Durability of organobentonite-amended liner for decelerating chloroform transport

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HIGHLIGHTS

- CTMAB-bentonite has the highest sorption capacity among six organobentonites.
- Adding 10% CTMAB-bentonite increased the duration of a bentonite liner by 88.5%.
- 70-cm 10% CTMAB-bentonite liner exhibited much better durability than 100-cm CCL.
- 65.8-cm 10% CTMAB-bentonite liner could sorb all chloroform in a 100-m landfill.

ARTICLE INFO

ABSTRACT

Chloroform is added to landfill for suppressing methane generation, which however may transport through landfill liners and lead to contamination of groundwater. To decelerate chloroform transport, the enhanced sorption ability of clay liners following organobentonite addition was tested. In this study, we used batch sorption to evaluate sorption capacity of chloroform to organobentonite, followed by column tests and model simulations for assessing durability of different liners. Results show that adding 10% CTMAB-bentonite (organobentonite synthesized using cetyltrimethylammonium bromide) increased the duration of a bentonite liner by 88.5%. CTMAB-bentonite consistently showed the highest sorption capacity (Q_m) among six typical organobentonites under various environmental conditions. The removal rate of chloroform by CTMAB-bentonite was 3.6—23 times higher than that by natural soils. According to the results derived by model simulation, a 70-cm 10% CTMAB-bentonite liner exhibited much better durability than a 100-cm compact clay liner (CCL) and natural bentonite liner evidenced by the delayed and lower peak of eluent concentration. A minimum thickness of 65.8 cm of the 10% CTMAB-bentonite liner could completely sorb the chloroform in a 100-m-high landfill. The 10% CTMAB-bentonite liner exhibiting much better durability has the promise for reducing environmental risk of chloroform in landfill.

1. Introduction

Biodegradation of disposed wastes emits a large amount of potentially explosive methane to the atmosphere (Kjeldsen and Fischer, 1995; Abushammala et al., 2013; Di Trapani et al., 2013; USEPA, 2014). Chloroform is added to landfill to suppress the methanogenesis activity (Zhao et al., 2009). However, chloroform may transport to groundwater causing secondary pollution (Jimenez et al., 2002). Current landfill liners, such as compact clay liner (CCL) and Geosynthetic Clay Liner (GCL) were inadequate to prevent pollutants in leachates from penetration. Organic compounds can transport through liners via advection, dispersion, and diffusion (Lake and Rowe, 2000; Katsumi et al., 2001; Foose et al., 2002). Thus, the impermeable property of liners to water does not represent durability to organic compounds. Using traditional methods might overestimate their durability and hence results in pollutants release into the environment in a shorter period. In order to enhance the durability of liners, a potential solution is to add strong sorptive materials into the liners to enhance their ability of absorbing organic pollutants (Lorenzetti et al., 2005).

Organobentonites were reported to be an excellent adsorbent

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for various types of organic pollutants in the aqueous phase (Zhu et al., 1998, 2000, 2008; Zhou et al., 2011; Nourmoradi et al., 2012) and could be used as amendments to improve durability of liners. Organobentonites were usually produced by replacing the metal ions in the interlayers with a cationic surfactant and would present different sorption properties based on the type of surfactants used during synthesis (Zhu et al., 2008; Zhu and Zhu, 2008). Researchers also indicated that adding organobentonite into landfill liner could retard organic compounds in leachate (Lo and Mak, 1998; Lorenzetti et al., 2005). However, there exists little evidence showing which organobentonite is more suitable for landfill liner amendments on the purpose of decelerating chloroform migration. Additionally, little information is known about how the conditions of leachate at landfill bottom, including coexistent organic chemicals, temperature, ionic strength of leachate, and humic acid, affect the sorption characteristics of organobentonites to a certain extent and lower the durability of liners to organic compounds.

In addition, there is a tradeoff between low permeability and good sorption capacity. Increasing the amount of organobentonite in liner increased the hydraulic conductivity as well as the sorption capacity of the liner. Lorenzetti et al. (Lorenzetti et al., 2005) found that when the percentage of HDTMA-bentonite and BTEA-bentonite increased from 0 to 80%, the hydraulic conductivity of liners increased by two to three orders of magnitude. A larger hydraulic conductivity presents a higher velocity of flow and this may limit the sorption capacity of liner. Accordingly, more organic pollutants transport through the liner via water permeation, and then the durability of the landfill liner is degraded.

Therefore, this study aimed to identify a suitable organobentonite and its optimal amount used for landfill liners. We compared the removal efficiency of chloroform by six different organobentonites, and tested their performance under various environmental conditions. By using column tests and model simulations, we investigated the transport of chloroform through different kinds and thicknesses of liner materials, where the durations of chloroform in the liners were estimated. The results of this study provide essential data for optimizing landfill liner design in order to minimize the environmental risk from chloroform.

2. Materials and methods

2.1. Materials

The bentonite used in this study was obtained from Inner Mongolia, China. Its cation exchange capacity (CEC) was 1.084 mmol/g (Wu and Zhu, 2012). Three common soils including red soil, black soil, and paddy soil were collected from Jiangxi, Zhejiang, and Heilongjiang provinces, respectively. The bentonite and three soils were ground to a less than 100 mesh powder and dried at 70 °C for 24 h. Tetramethylammonium bromide (TMAB), octyltrimethylammonium bromide (OTMAB), dodecyl trimethylammonium bromide (DTMAB), CTMAB, and chloroform were all of analytical grades, which were purchased from the Sinapharm Chemical Reagent Co. Ltd, Shanghai, China. The molar volume, density, $\log K_{ow}$, and water solubility of chloroform were 79.6 cm³, 1.492 g/cm³, 1.97, and 2096 mg/L, respectively.

2.2. Organobentonite synthesis

Organobentonites were synthesized by using the wet method described in the supplementary data. The single-cation organobentonites were designated as surfactant-bentonites, i.e., CTMAB-bentonite represents the organobentonite synthesized using CTMAB. The dual-cation organobentonites were identified by the amount of surfactants as a percentage of the bentonite's CEC

followed by the surfactant type. For example, 60CTMAB/40TMAB-bentonite denoted that this organobentonite was synthesized with CTMAB and TMAB, and the amounts of the surfactants were 60% and 40% of the bentonite's CEC, respectively.

2.3. Chloroform sorption

The procedure of the sorption study was adapted from an OECD method (OECD, 2000). The details are provided in the supplementary data. The influence of the temperature on the chloroform removal was studied by using the solution with an initial concentration of 0–2 mg/L at 288–308 K. Na^+ and NO_3^- (0–1 mM) were used as representative ions. The influence of humic acid on the chloroform removal was tested under the solution concentration of 0–500 mg/L humic acid.

In order to estimate the maximum capacity (Q_m) of materials in sorption, the Langmuir model was employed to delineate the experimental sorption isotherm. A linear model was used to estimate the sorption capacity (K_d). The models were described in the supplementary data.

2.4. Column tests and chloroform transport simulation

Column tests were conducted in glass columns with an inside diameter of 2.5 cm. First, 15 g quartz sand was laid at the bottom of each column. Second, 15 g soil was put on the top of the quartz sand. Third, the barometric pressure was adjusted to confine the soil. Finally, 10 g quartz sand was placed on top of the soil. During the experiment period, the upper solution was maintained at 15 cm. During the test period, each column was covered by a glass cap in order to avoid chloroform volatilization. The upper liquid was replaced regularly to make sure the concentration of chloroform maintained at the same level. The effluent was collected by glass tubes, and the chloroform concentration was measured in every 10 mL effluent.

A similar column test was conducted to evaluate the loss of surfactant from CTMAB-bentonite. The same mass of quartz sand and soils were set layer by layer as mentioned above in the same glass columns. In this experiment, we used solution containing 0.5 M of $NaNO_3$ as the ions in leachate. The effluent was collected every 20 mL, and its CTMAB concentration was measured.

A one-dimensional transport model simulating the transport of chemicals in a porous medium was used to evaluate the performances of different liners for a long period. Contaminants transport through liners via advection, dispersion, and sorption could be described by the following equation (Voudrias, 2002):

$$\frac{\partial C}{\partial t} = -v\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} - \frac{\rho_b}{n}\frac{\partial S}{\partial t} \tag{1}$$

where C is the concentration of solute in the aqueous phase (mg/L), S is the amount of solute sorbed on a sorbent (mg/g), v is the linear velocity of water (cm/y), x is the distance (cm), D is the dispersion coefficient (cm²/y), ρ_b is the bulk dry density of the porous media (g/cm³), and n presents the porosity. The change of C with time and distances were modeled as follows:

$$C(x, t) = C_0 A(x, t), \text{ for } 0 < t \leq t_0 \tag{2}$$

$$C(x, t) = C_0 A(x, t) - C_0 A(x, t-t_0), \text{ for } t > t_0 \tag{3}$$

$A(x,t)$ was described as equation (S8) in the supplementary data. In the simulations, t_0 was set to 2 years and the hydraulic conductivity of the liner (K) was measured by using a falling head method following ASTM D4491-99a (ASTM-D4491-99a, 2014) and