



## Trichloroethylene (TCE) adsorption using sustainable organic mulch

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### ABSTRACT

Soluble substrates (electron donors) have been commonly injected into chlorinated solvent contaminated plume to stimulate reductive dechlorination. Recently, different types of organic mulches with economic advantages and sustainable benefits have received much attention as new supporting materials that can provide long term sources of electron donors for chlorinated solvent bioremediation in engineered biowall systems. However, sorption capacities of organic mulches for chlorinated solvents have not been studied yet. In this study, the physicochemical properties of organic mulches (pine, hardwood and cypress mulches) were measured and their adsorption capacity as a potential media was elucidated. Single, binary and quaternary isotherm tests were conducted with trichloroethylene (TCE), tetrachloroethylene (PCE), trans-dichloroethylene (trans-DCE) and cis-dichloroethylene (cis-DCE). Among the three tested mulches, pine mulch showed the highest sorption capacity for the majority of the tested chemicals in single isotherm test. In binary or quaternary isotherm tests, competition among chemicals appears to diminish the differences in  $Q_e$  for tested mulches. However, pine mulch also showed higher adsorption capacity for most chemicals when compared to hardwood and cypress mulches in the two isotherm tests. Based upon physicochemical properties of the three mulches, higher sorption capacity of pine mulch over hardwood and cypress mulches appears to be attributed to a higher organic carbon content and the lower polarity.

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### 1. Introduction

Since trichloroethylene (TCE) was first detected in late 1970s, it has been identified as one of the most common contaminants in U.S. Superfund sites [1]. The agency for the Toxic Substances and Disease Registry has reported that TCE was present in 852 of 1430 National Priority List sites in 1997 [2]. The EPA has set 5 ppb\* for the maximum level contamination (MCL) of TCE. TCE contamination has been a great concern because of its high solubility in water ( $1100 \text{ mg L}^{-1}$  at  $25^\circ\text{C}$ ) and resistance to biological degradation. A small amount of TCE can contaminate a large amount of ground water for a long time [3].

For TCE contaminated soil and groundwater remediation, biotic and abiotic methods have been employed. The biotic removal of TCE utilizes microorganisms to dechlorinate tetrachloroethylene (PCE) and TCE into less chlorinated by-products such as dichloroethylene (DCE) and vinyl chloride (VC) in aerobic or anaerobic environments. The abiotic removal methods for TCE include the chemical oxidation/reduction of TCE [4] or the physical adsorption using various adsorbents. Among those methods, the adsorption process is one of the most commonly used techniques for the purification of TCE con-

taminated groundwater. Particularly, various adsorbents have been employed to mitigate the migration of TCE in subsurface aquifers. The most popular media for TCE adsorption has been activated carbon in both granular and powdered forms. However, even though the activated carbon shows the highest sorption capacity for TCE, it has been reported that the activated carbon cannot enhance the decomposing of adsorbed TCE into harmless substances [5,6]. Many researchers reported that the strong sorption of organic chemicals by the activated carbon decreased their bioavailability [7]. Also, the activated carbon cannot provide an alternative carbon source for microorganisms to degrade TCE even if it has high organic carbon content [5,8]. It is also expensive for field application.

Other available adsorbents for TCE are soils, peat moss [8,9], organo-clays [10,11], polymeric adsorbent [12,13], zeolites [14,15] and other carbon materials [16,17]. Among them, wood materials have recently received much attention. Since organic mulches are plentiful, inexpensive and readily available, the use of mulch for the removal of organic pollutants is gaining much attention as a simple, effective and economical means of treatment at Superfund sites [18]. Typically, mulch or peat moss has been installed in trenches as biowall [19,20], or biological filter media for volatile organic compounds [21]. Previous field studies also demonstrated that the application of mulches in permeable reactive barrier enhanced anaerobic bioremediation of chlorinated solvents in groundwater [22].

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Wood mulches are composed of many biopolymers, and their biological properties are mainly determined by the chemical composition of the cell wall. Wood cell walls are mainly composed of three polymeric components: cellulose, hemicelluloses and lignin [23]. Among biopolymers, lignin is known to have a high affinity and sorption capacity for nonionic organic compounds [24]. Moreover, mulch is rich in carbon and can provide an alternative carbon source for microorganisms to degrade chlorinated solvents anaerobically [25]. However, while organic mulch has shown its potential for anaerobic bioremediation of chlorinated solvents, the adsorption capacity of mulch for chlorinated solvents has not been studied yet.

This study aimed to explore the adsorption capacity of organic mulches (hardwood, pine and cypress mulches) for TCE removal. These mulches are by-products of wood and lumber industries and are the most common mulches in the United States. These mulches were selected as potential supporting materials for the biowall where anaerobic reductive dechlorination takes place. Sorption capacities of mulches were tested with four chemicals: TCE, PCE, trans-DCE and cis-DCE. First, single isotherm tests for each type of mulch were conducted to obtain its adsorption capacity. Then binary and quaternary isotherm experiments were conducted and results were compared to those from the single isotherm test.

## 2. Experimental

### 2.1. Sorbents and sorbates

The pine, hardwood and cypress mulches were purchased from Ohio Mulch (Cincinnati, OH, USA). To obtain homogenized mulches, the mulches were first washed several times with deionized water. Sand, fine debris and easily leachable materials were removed with the rinsing. The rinsed mulches were autoclaved two times to remove any existing bacterial and fungal spores and then dried at 60 °C. Completely dried mulches were grounded using a mechanical blender and then sieved with #10 mesh (2 mm) and #16 mesh (1.18 mm) sieves. Finally, the sieved mulches were autoclaved again and then were used to characterize physicochemical properties and for isotherm testing.

The carbon, hydrogen and nitrogen contents were determined with an Elemental Analyzer equipped with an inductive furnace analyzer (PerkinElmer 2400). Structural characteristics of the three mulches, including the Brunauer, Emmett and Teller (BET) surface area, porosity, and pore size distribution, were measured using nitrogen adsorption and desorption isotherms. A Tristar 3000 (Micromeritics, GA, USA) pore size analyzer was used, and all samples were purged with nitrogen gas for 2 h at 150 °C using a Flow Prep 060 (Micromeritics, GA, USA) before analyses. Surface area was measured with the multi-point BET method. Total pore volume was measured at  $P/P_0 = 0.95$  and meso-pore volume was calculated as the difference between total pore volume and micro-pore volume [26]. The pH, water content (WC), and bio-material content (BC) of the mulches were determined according to APHA [27]. Cation exchange capacity (CEC) was measured by the ammonium acetate method [28]. Considering their coexistence in contaminated soil and groundwater, four chemicals (TCE, PCE, trans-DCE and cis-DCE; Sigma–Aldrich Co.) were selected for adsorption tests.

### 2.2. Single solute adsorption isotherm test

Batch isotherm tests were conducted with Teflon-lined screw cap bottles to evaluate the adsorption capacity of organic mulches for all four tested chemicals. To minimize volatilization loss of tested chemicals, all bottles were filled up to remove head space

**Table 1**  
GC/MS analysis methods.

Chemical	TCE	PCE	trans-DCE	cis-DCE
Initial temperature (°C)	80	130	40	50
Hold time at the beginning (min)	5.5	5.5	5.5	4.5
Ramp (°C min <sup>-1</sup> )	20	20	40	40
End temperature (°C)	190	190	190	190
Hold time in the end (min)	2.0	2.0	2.0	2.0
Solvent delay time (min)	3.5	3.2	4.75	4.9
Carry gas (helium) flow rate (mL min <sup>-1</sup> )	0.4	0.4	0.4	0.4

Note: In cis-DCE program, detector is off during 4–8 min.

and three to six blank samples were also added at each sampling point.

To obtain an adsorption equilibrium time for each chemical on the mulches, preliminary isotherm tests were conducted with each chemical. Sample bottles were placed in a rotary tumbler at 12 rpm. Then samples were harvested at days 1, 2, 3, 5, 7, and 10 and liquid phase concentrations of the tested chemicals were monitored.

For the single isotherm tests for each chemical (PCE, TCE, cis-DCE and trans-DCE), samples with varied amounts of mulch mass were prepared. All chemical solutions were prepared with deionized water (18.2 MΩ) and the initial concentration was 50 mg L<sup>-1</sup>. All isotherm tests were conducted under room temperature (20 °C). After samples reached adsorption equilibrium time, liquid phase chemical concentrations were monitored and the adsorbed amount of chemicals on different mulches was calculated.

### 2.3. Binary and quaternary solutes adsorption isotherm test

In TCE contaminated groundwater or soil, chemicals from the anaerobic reductive dechlorination pathway coexist with TCE and the mixed condition may have competitive adsorption on adsorbents. Therefore, after obtaining single solute isotherm results, both binary isotherm tests (combination of TCE and PCE; TCE and cis-DCE) and quaternary isotherm tests were conducted with three different mulches. Test conditions were identical to those of the single isotherm test.

### 2.4. Analytical methods

A Hewlett-Packard model 6890 gas chromatograph equipped with a mass selective detector (MSD) was used to measure the concentration of TCE, PCE, cis-DCE and trans-DCE solutions. The HP-624 column for volatile organic compounds (30.0 m × 250 μm × 0.25 μm nominal; Restek RTX-5) was used. The total flow was 6.7 mL min<sup>-1</sup>. The set point temperature of the heater was 260 °C and pressure was 2.82 psi. Detector and injector temperatures were held at 250 and 220 °C, respectively. To monitor liquid phase chemical concentration, 2 ml of samples were collected from each bottle and chemicals were extracted by methylene chloride for GC analysis. GC/MS analysis methods are shown in Table 1.

### 2.5. Adsorption models

The mass balance expression used to determine the amount of adsorbates retained by adsorbents was calculated using aqueous-phase concentration of adsorbates.

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

where  $Q_e$  is the equilibrium adsorbent-phase concentration of adsorbate, mg g<sup>-1</sup>;  $C_e$  is the aqueous-phase concentration of adsorbate at equilibrium, mg L<sup>-1</sup>;  $C_0$  is the initial adsorbate concentration, mg L<sup>-1</sup>;  $V$  is the volume of aqueous-phase adsorbate solution, L; and  $M$  is the mass of adsorbent, g.

**Table 2**  
Physicochemical properties of the organic mulches used in this study.

Elements	Type of mulch		
	Pine	Hardwood	Cypress
Carbon (%)	51.62	43.23	19.05
Hydrogen (%)	4.99	5.44	1.98
Nitrogen (%)	0.68	0.31	0.36
Oxygen (%)	43.09	50.65	78.60
Atomic ratio [(N+O)/C]	0.84	1.19	4.14
Atomic ratio [O/C]	0.83	1.17	4.12
BET surface area (m <sup>2</sup> g <sup>-1</sup> )	0.6195	1.0972	1.3725
Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	0.0012	0.0078	0.0121
Micro-pore volume (cm <sup>3</sup> g <sup>-1</sup> )	0.00006	0.00016	0.00008
Meso-pore volume (cm <sup>3</sup> g <sup>-1</sup> )	0.001119	0.007581	0.011801
Water content (%)	49.4 ± 9.5	55.9 ± 6	36.9 ± 4.6
Biomaterial content (%)	11.2 ± 0.8	14.7 ± 0.4	5.3 ± 0.4
Cation exchange capacity (mequiv. (100 g) <sup>-1</sup> )	10.8 ± 2.5	42.3 ± 3.4	20.5 ± 2.5
Conductivity (mS cm <sup>-1</sup> ), at 25 °C	0.17 ± 0.06	0.36 ± 0.01	0.25 ± 0.01
pH	4.26 ± 0.08	7.43 ± 0.28	5.15 ± 0.06

In order to quantify the adsorption capacity of the mulches, obtained experimental data were fitted according to the Freundlich and Langmuir isotherm equations.

$$\text{Freundlich isotherm: } Q_e = K_f C_e^{1/n_f} \quad (2)$$

$$\text{Langmuir isotherm: } Q_e = \frac{S_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where  $K_f$  is the Freundlich constant indicative of adsorptive capacity,  $(\text{mg kg}^{-1})(\text{mg L}^{-1})^{-1/n_f}$ ;  $n_f$  is the Freundlich constant related to adsorption intensity;  $K_L$  ( $\text{mg}^{-1}$ ) is the Langmuir isotherm constant related to the equilibrium constant or binding energy; and  $S_m$  ( $\text{mg g}^{-1}$ ) is the amount of sorption corresponding to complete surface coverage.

### 3. Results and discussions

#### 3.1. Physicochemical properties of the experimental mulches

Physicochemical properties of the three types of organic mulches (cypress, hardwood, and pine mulches) were examined. Based on BET surface area measurements, these three mulches showed surface areas between 0.62 and 1.37 m<sup>2</sup> g<sup>-1</sup>, which are slightly higher than the previous study with aspen wood bark (0.62 m<sup>2</sup> g<sup>-1</sup> [26]). Among the three mulches, cypress mulch showed the relatively highest surface area (1.37 m<sup>2</sup> g<sup>-1</sup>). This might be related to the fibrous character of the experimental cypress mulch, which gives more surface area under the same unit mass. After cypress mulch, hardwood mulch showed a higher surface area than pine mulch.

Among the three mulches, pine mulch had the highest carbon content. After pine mulch, hardwood mulch showed a higher carbon content than that of cypress mulch. Based on the results of elemental composition analysis, atomic ratios [(N+O)/C, (O/C)] were calculated in order to measure the polarity of the three mulches [29]. It has been reported that polarity was one of the most important compositional parameters governing sorption of hydrophobic organic compounds in soil [26,30,31]. In their study with chemically treated wood, Xing et al. reported that the lowest polarity [(O+N)/C or (O/C)] represented the highest  $K_{oc}$  (the soil-water partition coefficient, determining the mobility of organic chemicals in soil) values as well as the highest sorption capacity with chemically treated wood [26]. The mass atomic ratio revealed that pine mulch showed the lowest polarity [(N+O)/C, (O/C)] while cypress mulch showed the highest polarity. For cation exchange capacity of mulch, the hardwood mulch showed the highest CEC among the three mulches. The physicochemical properties of the

mulches used in this study were measured and are summarized in Table 2.

#### 3.2. Single adsorption isotherm

For all selected chemicals (PCE, TCE, trans-DCE and cis-DCE), preliminary isotherm tests were conducted with different mulches to elucidate equilibrium time. Based on the preliminary adsorption results (data not shown), approximately all the equilibria were reached after 1 day for all tested chemicals with all three mulches. However, a 2 day equilibrium time was selected to ensure enough equilibrium time for all isotherm tests.

To assess the adsorption capacity of different mulches, a single solute adsorption isotherm experiment was conducted with varied mulch dosages from 0.2 g per vial to 5 g per bottle. The collected data were correlated to the linearized Freundlich and Langmuir isotherm models to obtain adsorption kinetics. The rearranged equations are shown as follows.

$$\text{Linearized Freundlich isotherm: } \log(Q_e) = \log(K_f) + \frac{1}{n_f} \log(C_e) \quad (4)$$

$$\text{Linearized Langmuir isotherm: } \frac{C_e}{Q_e} = \frac{1}{K_L S_m} + \frac{C_e}{S_m} \quad (5)$$

Fig. 1 shows the linear relation between  $Q_e$  and  $C_e$  with linearized Freundlich isotherm model and compares the adsorption capacity of different mulches. Among the three mulches, overall, pine mulch showed higher adsorption capacity than hardwood and cypress mulches. Table 3 shows the Freundlich and Langmuir isotherm coefficients of single solute adsorption on different mulches. Both models adequately described the adsorption data (over 0.9 regression coefficients) and also showed pine mulch had better adsorption capacity. A detailed analysis of both Freundlich and Langmuir isotherm coefficients suggested that PCE and TCE had a higher affinity to all three mulches than trans-DCE and cis-DCE. Among the four tested chemicals, trans-DCE was the most difficult to be adsorbed by all three mulches. Table 4 shows  $Q_e$  and removal efficiency for different mulches. In single isotherm test, pine mulch showed the highest  $Q_e$  (2181.52  $\mu\text{g g}^{-1}$ ) followed by cypress mulch (1511.4  $\mu\text{g g}^{-1}$ ) and hardwood mulch (1300.6  $\mu\text{g g}^{-1}$ ) for PCE; for TCE, the  $Q_e$  decreases in the following order: pine mulch (1076.0  $\mu\text{g g}^{-1}$ ), cypress mulch (942.7  $\mu\text{g g}^{-1}$ ), and hardwood mulch (540.9  $\mu\text{g g}^{-1}$ ); for trans-DCE, the  $Q_e$  decreases in the following order: hardwood mulch (510.4  $\mu\text{g g}^{-1}$ ), cypress mulch (451.3  $\mu\text{g g}^{-1}$ ), and pine mulch (369.1  $\mu\text{g g}^{-1}$ ); and for cis-DCE, the  $Q_e$  decreases in the following order: pine mulch (696.3  $\mu\text{g g}^{-1}$ ),

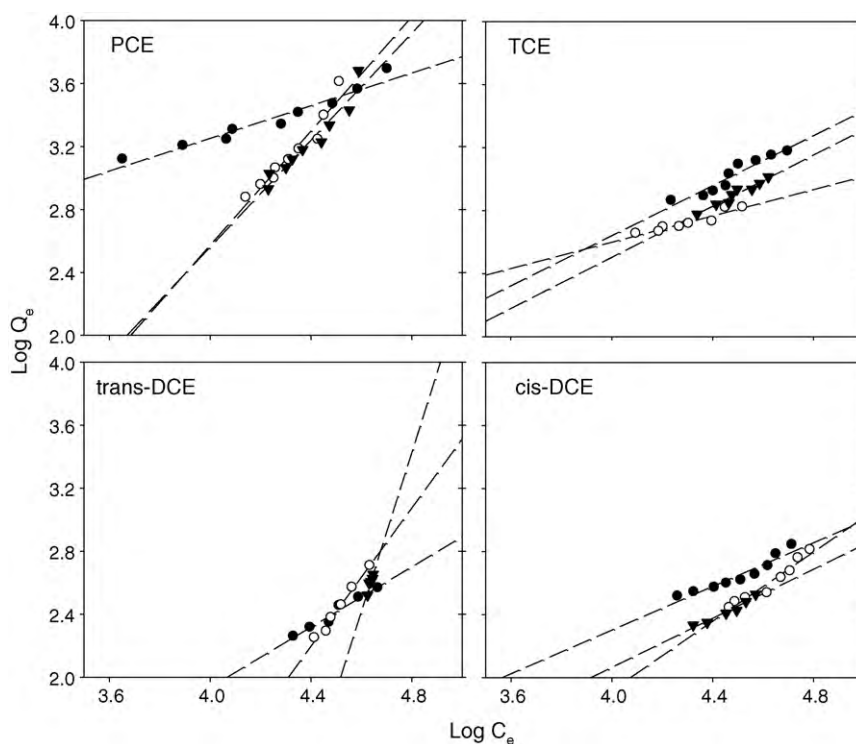


Fig. 1. log–log single chemical adsorption isotherm for different mulches (●—pine; ○—hardwood; ▼—cypress).

hardwood mulch ( $574.3 \mu\text{g g}^{-1}$ ), and cypress mulch ( $337.4 \mu\text{g g}^{-1}$ ). Under the same initial conditions, pine mulch adsorbed the largest amount of PCE, TCE and cis-DCE according to the above results.

Zytner [8] reported that there is a corresponding increase in the adsorption capacity of adsorbent as its organic carbon content, CEC and surface area increase. Among three mulches, pine mulch has the highest organic carbon content (51.62%), while hardwood mulch and cypress mulch had 43.23% and 19.05% of organic carbon content, respectively [8]. All three mulches showed small surface areas (between  $0.62$  and  $1.37 \text{ m}^2 \text{ g}^{-1}$ ) that would not make a significant difference in adsorption capacity. Furthermore, CEC, which is important for metal ion adsorption, appears not to be important. Therefore, the high organic carbon content of pine mulch affected the adsorption capacity for chlorinated solvents. Polarity  $[(O+N)/C$  or  $(O/C)]$  has also been considered an influencing parameter on the adsorption of organic chemicals. It was reported that lower polarity presented the higher sorption capacity with chemically treated wood [26]. Among three mulches, pine mulch showed the low-

est polarity (0.84 or 0.83) followed by hardwood mulch (1.19 or 1.17) and cypress mulch (4.14 or 4.12). Higher sorption capacity of pine mulch over hardwood mulch and cypress mulch appears to be attributed to a higher organic carbon content and the lowest polarity.

### 3.3. Binary and quaternary solutes adsorption isotherm

Figs. 2 and 3 show the binary and quaternary tests of adsorption under linearized Freundlich isotherm model, respectively. In the binary isotherm tests, similar to the isotherm results of single solute isotherm tests, pine mulch had higher adsorption capacity for most chemicals than those of hardwood and cypress mulches. Fig. 2 shows that the amount of adsorbed chemicals on mulches is in direct proportion to the y axis intersection. According to the results, PCE is most likely to be adsorbed by all three mulches followed by TCE. trans-DCE and cis-DCE showed little affinity to the tested mulches.

**Table 3**  
Langmuir and Freundlich isotherm constants and correction coefficients ( $r^2$  values) for single solute adsorption on different mulches (a: Freundlich isotherm coefficients; b: Langmuir isotherm coefficients).

Chemical	Pine			Hardwood			Cypress		
	$K_f$	$1/n_f$	$r^2$	$K_f$	$1/n_f$	$r^2$	$K_f$	$1/n_f$	$r^2$
(a)									
PCE	14.93	0.518	0.943	$2.1 \times 10^{-5}$	1.813	0.934	$5.9 \times 10^{-5}$	1.697	0.924
TCE	0.292	0.793	0.907	8.453	0.417	0.900	0.189	0.811	0.944
trans-DCE	0.013	0.956	0.963	$3.4 \times 10^{-8}$	2.195	0.984	$1.6 \times 10^{-21}$	5.046	0.889
cis-DCE	0.339	0.647	0.913	0.003	1.098	0.947	0.089	0.692	0.911
Chemical	Pine			Hardwood			Cypress		
	$S_m$	$K_L$	$r^2$	$S_m$	$K_L$	$r^2$	$S_m$	$K_L$	$r^2$
(b)									
PCE	1.931	$7.8 \times 10^{-5}$	0.979	0.552	-0.00013	0.911	0.589	-0.000141	0.971
TCE	1.261	0.00012	0.914	2.398	$3.6 \times 10^{-5}$	0.914	1.233	-0.000701	0.959
trans-DCE	1.046	0.0006	0.967	0.456	$-5.4 \times 10^{-5}$	0.985	0.198	$-2.9 \times 10^{-5}$	0.899
cis-DCE	1.546	$9.8 \times 10^{-5}$	0.930	0.911	-0.000163	0.946	1.445	0.000146	0.957

**Table 4**  
Comparison of  $Q_e$  and removal efficiency for different mulches in single, binary and quaternary experiment.

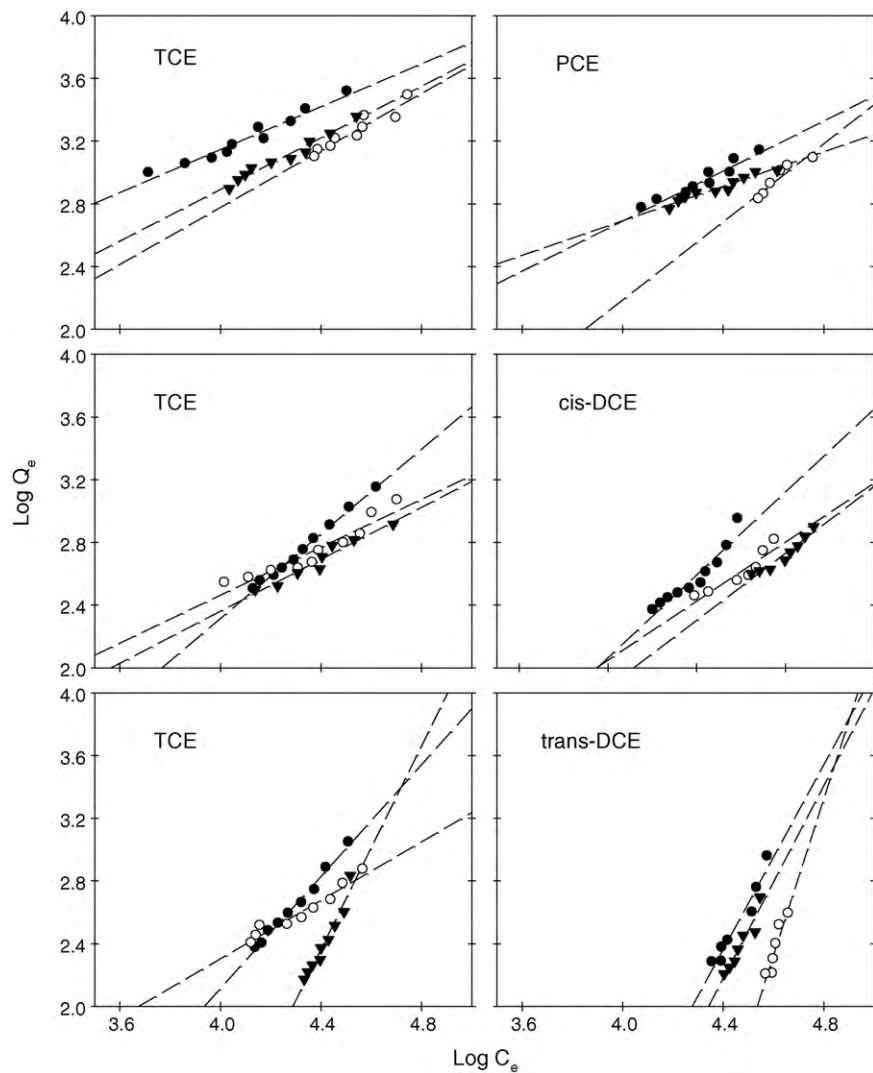
Adsorbates	Mixture type	Pine		Hardwood		Cypress	
		$Q_e$ ( $\mu\text{g g}^{-1}$ )	RE (%)	$Q_e$ ( $\mu\text{g g}^{-1}$ )	RE (%)	$Q_e$ ( $\mu\text{g g}^{-1}$ )	RE (%)
TCE	Single	1076.0	49.3	540.9	32.5	942.7	39.3
	Binary <sup>a</sup>	999.3	48.5	1104.3	37.4	930.0	43.5
	Binary <sup>b</sup>	1053.3	54.0	974.0	39.1	830.1	41.1
	Binary <sup>c</sup>	768.0	43.6	606.6	33.7	401.2	25.4
	Quaternary	1394.8	51.3	1314.5	34.4	1407.1	43.5
PCE	Single	2181.5	74.1	1300.6	67.7	1511.4	74.5
	Binary <sup>a</sup>	2104.2	73.5	2292.5	60.0	1577.0	70.6
	Quaternary	3879.1	70.9	3295.0	58.0	3215.2	67.7
cis-DCE	Single	696.3	26.2	574.3	21.2	337.4	19.3
	Binary <sup>b</sup>	599.3	30.4	555.0	22.6	688.1	18.0
	Quaternary	916.2	29.0	553.9	17.4	972.0	24.9
trans-DCE	Single	369.1	16.3	510.4	22.1	451.3	28.6
	Binary <sup>c</sup>	571.9	30.7	330.2	16.82	298.1	19.0
	Quaternary	533.5	22.4	516.4	20.9	516.4	23.6

Mulch weight is 1.0 g; initial concentration is 50 mg L<sup>-1</sup>; RE stands for removal efficiency, calculated using equation:  $RE = (C_0 - C_e)/C_0 \times 100\%$ .

<sup>a</sup> Binary of TCE and PCE.

<sup>b</sup> Binary of TCE and cis-DCE.

<sup>c</sup> Binary of TCE and trans-DCE.



**Fig. 2.** log–log binary adsorption isotherm for different mulches (●—pine; ○—hardwood; ▼—cypress).

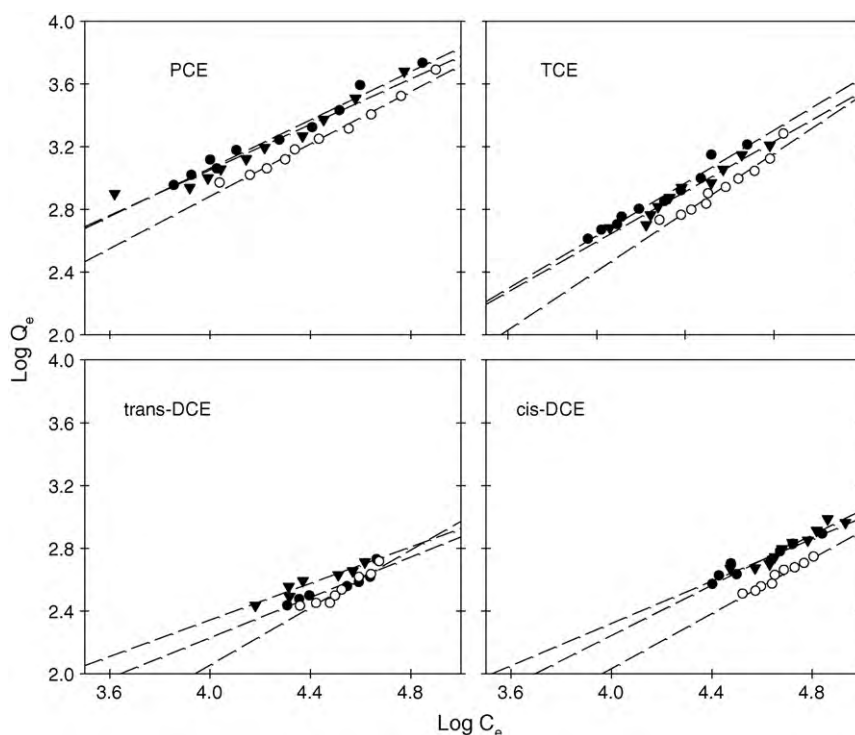


Fig. 3. log-log quaternary adsorption isotherm for different mulches (●—pine; ○—hardwood; ▼—cypress).

The removal efficiencies, percent mass of chemicals removed by mulch, are shown in Table 4. Among the tested mulches, pine mulch had the highest removal efficiency for most tested chemicals in all isotherm tests, followed by hardwood mulch and cypress mulch. The removal efficiencies of tested chemicals in binary and quaternary isotherm results were lower than those of single isotherm tests for all mulches. The slight decrease in removal efficiencies of binary and quaternary isotherm tests suggests that there was adsorption competition among adsorbates onto adsorbent surfaces. The multi-components adsorption is a complicated process because of the solute–surface interactions. Mixture of adsorbates has to compete to be adsorbed onto media in the binary or quaternary system, while a single component can reach saturation in the same solution. However, compared to the single solute isotherm test results, there was not significant difference in both the adsorption capacity of three mulches and the chemical removal efficiency in binary and quaternary isotherm tests. All tested chemicals did not show any significant mixture effects on adsorption capacity and affinity changes. Affinity of each chemical to the tested mulches showed the same trend with that of single solute isotherm tests. Larger molecular weight chemicals (PCE and TCE) appear to be more adsorbed on mulch surfaces compared to trans-DCE or cis-DCE which have smaller molecular weights.

#### 3.4. Comparison of sorption capacity of mulches to other adsorbents

For its high efficiency to remove various organic contaminants, activated carbon has been widely used. Zytner [8] tested granular activated carbon (GAC), peat moss, organic top soil, and sandy loam soil for TCE adsorption. The results reported that GAC had the highest sorption capacity followed by peat moss, organic top soil and sandy loam soil [8]. The organic carbon content of GAC was reported to be much higher (74.1%) than those of organic mulches (pine, 51.6%; hardwood, 43.2%; cypress, 19.1%). GAC is also reported to possess a much higher surface area,  $1300 \text{ m}^2 \text{ g}^{-1}$ , than that of the

tested mulches in this study (between  $0.62$  and  $1.37 \text{ m}^2 \text{ g}^{-1}$ ). The Freundlich adsorption coefficients  $K_f$  is 81076 for GAC while the adsorption coefficients for tested mulches are below 10 as shown in Table 3. However, activated carbon can only physically adsorb chlorinated solvents from liquid or gas phase into solid phase. The high content of organic carbon cannot provide an electron donor for microorganisms to anaerobically degrade TCE [5]. In addition, many researchers reported that strong adsorption of organic compounds on adsorbents significantly decreases biological availability of adsorbed compounds [7]. Therefore, the adsorption capacity of GAC implemented to biowall systems may not be regenerated by enhanced biological activity and exhausted activated carbon would need to be replenished.

A slight difference in adsorption capacity was reported for peat moss as compared to tested mulches. The  $K_f$  of both tested mulches and peat moss was less than 0.5% of that of GAC. The physiochemical properties of peat moss (organic carbon content 49.4% and surface area  $0.4 \text{ m}^2 \text{ g}^{-1}$  [8]) were similar to those of tested mulches in this study.

Aggarwal et al. [3] demonstrated clay minerals and especially smectites as potential sorbents of organic compounds because they are abundant in soils and aquifer materials and have large surface areas. Zhao and Vance [11] illustrated that organo-clays had roughly 20% organic carbon content, and  $15\text{--}87 \text{ m}^2 \text{ g}^{-1}$  surface areas. Based on the properties of clays and adsorbed phase TCE on it, mulches have a higher capacity of adsorption than clays [11].

As a cost-effective substrate, mulches only cost from  $\$0\text{--}0.55/\text{kg}$ , while the price of GAC is  $\$2.0\text{--}4.0/\text{kg}$  [25,32]. Being both plentiful and inexpensive, mulches showed a high potential to provide adsorption and sequential degradation of TCE from contaminated soil and groundwater.

#### 4. Conclusions

Adsorption capacity of pine, hardwood and cypress mulches for PCE, TCE, trans-DCE, and cis-DCE was monitored with single,

binary and quaternary isotherm tests. According to the isotherm experiment results, PCE showed the highest affinity to all tested mulches, followed by TCE and cis-DCE/trans-DCE. Among the three mulches, pine mulch showed better adsorption capacity for most tested chemicals than hardwood mulch and cypress mulch in single solute isotherm tests. High organic carbon content and low polarity of pine mulch may explain its higher effectiveness for chlorinated solvents adsorption over other two tested mulches. Other physicochemical properties of the three tested mulches, such as surface area and total pore volume, were similar and appear to have little effect on the adsorption capacity. In binary and quaternary isotherm tests, adsorption capacity of all tested mulches showed slight differences from single solute tests due to adsorption competition among adsorbates onto adsorbent surfaces. Both Freundlich and Langmuir isotherm models fit all adsorption isotherm data well. Overall, compared to other adsorbents for the removal of chlorinated solvents, organic mulches show promising adsorption capacity, economic advantages, and sustainable benefits for TCE bioremediation.

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### References

- [1] F.D. Schaumburg, Banning trichloroethylene—responsible reaction or overkill, *Environ. Sci. Technol.* 24 (1990) 17–22.
- [2] R.E. Doherty, A history of the production and use of carbon tetrachloride, tetrachloroethylene, trichloroethylene and 1,1,1-trichloroethane in the United States: Part 2—trichloroethylene and 1,1,1-trichloroethane, *Environ. Forensics* 1 (2000) 83–93.
- [3] V. Aggarwal, H. Li, S. Boyd, B.J. Teppen, Enhanced sorption of trichloroethene by smectite clay exchanged with Cs<sup>+</sup>, *Environ. Sci. Technol.* 40 (2006) 894–899.
- [4] J. Gotpagar, E. Grulke, T. Tsang, D. Bhattacharyya, Reductive dehalogenation of trichloroethylene using zero-valent iron, *Environ. Prog.* 16 (1997) 137–143.
- [5] N. Yoichi, Q. Li, N. Wataru, S. Eui, O. Mitumasa, Biodegradation of trichloroethylene (TCE) adsorbed on granular activated carbon (GAC), *Water Resour.* 34 (2000) 4139–4142.
- [6] J.E. Kilduff, T. Karanfil, Trichloroethylene adsorption by activated carbon preloaded with humic substances: effects of solution chemistry, *Water Res.* 36 (2002) 1685–1698.
- [7] M. Alexander, *Biodegradation and Bioremediation*, 2nd edn, Academic Press, California, 1995, pp. 121–122.
- [8] R.G. Zytner, Adsorption desorption of trichloroethylene in granular media, *Water Air Soil Pollut.* 65 (1992) 245–255.
- [9] S.M. Steinberg, J.S. Schmeltzer, D.K. Kreamer, Sorption of benzene and trichloroethylene (TCE) on a desert soil: effects of moisture and organic matter, *Chemosphere* 33 (1996) 961–980.
- [10] G.Y. Sheng, X.R. Wang, S.N. Wu, S.A. Boyd, Enhanced sorption of organic contaminants by smectitic soils modified with a cationic surfactant, *J. Environ. Qual.* 27 (1998) 806–814.
- [11] H.T. Zhao, G.F. Vance, Sorption of trichloroethylene by organo-clays in the presence of humic substances, *Water Res.* 32 (1998) 3710–3716.
- [12] P. Liu, C. Long, Q.F. Li, H.M. Qian, A.M. Li, Q.X. Zhang, Adsorption of trichloroethylene and benzene vapors onto hypercrosslinked polymeric resin, *J. Hazard. Mater.* 166 (2009) 46–51.
- [13] Z.H. Fei, J.L. Chen, G.D. Gao, C. Long, A.M. Li, Q.X. Zhang, Adsorption of chloroform and trichloroethylene in water with a new kind of hypercrosslinked resins, *Chin. J. Polym. Sci.* 22 (2004) 425–430.
- [14] S. Kleinedam, C. Schüth, P. Grathwohl, Solubility-normalized combined adsorption-partitioning sorption isotherms for organic pollutants, *Environ. Sci. Technol.* 36 (2002) 4689–4697.
- [15] J. Farrell, C. Manspeaker, J. Luo, Understanding competitive adsorption of water and trichloroethylene in a high-silica Y zeolite, *Micropor. Mesopor. Mater.* 59 (2003) 205–214.
- [16] V.W. Langer, K.S. Novakowski, A.D. Woodbury, Sorption of trichloroethene onto styrolites, *J. Contam. Hydrol.* 40 (1999) 1–23.
- [17] J.J. Yu, S.Y. Chou, Contaminated site remedial investigation and feasibility removal of chlorinated volatile organic compounds from groundwater by activated carbon fiber adsorption, *Chemosphere* 41 (2000) 371–378.
- [18] M.B. Henry, C.D. Downey, R.D. Griffiths, M. Krumholz, R.J. Gonzales, S.K.E. Becvar, Design of mulch biowalls for enhanced in situ anaerobic bioremediation, in: *Proceedings of the Eighth International In Situ and On-Site Bioremediation Symposium*, Baltimore, MD, 2005, Paper L-05.
- [19] H. Shen, J.T. Wilson, Trichloroethylene removal from groundwater in flow-through columns simulating a permeable reactive barrier constructed with plant mulch, *Environ. Sci. Technol.* 41 (2007) 4077–4083.
- [20] Y. Seo, P.L. Bishop, The monitoring of biofilm formation in a mulch biowall barrier and its effect on performance, *Chemosphere* 70 (2008) 480–488.
- [21] J.S. Ergas, D.E. Schroeder, P.Y.D. Chang, L.R. Morton, Control of volatile organic compound emissions using a compost biofilter, *Water Environ. Res.* 67 (1995) 816–821.
- [22] Air Force Center for Environmental Excellence Brooks City-Base, Texas, Ellsworth Air Force Base Rapid City, South Dakota, Treatability Study Work Plan for Bioremediation of Chlorinated Solvent Using a Permeable Reactive Biowall at the BG05 Site, Ellsworth Air Force Base, South Dakota, 2005.
- [23] A.A. Mackay, P.M. Gschwend, Sorption of monoaromatic hydrocarbons to wood, *Environ. Sci. Technol.* 34 (2000) 839–845.
- [24] D.R. Garbarini, L.W. Lion, Influence of the nature of soil organics on the sorption of toluene and trichloroethylene, *Environ. Sci. Technol.* 20 (1986) 1263–1269.
- [25] Air Force Center for Environmental Excellence Brooks City-Base, Texas, Naval Facilities Engineering Service Center Port Hueneme, California, Environmental Security Technology Certification Program Arlington, Virginia, Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents, 2004, August.
- [26] L.Y. Huang, T.B. Boving, B.S. Xing, Sorption of PAHs by aspen wood fibers as affected by chemical alterations, *Environ. Sci. Technol.* 40 (2006) 3279–3284.
- [27] American Public Health Association (APHA), American Water Works Association and Water Environment Federation, Standard Methods for the Examination of Water and Wastewater, 20th edn, 1998, Washington, DC, USA.
- [28] H. Ciesielski, T. Sterckeman, A comparison between three methods for the determination of cation exchange capacity and exchangeable cations in soils, *Agronomie* 17 (1997) 9–16.
- [29] B. Xing, W.B. McGill, M.J. Dudas, Cross-correlation of polarity curves to predict partition coefficients of nonionic organic contaminants, *Environ. Sci. Technol.* 28 (1994) 1929–1933.
- [30] T.B. Boving, W. Zhang, Removal of aqueous-phase polynuclear aromatic hydrocarbons using aspen wood fibers, *Chemosphere* 54 (2004) 831–839.
- [31] B.L. Chen, E.J. Johnson, B. Chefetz, L.Z. Zhu, B.S. Xing, Sorption of polar and nonpolar aromatic organic contaminants by plant cuticular materials: role of polarity and accessibility, *Environ. Sci. Technol.* 39 (2005) 6138–6146.
- [32] A. Jang, Y. Seo, P.L. Bishop, The removal of heavy metals in urban runoff by sorption on mulch, *Environ. Pollut.* 133 (2005) 117–127.