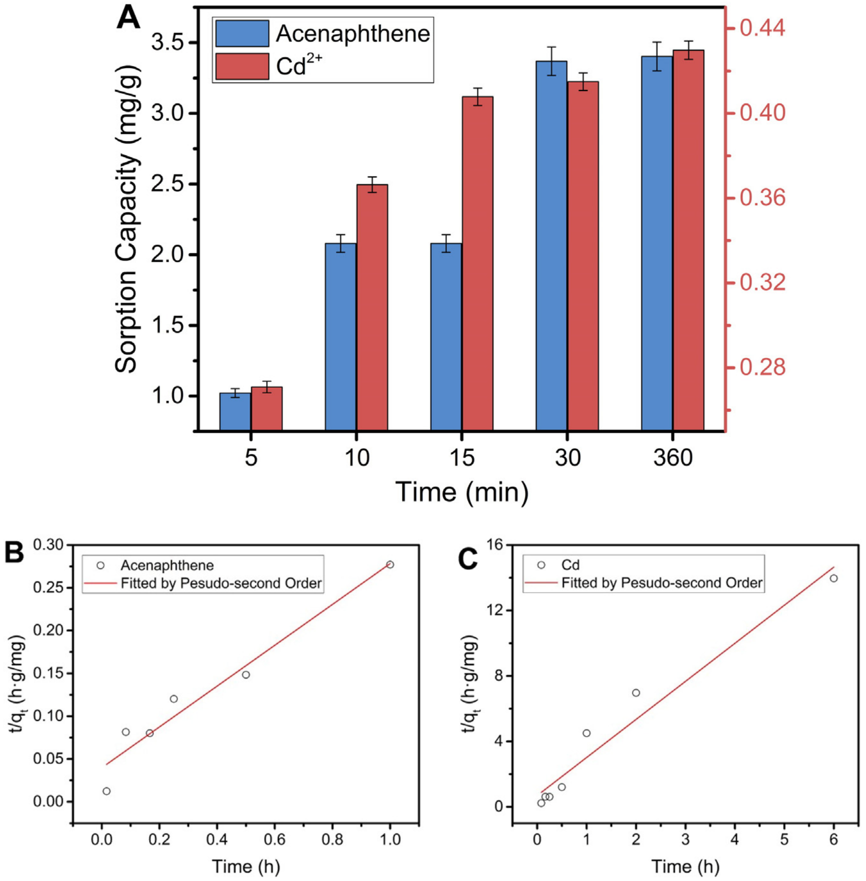

Fig. 4. (A) Sorption capacity of acenaphthene and Cd^{2+} versus time; and sorption kinetics fitted by pseudo-second order of (B) acenaphthene; (C) Cd^{2+} onto Mag-PCMA-T in solution at pH 7, symbols represent experimental data, and red line represents model prediction. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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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

2012); or/and the hydrogen bond between carboxylic groups on NOM and poly (ethylene oxide) groups on surfactants (Wang et al., 2011).

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 Fig. 4A. The pseudo-second order (Fig. 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.

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

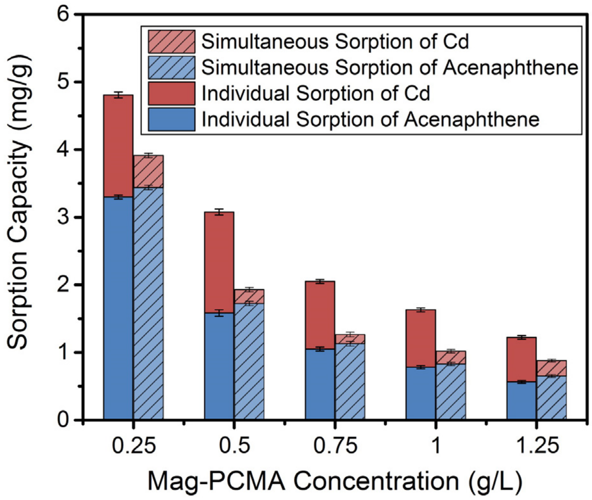

Fig. 5. Simultaneous sorption of Cd^{2+} and acenaphthene as a function of adsorbent dose with a fixed initial concentration of 1 mg/L Cd^{2+} and acenaphthene equally. Individual sorption capacity of Cd^{2+} and acenaphthene under same conditions are presented for comparison.

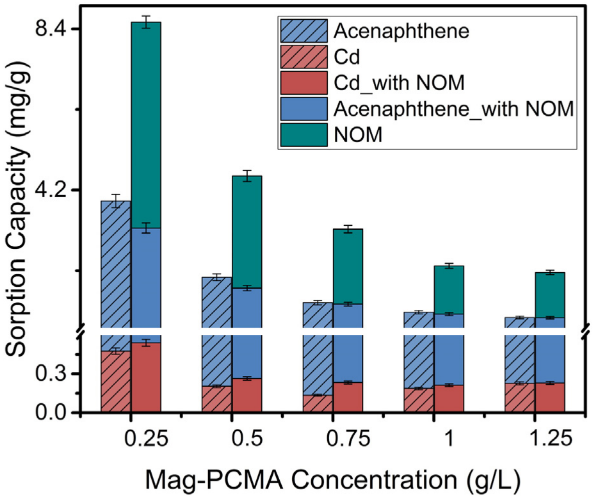

Fig. 6. Simultaneous sorption of Cd^{2+}, acenaphthene and NOM as a function of adsorbent dose with a fixed initial concentration of 1 mg/L of Cd^{2+} and acenaphthene equally in the presence of 20 mg/L NOM.

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 Fig. 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.

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 Fig. 7, as pH increased, the simultaneous sorption of both Cd^{2+} and

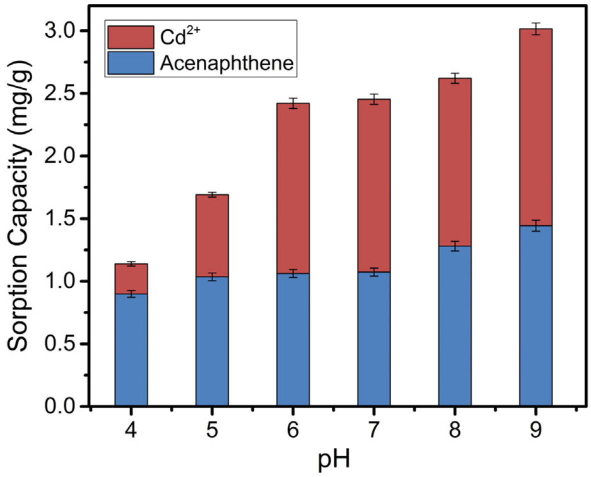

Fig. 7. Simultaneous sorption of Cd^{2+} and acenaphthene as a function of pH.

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acenaphthene increased, with a particularly significant increase in Cd^{2+} sorption. As indicated in Fig. 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, 2002).

3.6. Effect of water hardness on simultaneous removal

Water hardness is usually expressed as the total amount of Ca^{2+} and Mg^{2+} 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, Ca^{2+} and Mg^{2+} may also compete with simultaneous sorption of Cd^{2+} and acenaphthene (Kikuchi et al., 1992). Fig. 8 shows the simultaneous removal performance of Cd^{2+} and acenaphthene using Mag-PCMA-T in the presence of different concentrations of Ca^{2+} or Mg^{2+}. No significant difference was found on the sorption capacity of acenaphthene with either Ca^{2+} or Mg^{2+} concentrations up to 50 mg/L. However, the sorption capacity of Cd^{2+} sharply decreased when more Mg^{2+} was present, while no obvious change was observed with Ca^{2+} presence. Previous studies indicate that alkaline earth metal ion and Ca^{2+} complexes with Triton X-100 showed low formation constant (Kikuchi et al., 1992), suggesting less competitive sorption would be observed between Cd^{2+} and Ca^{2+}.

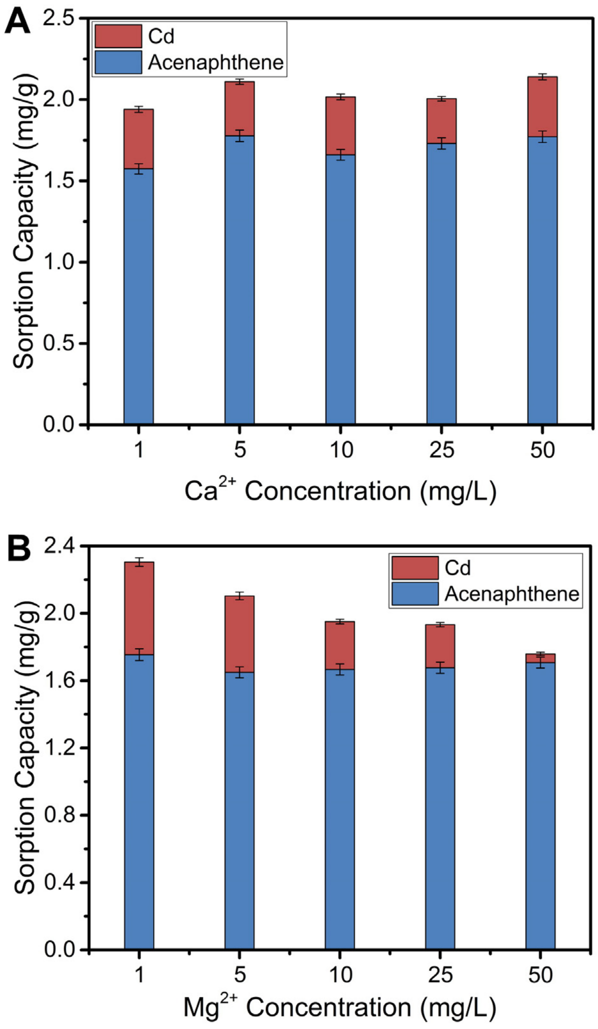

Fig. 8. Simultaneous sorption of Cd^{2+} and acenaphthene in the presence of (A) Ca^{2+} (from 1 mg/L to 50 mg/L) and (B) Mg^{2+} (from 1 mg/L to 50 mg/L) at pH 7.

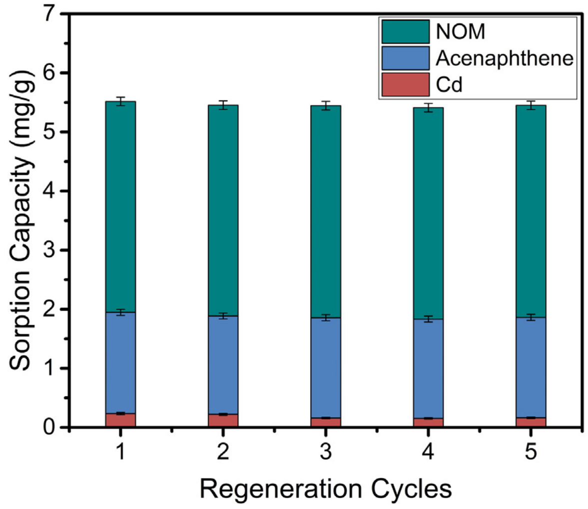

Fig. 9. Sorption of acenaphthene onto Mag-PCMA-T during five regeneration cycles.

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 Cd^{2+} was extracted by dilute acid (1% HCl). The simultaneous removal performance of acenaphthene, NOM and Cd^{2+} mixed solution during five continuous cycles of regeneration and reuse are shown in Fig. 9. No significant losses of sorption capacity of all these three compounds were observed for the regenerated Mag-PCMA-T up to 5 cycles, indicating good reusability of Mag-PCMA-T.

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

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approach for simultaneous decontamination of PAHs, metal ions and NOM.

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