Modeling the influence of ethanol on the adsorption and desorption of selected BTEX compounds on bentonite and kaolin

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Abstract

The influence of ethanol on the adsorption capacity and desorption kinetics of benzene and toluene on bentonite and kaolin through modeling and experimental study was investigated. The results showed that the adsorption capacity of both soils for the target compounds decreased as ethanol content increased. As ethanol content increased from 0 to 50%, the adsorption capacity for benzene and toluene on bentonite decreased from 3.6 to 0.54 $\mu g^{n+1}/(L^n \cdot g)$ (by 85%) and 1.91 to 0.01 $\mu g^{n+1}/(L^n \cdot g)$ (by 99.5%), respectively. For benzene and toluene adsorption on kaolin, the adsorption capacity decreased by 86.5% (from 0.26 to 0.04 $\mu g^{n+1}/(L^n \cdot g)$) and 98.2% (from 0.13 to 0.002 $\mu g^{n+1}/(L^n \cdot g)$), respectively, as ethanol content increased from 0 to 50%. In addition, the desorption rate of benzene and toluene from bentonite decreased by about one order of magnitude as the ethanol increased from 0 to 25% and 0 to 50%, respectively. It can be inferred that ethanol could affect the effectiveness of natural attenuation processes that rely on adsorption to soils as a containment technique for benzene and toluene by retarding the adsorption to soils and remobilizing compounds that had already been adsorbed to soils.

Key words: benzene; toluene; ethanol; soil; adsorption; desorption

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Introduction

Petroleum products are a major source of groundwater contamination (USEPA, 2010). The main source of this contamination is from leaking underground storage tanks (USTs) (USEPA, 2010; Nadim et al., 2001), which are commonly used to store petroleum products. There are about 607,000 confirmed leaking UST sites in the U.S. (USEPA, 2010). Other causes for groundwater contamination by petroleum products are from improper disposal, pipe breaks, and spills at extractions wells, refineries, distribution terminals and during transportation (Nadim et al., 2001). Gasoline, a major petroleum product, consists of a mixture of hydrocarbons that are toxic to humans. Benzene, toluene, ethylbenzene and xylene (BTEX) are monocyclic aromatic hydrocarbons that are found in gasoline and are highly toxic (USGS, 2010). Human exposure to these compounds can cause kidney and liver damage, nervous disorders, and reproductive harm (USDHHS, 2004; Caprino and Togna, 1998). Benzene is also classified as a human carcinogen (Caprino and Togna, 1998; Smith, 1996). Research has shown that benzene is known to cause leukemia and can alter blood cell counts in people below 1 part per million exposures (Lan et al., 2004).

To protect the public, these compounds must be removed from groundwater before it can be used as a drinking water source. At many contaminated sites, natural attenuation processes which rely on adsorption of the contaminants to soils and biodegradation of the contaminants by microorganisms are employed as containment and treatment techniques. Research has shown that the migration of hydrophobic gasoline components in the subsurface is retarded by their adsorption to organic matter in soils (Brown and Burris, 1996; Zhu et al., 2004). The effectiveness of adsorption as a natural attenuation processes depends, among other things, on gasoline composition or formulation, soil organic matter, and presence of organic solvents (Chen et al., 2000; Delle, 2001). It is very important to accurately estimate the extent of contaminant removal or containment by natural attenuation processes to make site decisions that are protective of the public and the environment. In particular, this is critical in light of the projected sharp increase in the use of ethanol over the coming years due to its use as fuel and/or fuel oxygenate, replacing methyl *tert*-butyl ether (MTBE).

Ethanol, an organic solvent, is completely miscible in water and could affect the physicochemical properties

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of groundwater, soil surface chemistry, and the fate and transport of gasoline components in the subsurface. When the gasoline-ethanol mixture comes in contact with water, the ethanol will partition to the water phase (Corseuil et al., 2004; USEPA, 2009). The partitioning into the water phase decreases the polarity of the water and can increase the solubility of BTEX compounds (Capiro et al., 2007; Heermann and Powers, 1998; Williams et al., 2003), a process known as a cosolvent effect. Additionally, ethanol is completely miscible with nonaqueous phase liquid (NAPL) such as gasoline (Lee, 2008). When a cosolvent, such as ethanol, is introduced into the two-phase NAPL-water system, it could enhance the solubility of ethanol-free NAPL (Lee, 2008; Kiven, 2005).

Research has been conducted on the effect of ethanol and BTEX compounds in the subsurface. Ruiz-Aguilar et al. (2003) reported that at sites contaminated with ethanol-gasoline mixture of 10% ethanol by volume, the plume lengths of benzene were 69% longer when compared to a site contaminated with gasoline not containing ethanol. The same study also found that toluene plumes were 39% longer in the presence of the ethanol-gasoline mixture. The retardation of biodegradation of BTEX compounds has been attributed to the preferential degradation of ethanol over BTEX compounds in aquifers. Ethanol is degraded first and depletes the oxygen and electron acceptors, leaving BTEX compounds without the nutrients to be degraded by natural attenuation processes, or greatly slowing the degradation process (Da Silva and Alvarez, 2002; Chen et al., 2008; Lawrence et al., 2009; Mackay et al., 2006).

Along with the retardation of BTEX biodegradation, the cosolvency effects of ethanol on BTEX compounds also play an important role in the subsurface. Corseuil et al. (2004) reported that for a water-ethanol solution of 20% ethanol content, the solubility of benzene, toluene, and *o*-xylene increased by 29%, 34%, and 80%, respectively. Da Silva and Alvarez (2002) measured the effect that different concentrations of ethanol had on the adsorption of BTEX compounds to soil. The findings showed that at 1% ethanol content, there were no significant signs of decreased adsorption retardation. However, it did show that at 50% ethanol, there was a significant decrease in BTEX retardation.

A significant amount of work has been done to understand the influence of ethanol on aqueous solubility of BTEX compound and their adsorption on soil. There is limited data on the influence of ethanol on desorption of BTEX compounds from soil, where both modeling and experimental work is conducted simultaneously, although the such data are very important at UST sites that had already been contaminated with gasoline components. This is because as ethanol replaces MTBE as a fuel-oxygenate and/or ethanol becomes a major component of gasoline, ethanol-gasoline mixture releases at these sites could remobilize the BTEX compounds that had already been adsorbed to soils. Considering the lack of such data, the main objective of this research is to investigate the influence of ethanol on the desorption kinetics of selected BTEX compounds, namely benzene and toluene, from soil

through modeling and experimental study. In addition, the effect of ethanol on adsorption capacity of soils for the target BTEX compounds will be investigated.

1 Experimental approach

A number of adsorption and desorption experiments were planned, designed, and conducted. During a typical adsorption experiment: (1) a measured mass of soil (0.03 g bentonite or 0.1 g kaolin) was added to 40 mL glass vials, (2) a 30 mL water-ethanol solution spiked with a target BTEX compound at concentrations of 25, 50, 100, 250, and 500 μg/L was added to the 40 mL glass vials, (3) the vials were sealed tightly and tumbled in a shaker at 200 r/min and kept at constant temperature of 25°C, (4) after 24 hr, the vials were removed and the contents were filtered using disposable syringes with 0.45 μm pore size, and (5) the samples were then analyzed using a Gas Chromatography (GC). The pH of the solution was measured at the beginning and end of the experiments. For experiments with bentonite, the pH values were measured as 8.8 ± 0.6 at the beginning of the experiments and 9.5 ± 0.3 at the end of the experiments. pH values of 6.4 ± 0.7 and 6.0 ± 0.4 were recorded for experiments with kaolin at the beginning and end of experiments, respectively. Step 1 to 5 was repeated for water-ethanol solutions containing 0%, 5%, 10%, 25%, and 50% ethanol by volume. All experiments were conducted in duplicate. These concentrations of ethanol were chosen to bracket ethanol concentrations anticipated in the environment. The 50% ethanol concentration represents a spill in which pure ethanol escapes in a localized area, while the 5% ethanol concentration represents the lower concentration of ethanol that may be seen as the spill advances further through the subsurface.

During a typical desorption experiment: (1) a measured mass of soil (0.03 g bentonite) was added to 40 mL glass vials, (2) 30 mL of the target BTEX compound at 500 μg/L was added to each vial, (3) the vials were then placed in a shaker at 200 r/min to equilibrate, (4) after 24 hr, the aqueous solution was separated from the soil by centrifuging for 30 min at 1875 r/min, (5) the aqueous solution was used to determine the equilibrium concentration and the soil remaining was used for the desorption studies, (6) a water-ethanol solution was added to each vial, (7) the vials were then tumbled in a shaker at 200 r/min and temperature of 25°C, and (8) samples were taken at different time intervals, between 1 hr and 8 days. Each sample was centrifuged for 30 min at a speed of 1875 r/min to separate the liquid from the soil. The samples were then analyzed using a GC. Step 6 through 8 was repeated for water-ethanol solutions containing varying concentrations of ethanol, 0%, 5%, 10%, 25%, and 50% by volume. All experiments were conducted in duplicate.

1.1 Analyses

Analyses of BTEX compounds were performed with a GC (6890, Agilent, USA) equipped with a flame ionization detector using EPA method 502.2 Revision 2.1. The GC

is coupled to an autosampler (CTC Combi-Pal, CTC Analytics AG, Switzerland). The CTC Combi-Pal is a multifunctional auto sampler for headspace, liquid injection, and solid phase micro-extraction systems. The samples were vigorously shaken for 15 min at 99°C in a separate compartment. From there, the auto sampler injected 1 mL of headspace sample into the GC. Nitrogen was used as a makeup gas at 23.2 mL/min, while hydrogen and air were used as carrier gases at 40.0 and 400 mL/min, respectively. The initial oven temperature was 40°C, which was kept constant for 5 min. After 5 min, the oven temperature was ramped at a rate of 10°C/min, holding for 3 min at each 10°C increment. The ramping continued until 250°C was reached.

In order to determine the total organic carbon (TOC) present in soils used in this study, bentonite and kaolin, a TOC analyzer (5000A, Shimadzu, Japan) with a solid sample module was used. The analyzer was set at 900°C, a temperature at which all the organic matter was oxidized and measured. Prior to analysis of the sample, the instrument was calibrated using 0, 1, 2.5 and 5 mg of glucose (40% carbon) and 0, 3.53, 8.83, 17.66 mg of Na_2CO_3 that contains about 0, 0.4, 1 and 2 mg of carbon.

The particle size of bentonite and kaolin was analyzed using a Particle Size Analyzer (PSA LS13320, Beckman Coulter, USA). The pump speed and run time of the analyzer for bentonite and kaolin were 35% and 93 sec respectively. The obscuration was around 9% for bentonite and 11% for kaolin. The particle diameter of bentonite and kaolin was calculated by taking the mean median and mode of the results obtained.

1.2 Materials

All chemicals and reagents used in this study were of analytical grade. Reagents used in this study were distilled deionized water, and ethanol (200 proof, HPLC/Spectrophotometric grade) from Sigma Aldrich, USA. Target compounds (benzene, toluene, and ethylbenzene) used in this research were purchased from Restek Corporation, USA. The purities for benzene and toluene are 99.9% and 99.8%, respectively.

The soils used were bentonite, purchased from Alfa Aesar, USA, and kaolin, purchased from Arcos Organics, USA. Comparison of bentonite and kaolin show that bentonite has 0.75% TOC content compared with 0.032%

for kaolin. In addition, bentonite has a smaller particle size distribution than that of kaolin. The D50 and D90 for bentonite were 4.44 and 21.08 μm, respectively. While the D50 and D90 for kaolin were 6.86 and 35.52 μm, respectively. D50 is the diameter in which 50% of the particles have a larger equivalent. Similarly, D90 is defined as the diameter in which 10% of the particles have a larger equivalent diameter.

2 Results and discussion

2.1 Influence of ethanol on adsorption capacity

The isotherm data were fitted to Langmuir and Freundlich models. The R^2 values for the Freundlich isotherms were consistently higher than the values for the Langmuir isotherms, and therefore, the Freundlich model is used to analyze the data. The adsorption capacity, k_F, and Freundlich constant, n, determined by fitting the experimental data to Freundlich model given in Eq. (1) are presented in Table 1. The results indicate that higher ethanol concentrations resulted in lower adsorption capacity of benzene and toluene for bentonite and kaolin used in this study. As ethanol content increased from 0 to 50%, the adsorption capacity for benzene and toluene on bentonite decreased by 85% and 99.5%, respectively. For benzene and toluene adsorption on kaolin, the adsorption capacity decreased by 86.5% and 98.2%, respectively, as ethanol content increased from 0 to 50%.

$$q_e = k_{Fe} C_e^{1/n} \tag{1}$$

where, q_e (μg/g) is the mass of adsorbate (target BTEX compound) per mass of adsorbent (soil) at equilibrium, k_{Fe} ($\mu g^{n+1}/(L^n \cdot g)$) represent the Freundlich adsorption capacity at equilibrium, C_e (μg/L) represents the concentration of the target BTEX compound at equilibrium and n is a Freundlich constant, which measures the affinity of the adsorbate for the adsorbent surface. The greater the adsorbate affinity for the surface, the lower the value of n and the concentration required to establish high adsorbent loading, resulting in a highly favorable isotherm.

Adsorption takes place in physical, chemical or electrostatic interactions (Voice and Weber, 1983). Since benzene and toluene do not have a charge, electrostatic forces usually do not play a role in the adsorption. The decrease in the adsorption capacity from 0 to 50% ethanol content

Table 1　Adsorption capacity for benzene and toluene onto bentonite and kaolin in the presence of varying concentrations of ethanol

Soil	Ethanol fraction (%)	k_F ($\mu g^{n+1}/(L^n \cdot g)$)		Freundlich constant n	
		Benzene	Toluene	Benzene	Toluene
Bentonite	0	3.60 ± 0.40	1.91 ± 0.16	1.19 ± 0.02	0.99 ± 0.01
	5	2.00 ± 0.28	1.19 ± 0.24	1.11 ± 0.06	1.01 ± 0.00
	10	1.79 ± 0.49	0.94 ± 0.20	0.99 ± 0.09	0.96 ± 0.08
	25	1.43 ± 0.53	0.09 ± 0.03	1.03 ± 0.08	0.75 ± 0.03
	50	0.54 ± 0.13	0.01 ± 0.00	1.17 ± 0.09	0.47 ± 0.00
Kaolin	0	0.26 ± 0.04	0.13 ± 0.01	1.07 ± 0.03	1.00 ± 0.03
	5	0.22 ± 0.04	0.05 ± 0.02	1.07 ± 0.04	0.92 ± 0.07
	10	0.13 ± 0.02	0.04 ± 0.02	1.03 ± 0.02	0.78 ± 0.15
	25	0.08 ± 0.02	0.01 ± 0.00	0.93 ± 0.06	0.68 ± 0.00
	50	0.04 ± 0.02	0.002 ± 0.000	0.93 ± 0.15	0.62 ± 0.03

Data represent mean ± one standard diviation from duplicate data.

can be explained by the cosolvency effect. In the presence of ethanol, there is a decrease in the polarity of water (Da Silva and Alvarez, 2002). Hydrophobic compounds, such as benzene and toluene, are highly non-polar, so a decrease in polarity of water can radically alter the stability of molecules in a solution (Voice and Weber, 1983). The decrease in adsorption capacity with increase in ethanol content may also be attributed to the swelling effects that cosolvents have on soils (Brusseau et al., 1991). Adsorption is dependent upon the surface and internal regions of organic matter in soil (Brusseau et al., 1991). When an organic solvent, such as ethanol, is introduced into a solution with soil, such as bentonite or kaolin, it causes the soils to swell. This swelling increases the thickness of the internal regions, which decreases the surface area to volume ratio (Brusseau et al., 1991), preventing the adsorption of benzene and toluene onto the organic matter of the soils.

2.1.1 Cosolvency power

The cosolvency power represents a hypothetical partition coefficient of hydrophobic compounds between a cosolvent and water. The cosolvency power of ethanol with respect to the target BTEX compounds can be modeled by the log-linear cosolvency equation (Nkedikizza et al., 1985).

$$\ln\left(\frac{k_{\mathrm{F}}^{\mathrm{c}}}{k_{\mathrm{F}}}\right) = -\sigma f^{\mathrm{c}} \tag{2}$$

where, $k_{\mathrm{F}}^{\mathrm{c}}$ ($\mu g^{n+1}/(L^n \cdot g)$) is the Freundlich adsorption capacity for target BTEX compound in a water-ethanol solution, while k_{F} ($\mu g^{n+1}/(L^n \cdot g)$) is the adsorption capacity in water in the absence of ethanol (0% ethanol fraction, f^{c}). σ is the cosolvency power for the target BTEX compounds.

From Eq. (2), it can be concluded that the adsorption capacity for hydrophobic compound in water-ethanol system, $k_{\mathrm{F}}^{\mathrm{c}}$, decreases as the fraction of ethanol increases. By plotting $\ln(k_{\mathrm{F}}^{\mathrm{c}}/k_{\mathrm{F}})$ vs. f^{c}, the cosolvency power of ethanol, σ, can be determined. The graph will yield a straight line with a slope of σ. Figure 1 shows the plot of $\ln(k_{\mathrm{F}}^{\mathrm{c}}/k_{\mathrm{F}})$ vs. f^{c} for benzene and toluene.

The data show that the cosolvency power of benzene (3.99) is lower than toluene (12.36) for ethanol with bentonite. Similarly, the cosolvency power of ethanol with kaolin is in the order benzene (4.58) < toluene (9.07). These results are expected because of the direct relationship between the $\log K_{\mathrm{ow}}$ and the cosolvency power (Corseuil et al., 2004). The $\log K_{\mathrm{ow}}$ for benzene and toluene is 2.13 and 2.69, respectively. In addition, the cosolvency power was found to be directly proportional to the $\log K_{\mathrm{oc}}$ and is inversely proportional to the water solubility of the target BTEX compounds tested in the current study (Table 2).

2.2 Comparison of adsorption capacity for bentonite and kaolin

Figure 2 represents the adsorption capacity of bentonite and kaolin for benzene and toluene. For both chemicals, larger adsorption capacity values are observed for ben-

Table 2 Correlation between cosolvency power (σ) and $\log K_{\mathrm{ow}}$, $\log K_{\mathrm{oc}}$, and water solubility (C_{s}) for benzene and toluene

Target BTEX compound	Soil	$\log K_{\mathrm{ow}}$	$\log K_{\mathrm{oc}}$	C_{s} (mg/L)	σ
Benzene	Bentonite	2.13	1.9	1780	3.99
	Kaolin				4.58
Toluene	Bentonite	2.69	2.0	515	12.37
	Kaolin				9.07
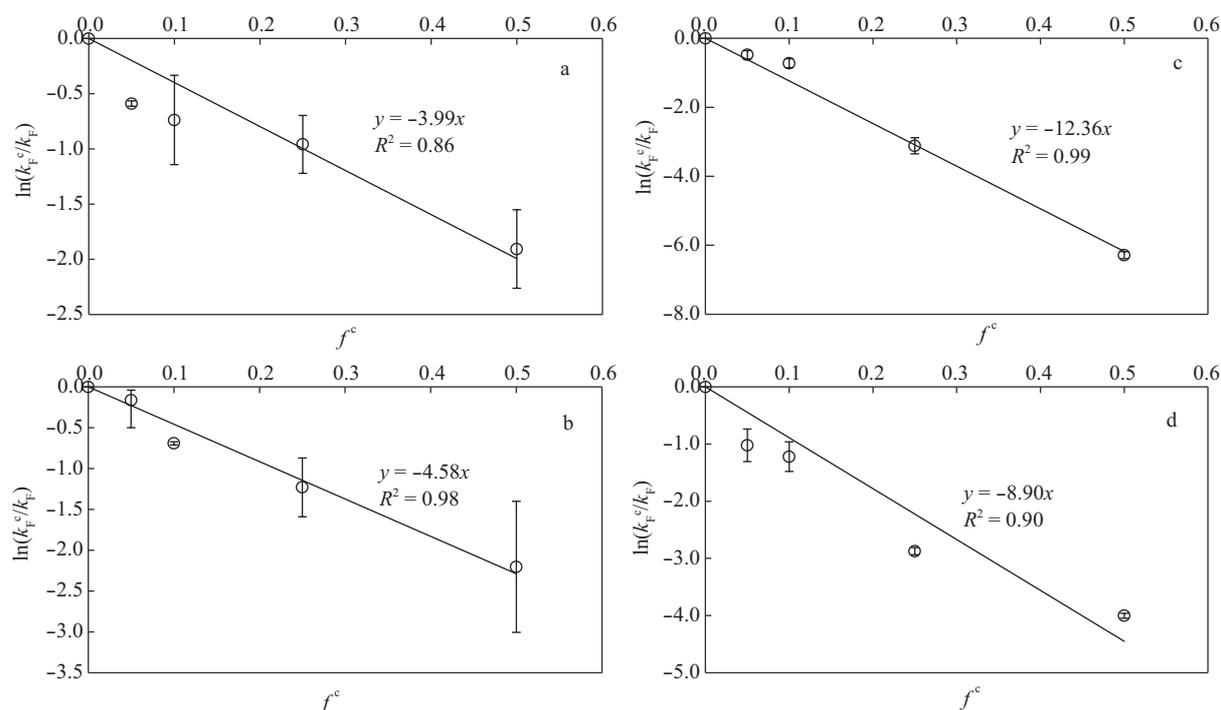
Fig. 1 Plot of $\ln(k_{\mathrm{F}}^{\mathrm{c}}/k_{\mathrm{f}})$ vs. f^{c}. (a) benzene with bentonite; (b) benzene with kaolin; (c) toluene with bentonite; (d) toluene with kaolin.
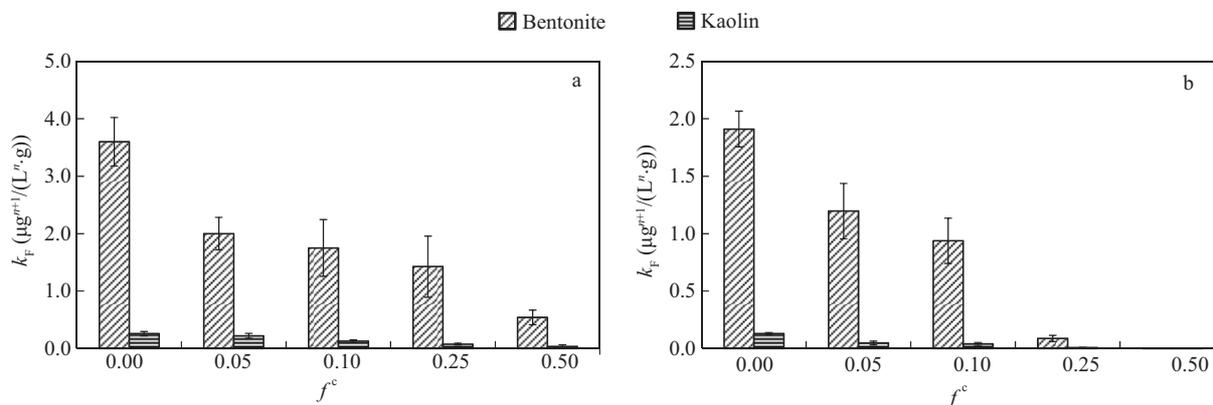
Fig. 2 Adsorption capacity of bentonite and kaolin for: (a) benzene and (b) toluene.

tonite at all ethanol-water content considered in this study, which has a higher percentage of organic carbon (0.75%), and smaller adsorption capacity values are observed in kaolin, which has a lower percentage of organic carbon (0.032%). These results are expected because the organic content is a critical factor in the adsorption capacity of a soil. In general, soils with higher organic carbon content have a higher adsorption capacity for nonionic organic compounds than soils or clay with lower organic carbon content (Bartelt-Hunt et al., 2003). Another important variable in adsorption is the particle size. There is an inverse relationship between the particle size and the adsorption capacity (Voice and Weber, 1983). A smaller particle size offers a larger surface area for adsorption of compounds. From an analysis on the particle size distribution, bentonite has smaller size particles than that of kaolin. The D50 and D90 for bentonite are 4.44 and 21.08 μm, respectively. For kaolin, the D50 and D90 are 6.86 and 35.52 μm, respectively.

The desorption of a given constituent from soil can be given by the first-order kinetics (Eq. (3)):

$$\frac{dC}{dt} = k_d(C_e - C) \tag{3}$$

where, k_d (sec^{-1}) is the desorption rate. A number of studies have reported that desorption rate from soils and sediments is biphasic in nature and consist of an initial rapid release of chemicals from liable sites that occurs over a few hours or days followed by a much slower release from non-liable sites which can take months or years (Carroll et al., 1994; Pignatello et al., 1993). In the current study, the desorption studies are conducted for eight days, and therefore, the k_d value in Eq. (1) is assumed to represent the release the target BTEX compounds from the liable sites. C (μg/L) represents the concentration of the target BTEX compound in a solution at a given time t. The expression for C and C_e can be obtained from isotherm models, such as Freundlich and Langmuir. In the current study, the experimental data from isotherm studies were fitted to both models and the R^2 values for the Freundlich model were consistently higher than the R^2 values for the Langmuir isotherm, and therefore, the Freundlich isotherm is used.

At equilibrium, the relationship between the target BTEX compound concentrations in a solution and ad-

sorbed to soil can be described using the Freundlich model given in Eq. (1). Rearranging Eq. (1) and solving for C_e results in Eq. (4). Similarly, the expression for concentration of the target BTEX compounds in a solution during desorption can be given by Eq. (5).

$$C_e = \left(\frac{q_e}{k_{Fe}}\right)^n \tag{4}$$

$$C = \left(\frac{q}{k_F}\right)^n \tag{5}$$

where, q (μg/g) is the mass of adsorbate (target BTEX compounds) per mass of adsorbent (soil) at a given time t (sec) during desorption. Substituting the expression given for C_e in Eq. (4) and for C in Eq. (5) into Eq. (3), results in Eq. (6). Multiplying Eq. (6) by (k_F^n/q_e^n) gives Eq. (7). Differentiation of the right hand side and re-arrangement of Eq. (7) results in Eq. (8).

$$\frac{\left(\frac{q}{k_F}\right)^n}{dt} = k_d\left(\left(\frac{q_e}{k_{Fe}}\right)^n - \left(\frac{q}{k_F}\right)^n\right) \tag{6}$$

$$\frac{\left(\frac{q}{q_e}\right)^n}{dt} = k_d\left(\left(\frac{k_F}{k_{Fe}}\right)^n - \left(\frac{q}{q_e}\right)^n\right) \tag{7}$$

$$\frac{\left(\frac{q}{q_e}\right)}{dt} = \frac{k_d}{n\left(\frac{q}{q_e}\right)^{n-1}}\left(\left(\frac{k_F}{k_{Fe}}\right)^n - \left(\frac{q}{q_e}\right)^n\right) \tag{8}$$

2.2.1 Method of solution to the desorption equation

Equation (8) is used to predict the desorption of target BTEX compounds, in terms of q/q_e, from soil for given desorption rate (k_d), Freundlich constant (n), and ratio of adsorption capacity at any time and equilibrium (k_F/k_{Fe}). The equation is an ordinary differential equation (ODE) with known initial condition. The solution to the ODE is obtained numerically using ode15s, an ODE solver available in MATLAB, version 7.7.04.471. Ode15s is a stiff and a variable-step solver based on the numerical

differentiation formula. The variable-step feature allows ode15s to control error by varying the step size during the simulation, reducing the step size to increase accuracy when a model's values are changing rapidly and increasing the step size to avoid taking unnecessary steps when the model's values are changing slowly. The k_d and k_F values are estimated by fitting experimental data obtained from desorption studies to model predictions using lsqcurvefit, an optimization function available in MATLAB.

2.2.2 Sensitivity of the desorption model

Sensitivity of the desorption model to k_d, n, and k_F/k_{Fe} is investigated. The following values are used as base values: $k_d = 10^{-5}$ sec^{-1}, $n = 0.99$, and $k_F/k_{Fe} = 0.90$. The sensitivity of the desorption model in relation to variation of selected parameters is tested while keeping constant other parameters at base values.

The influence of desorption rate, k_d, on q/q_e for k_d values of 10^{-7}, 10^{-6}, 10^{-5}, 10^{-4}, and 10^{-3} sec^{-1} is presented in Fig. 3a. The lines in the figure show successive increases in desorption of the constituent from adsorbent surface with increasing k_d, which is expected. However, increasing the Freundlich constant, n, from 0.8 to 1.20 did not affect desorption of adsorbate from adsorbent (Fig. 3b). This result is in agreement with the findings of Carter et al. (1995) who evaluated the influence of n on site energy distribution for preloaded adsorbents. They showed increase in n caused a decrease in the width of energy distribution site and increase in site energetics, resulting in no change in overall energies of adsorption. Figure 3c illustrates the influence of ratio adsorption capacities during desorption and at equilibrium on desorption from the adsorbent surface. The results in the figure show successive decrease in the ratio of k_F/k_{Fe} increased desorption.

The desorption data were fitted to the ODE given in Eq. (8) and the results are presented in Fig. 4 for benzene and toluene desorption from bentonite with varying concentrations of ethanol. The results in Fig. 4a–c represent the desorption for benzene from bentonite to a water-ethanol solution with 0, 10%, and 25% of ethanol by volume, respectively. While the desorption of toluene from surface of bentonite to a water-ethanol solution with 0, 25%, and 50% ethanol by volume is presented in Fig. 4d–f, respectively. The experimental data and the model predictions fitted with R^2 values in the range of 0.71 to 0.98.

The results indicate that as the ethanol content increased, the desorption rate, k_d, increased for both benzene and toluene. For benzene, as ethanol content increases from 0 to 25%, the k_d value increased from 1.9×10^{-5} to 1.7×10^{-4} sec^{-1}, close to one order of magnitude increase. Similarly, as ethanol content increases from 0 to 50% ethanol, the k_d value for toluene increased from 4.7×10^{-5} to 4.0×10^{-4} sec^{-1}. This is a significant finding for sites contaminated with BTEX compounds and where adsorption to soils is used as a natural attenuation process. The release of ethanol at such a site may remobilize BTEX compounds that has already been adsorbed to soils.

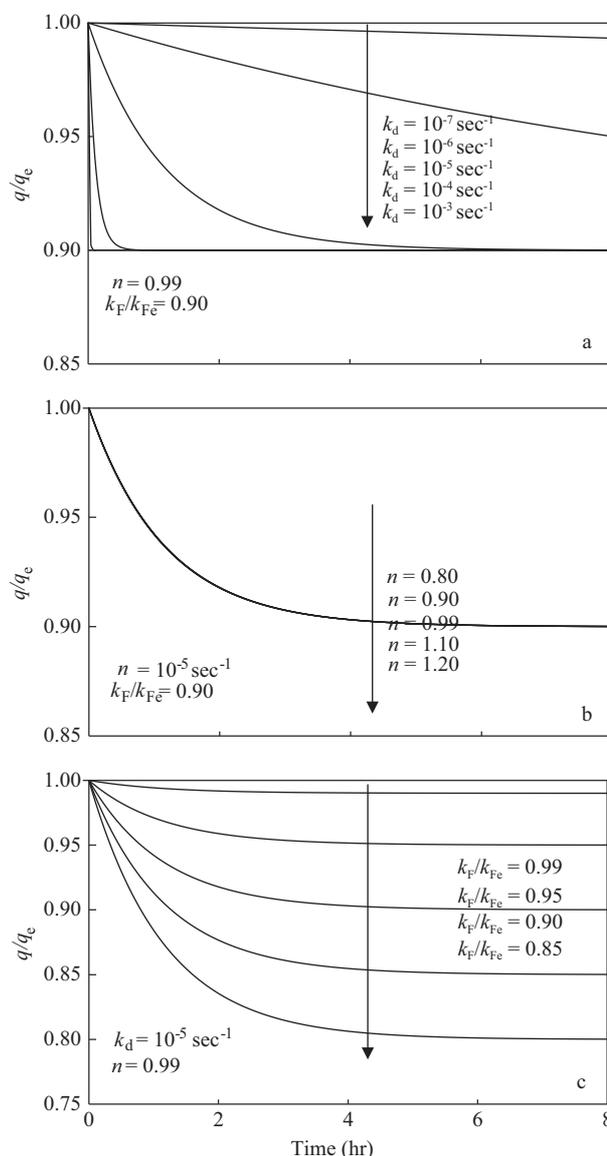In addition, ethanol fraction, f^c, was found to be directly

Fig. 3 Predicted effect of k_d (a), n (b), and k_F/k_{Fe} (c) on the desorption of adsorbate from adsorbent.

proportional to the logk_d (Fig. 5). Like cosolvency power, the desorption rate of benzene is less than that of toluene. On the basis of the properties of benzene and toluene, it can be inferred that desorption rate is directly proportional to logK_{ow} and logK_{oc} and is inversely proportional to the water solubility.

In summary, this study investigated the influence of ethanol on the adsorption capacity and desorption kinetics of benzene and toluene on bentonite and kaolin. For both soils, the adsorption capacity for the target BTEX compounds deceased as the ethanol content increased. The cosolvency power, a hypothetical partition coefficient of hydrophobic compounds between a cosolvent and water, for benzene and toluene with respect to ethanol is directly proportional to logK_{ow} and logK_{oc} and is inversely proportional to water solubility. The desorption rate of benzene and toluene from bentonite decreased by about one order of magnitude as the ethanol increased from 0 to 25% and 0 to 50%, respectively. Like cosolvency power, the desorption rate, k_d, is directly proportional to logK_{ow} and logK_{oc}
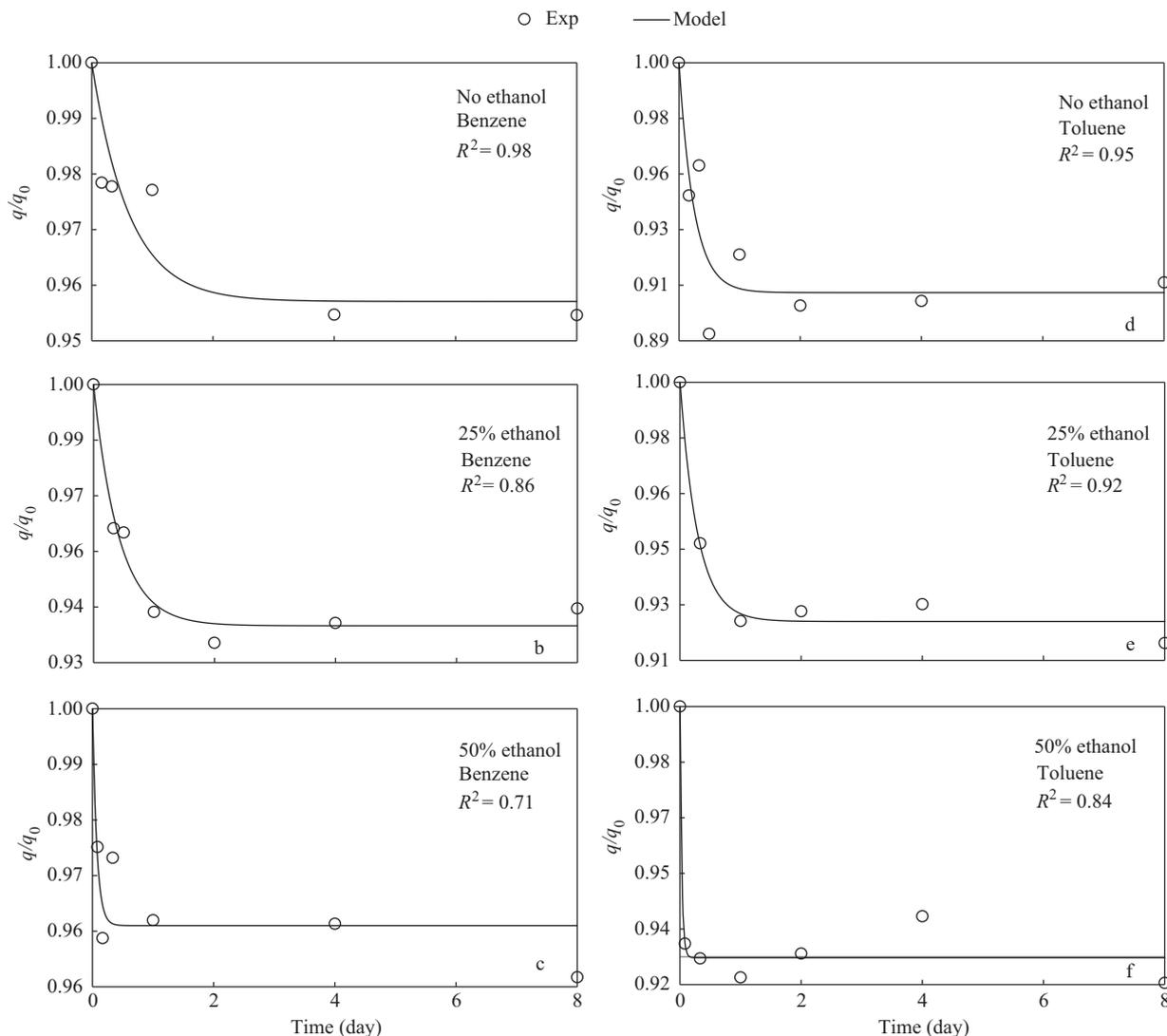
○ Exp   —— Model

Fig. 4   Desorption of benzene and toluene from bentonite to a solution containing varying concentration of ethanol.
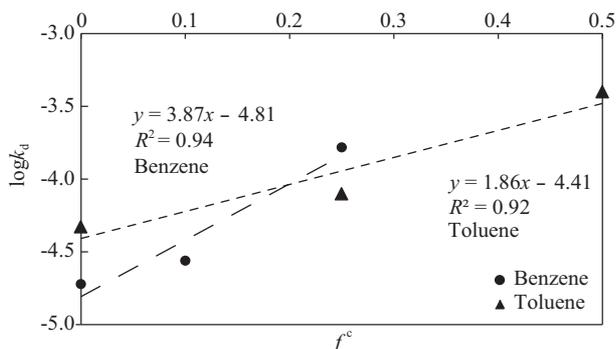

Fig. 5   Plot of $\log k_d$ vs. f^c.

and is inversely proportional to the water solubility. The findings of this research show that ethanol could affect the effectiveness of natural attenuation process that relies on adsorption to soils as a containment technique for BTEX compounds. In addition, ethanol could also remobilize BTEX compounds that had already been adsorbed to soils.

Acknowledgments

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