

Magnetic pollen grains as sorbents for facile removal of organic pollutants in aqueous media

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ABSTRACT

Plant materials have long been demonstrated to sorb organic compounds. However, there are no known reports about pollen grains acting as sorbents to remove hydrophobic organic compounds (HOCs) such as pesticides, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) from contaminated waters. We report a facile and effective method to remove HOCs from water using magnetized short ragweed (*Ambrosia artemisiifolia*) pollen grains. We dispersed the magnetized pollen grains in two different water samples – deionized (DI) and natural storm water to mimic real environmental conditions likely to be encountered during treatment. The magnetized pollen grains were readily separated from the aqueous media via a magnetic field after adsorption of the HOCs. We measured the adsorption of five representative HOCs (acenaphthene, phenanthrene, atrazine, diuron, and lindane) onto magnetized ragweed pollen in different aqueous matrices. We demonstrate that the adsorption capacity of the magnetized ragweed pollen can be regenerated to a large extent for reuse as a sorbent. Our results also indicate that the magnetized pollen grains are as effective as activated carbon (AC) in removing HOCs from both types of contaminated waters. The high HOC sorption of the ragweed pollen allows it to have potential remediation application in the field under realistic conditions.

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1. Introduction

Pollen grains are the physiological containers that produce the male gametes of seed plants, and have long been closely studied by plant physiologists [1–8], chemists [9], chemical engineers [10] and material scientists [11] for diverse reasons and applications. The outer layer (exine) of the grain is made of an extremely stable and complex biopolymer known as sporopollenin which is highly resistant to chemical attack, and has been functionalized for uses in ion exchange [12] and drug delivery [9]. For this study, short ragweed (*Ambrosia artemisiifolia*) was chosen as representative pollen to demonstrate the capability of pollen to act as sorbents for organic pollutants in aqueous media given its wide availability worldwide [13]. It is likely that other types of pollen can have similar sorption capabilities and thus production can be increased to meet demand for environmental remediation via harvesting from flowering seed plants. The potential for pollen grains to be used as sorbents has not been evaluated before.

Hydrophobic organic compounds (HOCs) including many pesticides, some pharmaceuticals, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) are ubiquitous envi-

ronmental contaminants and their presence in drinking water, stormwater [14,15], wastewater, soils and sediments poses a serious risk to human and local ecosystem health. One of the most commonly used sorbents for HOC removal in contaminated water is activated carbon (AC). However, current state-of-the-art regeneration of AC involves high temperatures [16] (up to 800 °C) and the resulting energy costs and carbon footprint [17] makes it appealing to look for a low-cost alternative of similar or better efficiency. Many novel polymeric sorbents have been developed [18–21], but the cost of their synthesis has generally made them not viable. Similarly, magnetic sorbents [22] utilizing carbon/iron oxide composites [23,24] have demonstrated potential as a promising new class of materials for environmental remediation of heavy metal ions and organic pollutants but use relatively expensive AC, carbon nanotubes or a carbon-based surfactants. Magnetic separation of the sorbent from the treated aqueous media by an external magnetic field is much easier, faster and cheaper than the traditional methods of filtration, centrifugation or gravitational separation. High reusability of the sorbent is also a desirable property.

2. Experimental



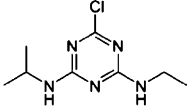
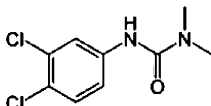
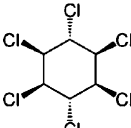
2.1. Materials

The five representative HOCs (acenaphthene, phenanthrene, atrazine, diuron, and lindane) chosen as sorbates were obtained

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Table 1
Properties of the five selected HOCs for sorption studies [42].

Class of compound	Compound name	Molecular weight (g/mol)	Structure, molecular formula or chlorine content	Octanol–water partition coefficient, log K_{ow} at 25 °C	Sorption partition coefficient, log K_{oc} at 25 °C in DI water
PAHs	Acenaphthene	154.207	 $C_{12}H_{10}$	3.92	5.38
	Phenanthrene	178.229	 $C_{14}H_{10}$	4.46	6.12
Pesticides	Atrazine	215.686	 $C_8H_{14}ClN_5$	2.68	2.24
	Diuron	233.097	 $C_9H_{10}Cl_2N_2O$	2.42	2.59
	Lindane	290.832	 $C_6H_6Cl_6$	3.76	3.30

from Chem Service Inc. (West Chester, PA). The physicochemical properties of the HOCs are given in Table 1. Iron(II) chloride, iron(III) chloride, hydrochloric acid, nitric acid, ethanol and aqueous ammonia were obtained from Fisher Scientific Inc. Short ragweed (*A. artemisiifolia*) pollen grains were purchased from Greer Labs (Lenoir, NC). Darco G-60 100 mesh activated carbon (AC) was purchased from Fisher Scientific. All chemicals and reagents were used as received with no further purification.

2.2. Synthesis and characterization of magnetic ragweed pollen grains

The synthesis of magnetized ragweed pollen was done in four steps. First, 13.32 g $FeCl_3 \cdot 6H_2O$ (Fisher), 19.88 g $FeCl_2 \cdot 4H_2O$ (Fisher), 5 mL 5 M HCl (Fisher), 40 mL Nanopure deionized water and 5 mL ethanol (Sigma–Aldrich) were mixed in a 100 mL flask followed by heating to 40 °C until the Fe salts were completely dissolved. Second, 0.5 g of the short ragweed (*A. artemisiifolia*) pollen grains (Greer Labs, Lenoir, NC) were dispersed in 15 mL of the iron chlorides solution and stirred for 2 h at room temperature. After the complexation of pollen and iron chloride salts, the residual dissolved Fe salts were filtered. The filter paper with collected pollen grains was rinsed with 100–200 mL of 18 M Ω Milli-Q water, until the visible rinseate was clear. The filtered samples were transferred back into a flask and 5 mL of 1 M ammonia solution was added. After 1 h the magnetized pollen grains were filtered again and rinsed with 200 mL of Milli-Q water. The magnetized ragweed pollen were left in a scintillation vial and put into a convection oven at 60 °C to dry overnight before use.

The diameters of both magnetized ragweed pollen and unmodified pollen grains were measured using a scanning electron microscope (SEM XL40 Sirion FEG Digital Scanning Microscope, FEI company, Hillsboro, OR) equipped with an Oxford energy-

dispersive X-ray spectroscopy (EDS) analysis system. A Leica 1510S cryostat (Leica Microsystems Inc., Bannockburn, IL) was used to cut open both types of pollen grains prior to imaging with EDS in order to determine the concentration of Fe inside and outside the pollen grains.

2.3. Characterization of water samples

Two types of water samples were used to determine the sorption behavior of the magnetized ragweed pollen in different aqueous matrices. Lab water samples were of the deionized form (DI water) treated by reverse osmosis on a Milli-Q Plus system (Millipore) to 18 M Ω cm resistivity while stormwater samples were collected from the influent to a stormwater treatment lagoon at the University of California Santa Barbara (UCSB). Stormwater was considered since it is a common transport pathway for PAHs and pesticides [14,15]. The characterization of the UCSB stormwater samples were done previously [25]. The composition of the stormwater is presented in Table 2. Briefly, total organic carbon (TOC) was measured using a Shimadzu TOC-V instrument (Shimadzu Scientific Instruments). The pH was measured using an Oakton pH meter (Ion 510 series, Fisher Scientific). Conductivity, resistivity, and total dissolved solids (TDS) were measured with a Fisher Scientific Traceable* Conductivity, Resistivity, and TDS Meter (Fisher Scientific). Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo iCAP 6300 ICP) was used to measure the concentration of five metal ions. Chloride ion concentration was determined by the argentometric method, following Standard Methods (19th Ed., Method 4500-Cl-B). Phosphate, sulfate, nitrite, and nitrate ions were measured via colorimetry (HACH portable DR/890, HACH Company, Loveland, CO). HCO_3^- was determined by titration via a phenolphthalein/total alkalinity test (model WAT-MP-DR, Lamotte Chemical Products, MD).

Table 2
Characteristics of the UCSB stormwater sample used.

	Units	UCSB storm runoff
pH		7.09
TOC	μM C	1564
UV ₂₅₄	cm ⁻¹	0.84
Conductivity	μS	591
Resistivity	MΩ	0.002
Total dissolved solids	mg/L	394
SO ₄ ²⁻	mg/L	110
Cl ⁻	mg/L	116.7
NO ₃ ⁻	mg/L	1.33
NO ₂ ⁻	mg/L	0.03
HCO ₃ ⁻	mg/L CaCO ₃	120.7
PO ₄ ³⁻	mg/L	5.73
K ⁺	mg/L	17.70
Na ⁺	mg/L	36.33
Ca ²⁺	mg/L	46.78
Mg ²⁺	mg/L	13.03
Fe ²⁺ and Fe ³⁺	mg/L	0.02
Ionic strength	eq./L	9.63 × 10 ⁻³

2.4. Sorption isotherms of HOCs onto pollen and AC in contaminated waters

Batch sorption experiments were conducted using 15 mL test tubes with Teflon-lined screw caps. Each test tube was dosed with 5 mg of the magnetized pollen or AC and 10 mL of contaminant in either DI or storm water. All sorption studies were performed within the solubility range [26] of the HOCs used as reported in Table 3 and the batches were run at room temperature on a roller table at 60 rpm to mix vials end over end to disperse the sorbent throughout the aqueous phase. Mixing was done for 24 h to achieve equilibrium. Magnetized ragweed pollen was magnetically separated from the aqueous phase while unmodified pollen and AC were allowed to settle by gravity to the bottom of the test tube. The final pH of the supernatants after the sorption experiments were measured to be between 6.3 and 6.5 for the DI waters, while the storm waters were at pH 7.09 before and after the 24 h equilibration. Our data showed that the pH values of the mixtures were constant throughout the sorption process. The final aqueous concentration of HOC after equilibration was determined by one of three analytical instruments: gas chromatograph mass spectrometer GC–MS (Saturn 2100T, Varian Inc., Walnut Creek, CA), high performance liquid chromatography (HPLC) system (SPD-M10AVP, Shimadzu, MD), or UV–Vis spectrometer (BioSpec 1601, Shimadzu, MD). Acenaphthene and lindane concentrations in the aqueous phase were analyzed using solid phase microextraction (SPME) and GC–MS. A 7 μm diameter PDMS fiber was used to extract the organic from the aqueous phase for 20 min and the fiber was placed in the injector and desorbed for 5 min. The GC–MS was initially set to 50 °C and held for 5 min. The column was then ramped to 320 °C at a rate of 12 °C/min and held for an additional 10 min. Atrazine and diuron concentrations were analyzed with HPLC. The UV detector of the HPLC monitored the absorbance at 222 nm for atrazine and 247 nm for diuron. The UV–Vis spectrophotometer was used to measure the concentration of phenanthrene in the water at 251 nm. A set of standards were equilibrated with each batch of

Table 3
HOC solubility in water and concentration ranges used for recovery experiments.

HOC	Solubility in water mg/L 20–25 °C [26]	Concentration range evaluated (mg/L)
Acenaphthene	3.8	0.5–3.0
Phenanthrene	1.1	0.2–1.0
Atrazine	30	1–20
Diuron	42	1–24
Lindane	17	1–6

sorption experiments to take into account any aging effects from the 24 h equilibration and a calibration curve was performed daily with a regression (R^2 value) of 0.98 or greater. Concentration of the organic compound sorbed to the magnetized ragweed pollen or activated carbon was calculated as the difference between the concentration dosed versus the equilibrated concentration left in the aqueous phase. Sorption isotherms and linear fits were analyzed using Origin Labs 8.1 software.

2.5. Recovery of organic contaminants from magnetized ragweed pollen

Acetone was used to extract a representative organic contaminant, acenaphthene, by sonicating the magnetized ragweed pollen with 3 mL of acetone in a Branson Ultrasonic Bath at 25 °C for 30 min. Extracts were analyzed via direct injection using a Varian 2100T GC–MS. The column was held at 50 °C for 5 min and ramped to 320 °C at 12 °C/min and held for an additional 10 min.

2.6. Reuse and regeneration of magnetized ragweed pollen

Magnetized ragweed pollen grains were mixed for four cycles of 24 h after being dosed with diuron. The aqueous phase was decanted each time and analyzed via HPLC for percent mass removed after each round of reuse. Between cycles the particles were not rinsed with solvent. Fresh diuron was added at the same concentration as the original solution to each round of sorption to investigate the number of times the sorbent could be reused without purification or regeneration in solvent. Methanol extractions of diuron from magnetized pollen were done in a separate study to examine regeneration capacity of the sorbent.

2.7. BET surface area analysis

AC, magnetized and unmodified pollen grains were analyzed with BET nitrogen adsorption (Tristar, Micromeritics Instruments, Norcross, GA) to determine the surface area of the materials.

3. Results and discussion

3.1. Coating of magnetite onto pollen

In Fig. 1, the successful coating of magnetite onto the short ragweed pollen grains is presented using SEM images. The presence of iron was confirmed by EDS in Fig. 2 and the elemental composition is listed in Table 4. EDS sampling was done on two different pollen grains – one iron-oxide coated and one uncoated. There are variations in the elemental composition from grain to grain, and in our EDS samples, the elemental composition values have an approximate ±10% standard deviation based on the multiple measurements taken. Natural ragweed pollen grains are composed mainly of carbon and oxygen with no iron. Fig. 3 shows that MRP

Table 4
Comparison of the average elemental composition of unmodified ragweed pollen grains with magnetized ragweed pollen by EDS. Standard deviations of the elemental composition is approximately ±10%.

Ragweed pollen			Magnetized ragweed pollen		
Element	Weight%	Atomic%	Element	Weight%	Atomic%
C	57.91	64.75	C	60.25	73.05
O	41.80	35.09	O	25.28	23.01
Na	0.22	0.13	Na	0.17	0.07
Si	0.07	0.03	Si	0.15	0.07
Cl	0.00	0.00	Cl	0.74	0.30
Fe	0.00	0.00	Fe	13.41	3.5
Totals	100.00		Totals	100.00	

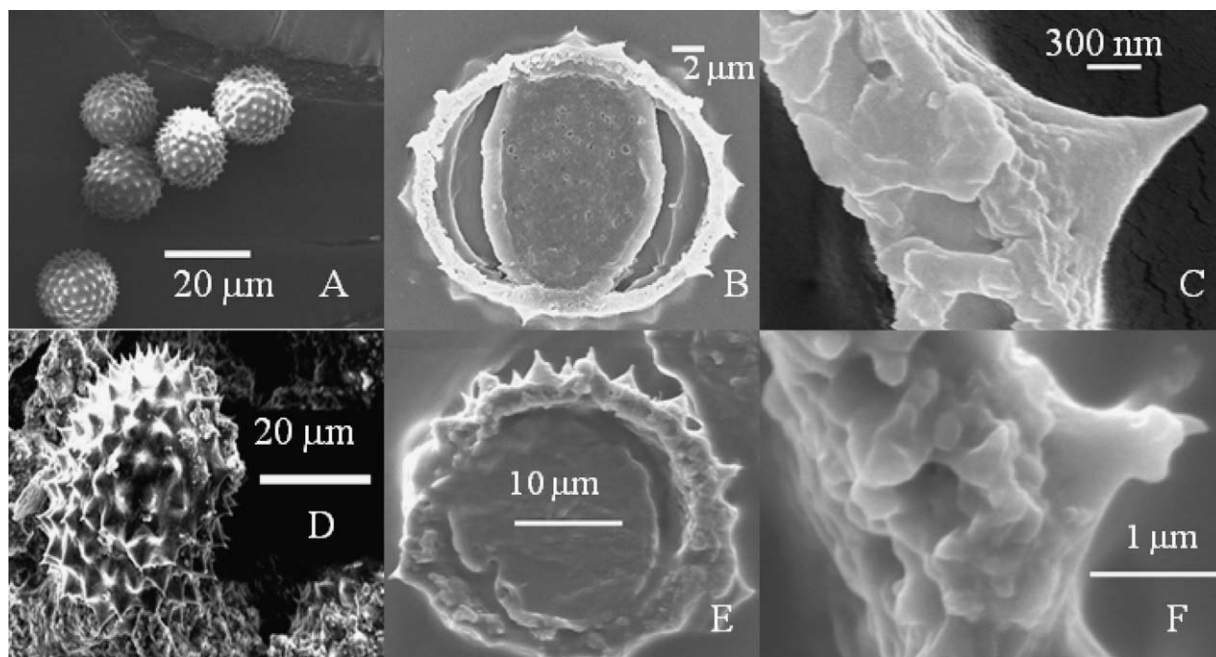


Fig. 1. SEM images of untreated (A–C) and magnetized (D–F) ragweed pollen grains. Close up views (E and F) of the sliced pollen grains show a deposit of magnetite on the outer and inner surfaces of the magnetized pollen exine. EDS spectra shows that the Fe composition in the magnetized ragweed pollen is ~4%. Fe is not within detectable limits in the untreated pollen.

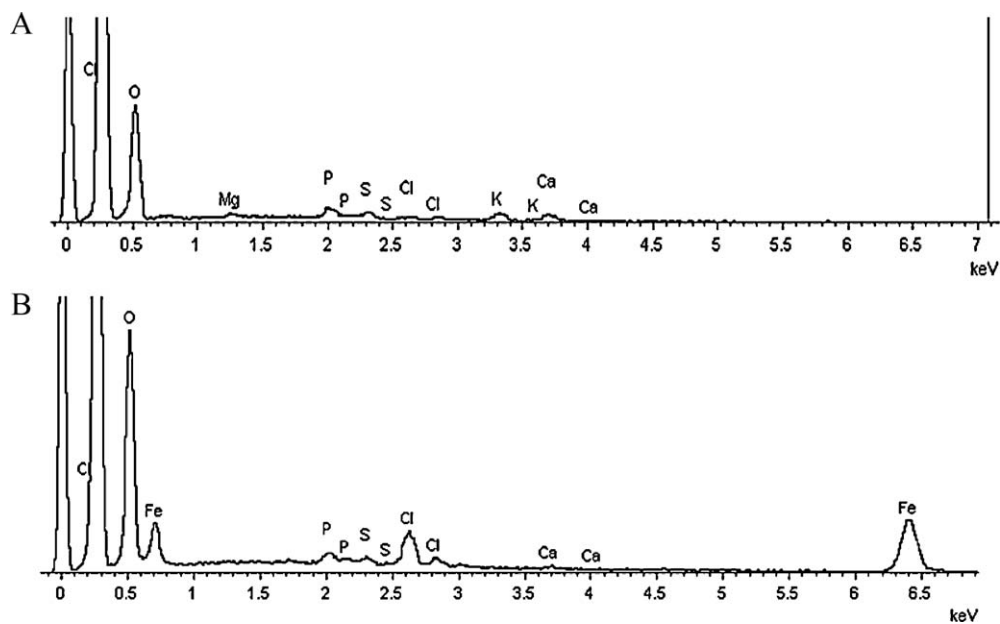


Fig. 2. EDS spectra of the pollen cross sections in Fig. 1C and F show the absence (A) and presence (B) of the Fe peak in untreated and magnetized pollen, respectively.

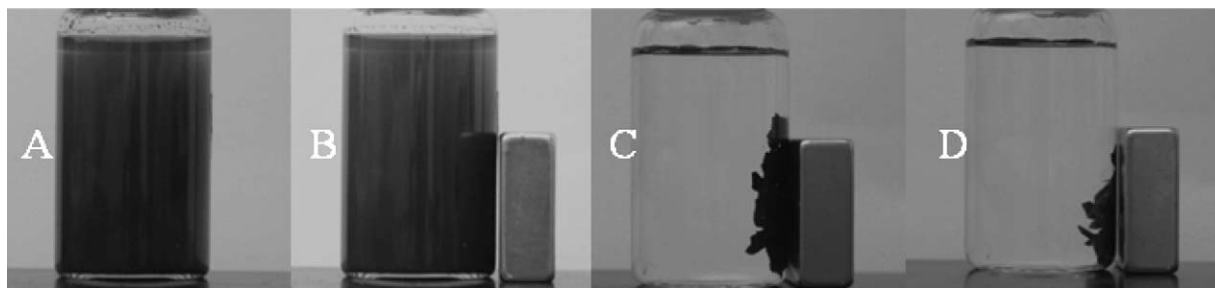


Fig. 3. Testing the recovery of the magnetized ragweed pollen from contaminated media by external magnetic field. (A) Magnetized ragweed pollen are introduced to a vial containing acenaphthene contaminated water. (B) A permanent magnet is placed next to the vial and starts to attract the magnetic pollen grains. (C) After 10 min, most of the pollen grains are on the right side of the vial. (D) Magnetized ragweed pollen remains attracted to the magnet 30 min after being first placed under an external magnetic field.

Table 5
Measured HOC sorption parameters from magnetized ragweed pollen (MRP) and activated carbon (AC) in DI water.

HOC	K_f (mg/g) (L/mg) ⁻ⁿ		n		Regression	
	MRP	AC	MRP	AC	MRP	AC
Acenaphthene	1.395 ± 0.008	1.247 ± 0.003	1.005 ± 0.030	0.953 ± 0.020	0.996	0.997
Phenanthrene	1.367 ± 0.011	1.371 ± 0.020	1.011 ± 0.030	1.008 ± 0.057	0.996	0.983
Atrazine	1.857 ± 0.015	1.965 ± 0.009	1.010 ± 0.020	1.003 ± 0.008	0.996	0.999
Diuron	1.144 ± 0.030	1.966 ± 0.030	1.109 ± 0.030	0.991 ± 0.030	0.996	0.996
Lindane	1.219 ± 0.070	1.289 ± 0.020	0.940 ± 0.14	1.098 ± 0.040	0.997	0.995

Table 6
Measured HOC sorption parameters from magnetized ragweed pollen (MRP) and activated carbon (AC) in stormwater.

HOC	K_f (mg/g) (L/mg) ⁻ⁿ		n		Regression	
	MRP	AC	MRP	AC	MRP	AC
Acenaphthene	2.032 ± 0.020	1.644 ± 0.025	0.915 ± 0.055	1.027 ± 0.066	0.975	0.976
Phenanthrene	1.487 ± 0.007	1.480 ± 0.012	0.948 ± 0.021	1.01 ± 0.037	0.997	0.992
Atrazine	1.692 ± 0.051	1.745 ± 0.091	1.031 ± 0.042	0.944 ± 0.073	0.986	0.954
Diuron	1.869 ± 0.025	1.863 ± 0.025	0.893 ± 0.022	0.946 ± 0.023	0.996	0.997
Lindane	1.429 ± 0.025	1.616 ± 0.014	1.062 ± 0.043	0.808 ± 0.025	0.989	0.995

has sufficient loading of iron oxides that the suspension acts like a ferrofluid [27] in the presence of an external magnetic field.

3.2. Isotherms modeling

We evaluated the sorption of the HOCs onto magnetized ragweed pollen by the batch equilibration method for both waters. Plotting C_e versus q showed a linear relationship for all sorbents. The log transformation of the Freundlich isotherm also produced plots with linear regression values >0.95. The best fit of the data suggests a Freundlich isotherm [26,28] due to its better correlation between the empirical parameters q and C_e :

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

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 (mg/g) (L/mg)⁻ⁿ, and n the measure of adsorption intensity (dimensionless). Eq. (1) can be linearized by taking the logarithmic form:

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

and compared to the experimental data for HOCs.

Comparison of the Freundlich exponent, n , for MRP in DI water and storm water suggests there is minimal competition for sorption in the presence of salts and natural organic matter as the values decreased an average of only 3% across all HOCs for MRP.

3.3. Sorbents' HOC sorption performance

Fig. 4 presents the sorption performance of MRP compared to that of AC for the HOCs in DI water, while Tables 5–7 list the Freundlich parameters as well as the average efficiency of contaminant removal from both types of sorbent together with

untreated ragweed pollen (URP) in the different aqueous matrices. There are multiple ways [29,30] to interpret the empirical relationships between sorption constant K_f , and the Freundlich exponent n . Schwarzenbach et al. [26] uses the value of n relative to 1 to determine the relative interactions of increased sorbate with sorbent. Values greater than 1 suggest a favorable free energy of further sorption in the presence of more sorbate. Values less than 1 are isotherms where the free energy of binding more sorbate decreases with increased concentration. The value of n is dimensionless and provides information about the multi-site binding on AC, MRP and URP. Figs. 4 and 5 and Tables 5 and 6 show that MRP behaves similarly to AC with regard to the sorption of HOCs in DI and storm waters. Both non-chlorinated and chlorinated HOCs sorbed to magnetized and untreated ragweed pollen as well as activated carbon, demonstrating ragweed pollen's potential to act as a non-specific organic contaminant sorbent in water. The outermost layer of the pollen grain, also known as the exine, is composed of sporopollenin which is a complex polymer made of carboxylic acids cross-linked with saturated and unsaturated aliphatic chains with varying amounts of aromatics [31,32]. Since sporopollenin contains polar, nonpolar, aliphatic and aromatic functional groups, the significant difference in sorption of the various HOCs to the two types of pollen is a result of the differences in interactions with the exine surface via dispersion (London) forces, polar interactions, and π - π interactions. There are large disparities in sorption capacity of the three adsorbents depending on the aqueous matrix, as shown in Table 7. We observed an enhanced sorption of organics in stormwater compared to DI water in most of our experimental conditions. We used the concentration of 1 mg/L for the HOC concentration as that was the closest we have to being environmentally relevant in contaminated waters [33]. This enhanced sorption can be attributed to the fact that natural waters contain organic matter, as measured by total organic carbon (TOC) in Table 2, which

Table 7
Percent recovery of HOC at one concentration compared with three sorbents untreated ragweed pollen (URP), magnetized ragweed pollen (MRP) and activated carbon (AC) in DI water and stormwater. All values presented are the average of a minimum of three data points with a standard deviation range of 0–5.3%.

	[HOC] (mg/L)	URP		MRP		AC	
		DI	Stormwater	DI	Stormwater	DI	Stormwater
Acenaphthene	1.0	62.2	100.0	72.4	100.0	62.2	94.3
Phenanthrene	1.0	67.2	95.0	67.9	80.0	72.5	77.5
Atrazine	1.0	94.9	98.6	94.1	98.6	95.1	93.6
Diuron	1.0	100.0	100.0	39.4	100.0	99.5	100.0
Lindane	1.0	49.5	68.4	55.6	84.6	61.3	79.1

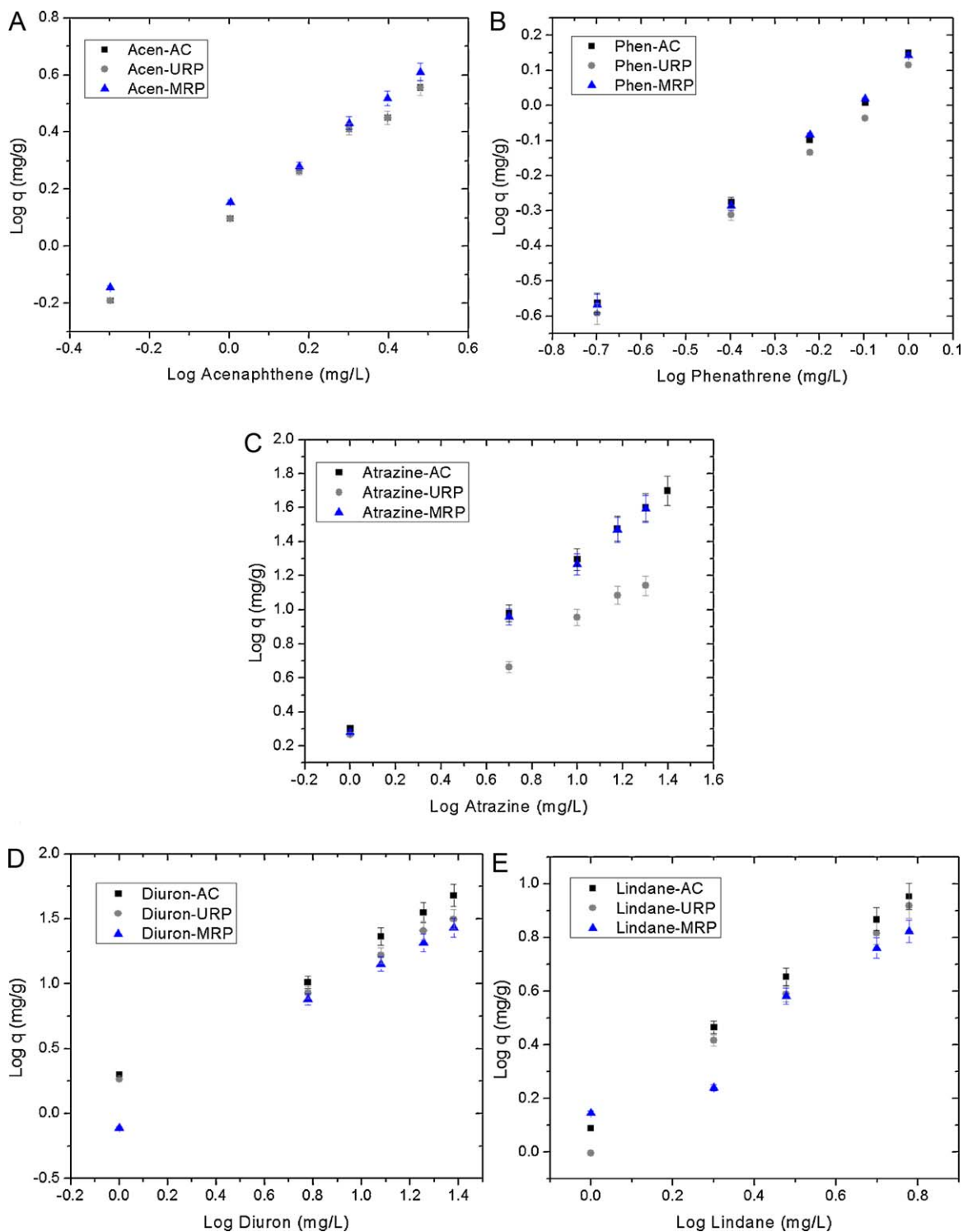


Fig. 4. Sorption isotherms for (A, B) PAHs and (C–E) pesticides using activated carbon (AC), untreated ragweed pollen (URP, without iron coating) and magnetized ragweed pollen (MRP) in DI water. Similar sorption capacity of all three sorbents is observed.

may bind to the HOCs. The possible interactions between the HOCs and TOC can be in the form of hydrogen bonding, van der Waals forces or hydrophobic association [34]. The binding of the HOCs to the TOC can enhance their overall sorption to the carbonaceous adsorbents via a two-step complexation–flocculation process [35]. The HOC–TOC complexes are first formed in several structural forms such as vesicle, membrane or micelle with hydrophilic exteriors and hydrophobic interiors [36]. Next, the presence of ions

such as Na^+ , K^+ , Ca^{2+} or Mg^{2+} promotes flocculation or aggregation of these complexes by screening the negative charges on the hydrophilic exterior, reducing the electrostatic repulsion and leading the complexes' sorption onto the adsorbents. Furthermore, previous studies for iron coated sorbents and plant cuticular materials showed enhancement of sorption of natural organic matter and nitroaromatics onto iron-oxides coated sand and soils over their uncoated counterparts [33,37]. As illustrated in Table 7, our

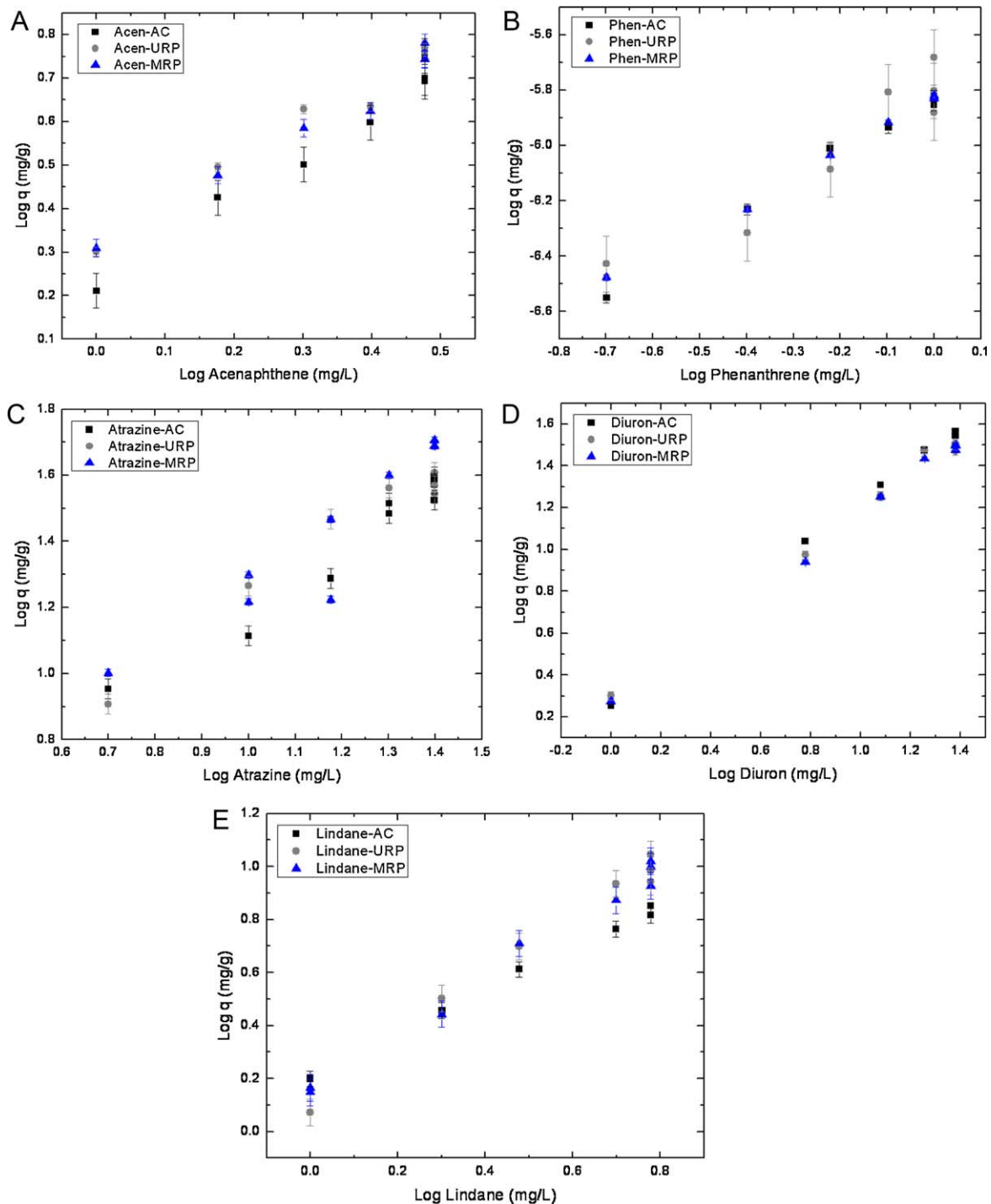


Fig. 5. Sorption isotherms for (A, B) PAHs and (C–E) pesticides using activated carbon (AC), untreated ragweed pollen (URP, without iron coating) and magnetized ragweed pollen (MRP) in stormwater.

results similarly had increased HOC sorption when comparing MRP to URP. While both the iron oxides coated and uncoated ragweed pollen are excellent candidates to serve as sorbents for organic contaminants, the magnetized form allows easier separation of the pollen grains from the treated water via a simple application of a magnetic field.

Comparison of Table 8 with Table 9 shows an increased amount of HOC partitioned onto the sorbent in the presence of natural organics and other ions common in natural waters.

Table 10 shows the concentration of Fe ions in the supernatants after the adsorption experiments. All contaminated water sam-

ples mixed with MRP had dissolved [Fe] of less than 1 mg/L; the stormwater had a background [Fe] of 0.02 mg/L. The [Fe] in the waters was not observed to affect the sorption capacity of the MRP compared to AC or URP.

3.4. Regeneration and reuse of MRP

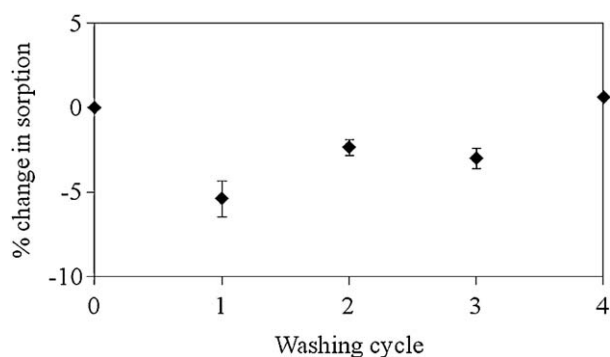
The ability to regenerate and reuse MRP using common organic solvents to extract the HOCs is of value since it will reduce the overall cost. In addition, the recovered HOCs may be either reused or disposed of safely in a more concentrated solution. Although

Table 8
Partition coefficient K_d in DI water.

HOC	URP		MRP		AC	
	Avg K_d	Std. dev.	Avg K_d	Std. dev.	Avg K_d	Std. dev.
Acenaphthene	3.19E+03	3.90E+02	4.36E+03	6.32E+02	3.19E+03	3.90E+02
Phenanthrene	3.42E+03	5.08E+02	3.98E+03	4.93E+02	4.33E+03	6.02E+02
Atrazine	3.62E+04	2.09E+03	3.12E+04	2.05E+03	3.45E+05	4.23E+05
Diuron	3.62E+03	1.47E+03	2.70E+03	8.37E+02	2.04E+05	1.96E+05
Lindane	3.52E+03	9.32E+02	4.55E+03	2.53E+03	5.22E+03	1.17E+03

Table 9
Partition coefficient K_d in stormwater.

Sorbent	URP		MRP		AC	
	Avg K_d	Std. dev.	Avg K_d	Std. dev.	Avg K_d	Std. dev.
Acenaphthene	6.00E+07	1.00E+03	8.86E+04	5.94E+04	2.57E+04	3.84E+03
Phenanthrene	4.42E+05	1.13E+06	1.08E+03	9.28E+02	6.32E+03	3.27E+02
Atrazine	1.32E+05	1.56E+05	4.12E+05	2.85E+05	1.90E+03	1.41E+02
Diuron	5.90E+03	1.60E+03	6.02E+03	1.43E+03	8.84E+03	2.26E+03
Lindane	8.51E+03	4.03E+03	9.62E+03	3.22E+03	4.29E+03	2.98E+03

**Fig. 6.** Percent change of sorption of diuron onto magnetized ragweed pollen for five regeneration cycles in DI water. The ideal reusable sorbent would show 0% change of sorption between regeneration cycles.

activated carbon can be regenerated, it typically requires high temperatures and more sophisticated reactors to recover the HOCs. As a proof of concept, the recovery of acenaphthene in our contaminated DI water samples was investigated using 3 mL of acetone, with a recovery rate of 81%, considering an initial acenaphthene concentration of 1 mg/L and 5 mg/L of MRP. We also evaluated the recovery of diuron (which is the least sorbed contaminant in our list of pesticides) from MRP in DI water using methanol extraction. MRP was found to be highly stable and reusable under the investigated sorption conditions, preserving over 90% of its initial diuron sorption capacity after five cycles of regeneration and reuse as shown in Fig. 6.

Table 10
Concentration of dissolved Fe ions in the HOC–water samples mixed with MRP.

HOC	Water type	[Fe] (mg/L)
None	DI	0.003
Acenaphthene	DI	0.01
Phenanthrene	DI	0.005
Atrazine	DI	0.03
Diuron	DI	0.02
Lindane	DI	0.03
None	Stormwater	0.02
Acenaphthene	Stormwater	0.03
Phenanthrene	Stormwater	0.02
Atrazine	Stormwater	0.02
Diuron	Stormwater	0.02
Lindane	Stormwater	0.02

3.5. Effect of AC and pollen grains' surface structure on sorption performance

Previous studies [38] have indicated that laboratory batch equilibrium adsorption tests tend to grossly overestimate by as much as three times the actual organic contaminant adsorption capacity of the activated carbon used commercially. Most laboratory test conditions involve the use of analytical grade fine granular activated carbon with high microporosities and surface areas, while field activated carbon is typically of lower grade coarser particles with smaller surface areas available for adsorption. The difference in sorption performance between commercially used activated carbon and laboratory grade activated carbon will mean that magnetized ragweed pollen may be a more competitive and efficient sorbent for HOCs than field-grade activated carbon. In our case, while the AC used is analytical grade with the BET surface area of 3350 m²/g (Table 11), it did not perform significantly better than both the magnetized and unmodified pollen grains. As a comparison, our iron-oxide coated pollen had a surface area of 0.678 m²/g and uncoated pollen had a surface area of 0.623 m²/g. Furthermore, pollen grains are known to shrink and expand considerably [39] to adjust their shape according to moisture content and environmental conditions in a process known as harmomegathy [40]. This suggests that BET measurement does not accurately portray the available adsorbent surface area, since the pore volume measurements are done in the gas phase and not in the aqueous environment. When pollen grains are released from the anther into the atmosphere, they equilibrate their hydration state with the surrounding environment in order to limit desiccation for the protection of the plant genetic material. The structure of the pollen wall is designed to allow the apertures to fold inwardly during harmomegathy thus reducing the rate of water loss via a contraction and effective sealing of exposed surface area [41]. This indicates that the actual surface areas of both iron-coated and unmodified pollen grains in the contaminated water samples could be much higher than the values obtained by the BET measurements in a humidity free N₂ environment.

Table 11
Measured surface area data for AC, MRP and URP.

Material	BET surface area (m ² /g)
AC	3350
MRP	0.678
URP	0.623

4. Conclusions

We have shown that magnetized pollen grains can be used as effective sorbents for HOCs to treat contaminated water, with similar levels of organic contaminants removal as traditional AC. The magnetization of the pollen simplifies its separation from the treated water. Ideal remediation sorbents should be cheap, easy and quick to produce and scale up, widely available, have a low carbon footprint, non-toxic, biologically degradable and come from renewable sources. Magnetized pollen grains fit these criteria well and can also be reused. The coating amount of iron oxides on the pollen grains can be optimized further to minimize cost and wastage without sacrificing their magnetic performance. Finally, pollen grains are widely distributed worldwide and species less allergenic than *A. artemisiifolia* may be harvested from fast growing flowering seed plants to increase production to meet demand for environmental remediation.

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