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Transport of Cr(VI) through clay liners containing activated carbon or acid-activated bentonite

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ABSTRACT

The potential of clays containing 3 or 6% granular activated carbon (GAC) or 3 or 6% acid-activated bentonite was assessed for use as a landfill liner-soil material. Permeability, batch adsorption and column tests were performed to evaluate the seepage properties, the Cr(VI) adsorption capacity and transport parameters of the soils. All soil specimens had a hydraulic conductivity of $<1\times10^{-7}$ cm/s at a certain range of moulding water content. The Cr(VI) adsorption was much larger than adsorption by the raw clay. The improved clay prevented effectively the transport of Cr(VI). The diffusion coefficient of Cr(VI) for liner-soil materials was back-calculated by a one-dimensional nonlinear advection–dispersion–reaction numerical transport program. This coefficient for the clay or the improved clay was 2.2×10^{-10} to 8.3×10^{-10} m^2/s. The improved clay may be used as a good barrier material to attenuate contamination of Cr(VI) in landfills.

1. Introduction

Leachate from solid-waste landfills was found to contain a number of heavy metal ions. These heavy metal ions may enter the aquifer underlying the landfill and thereby pose a potential threat to human health (He et al., 2006; Giannis et al., 2007; Qu et al., 2008). Modern landfills are designed with a barrier liner system beneath the solid waste, to control the permeation of leachate and minimize contamination of the environment. However, many heavy metal ions can pollute groundwater by diffusion through a block liner. Hence, there is a crucial need for the development of a new landfill liner that can effectively prevent the transport of heavy metal ions. A method of enhancing pollutants adsorption and thus minimizing the flux of leachate pollutants through liners is to amend the liners with materials capable of strongly adsorbing pollutants (Gullick and Weber, 2001; Bartelt-Hunt et al., 2005). Granular activated carbon (GAC) and acid-activated bentonite are both powerful adsorbents for contaminants (Wu, 2004; Hu and Yu, 2007; Lu et al., 2008). Increasing the adsorption capacity of clay liners reduces the pollutant advection velocity and the rate of solute diffusion during solute transport without requiring an increase in liner thickness. Although an adsorbed pollutant will eventually be desorbed from the liner, the mass flux from the bottom of the liner should be significantly reduced when GAC or acid-activated bentonite is a component of the liner.

To predict the transport of a pollutant through the improved clay liners, mass transport parameters such as seepage velocity, the diffusion coefficient of the pollutant, and the retardation factor of the liner-soil material to the pollutant should be identified. Among of these mass transport parameters, the retardation factor and diffusion coefficient are usually estimated using batch or column tests (Kim et al., 2003). For compacted clay liners, which have a very low hydraulic conductivity with a low hydraulic head, pollutants will be slowly transported and is controlled by diffusion through the liners. Most of the available data related to pollutants transport in clay liners were acquired from column experiments performed in which a low hydraulic head is used (Shackelford and Daniel, 1991; Shackelford and Redmond, 1993; Du et al., 2005a,b). Because of the blocked leachate collection system, leachate head can rise to a few meters high (Cooke et al., 2005). Although the liners have a very low hydraulic conductivity, the effect of advection to pollutants transport cannot be ignored at relatively high leaching.

In the process of pollutants transport through the liners, adsorption to liner-soil materials is a very important mechanism. Reliability of the measurement for diffusion coefficients of reactive solutes was related to assumption of adsorption isotherm and contaminant concentration. At relatively low concentrations of the solute, the adsorption behavior can be modeled with a linear model. However, in most practical applications, the solute concentrations will be higher and the resulting adsorption behavior will be nonlinear (Shackelford and Daniel, 1991). Hence, the appropriate migration equation is a nonlinear advection–dispersion–reaction equation.

In this paper, GAC and acid-activated bentonite were evaluated for their use as adsorptive amendments for trapping Cr(VI) in clay liners

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by conducting batch tests. For investigating the Cr(VI) transport through these improved clay liners, a series of laboratory column experiments was performed. Diffusion coefficients were determined by fitting the measured concentration to the one-dimensional nonlinear solute transport numerical results.

2. Materials and methods

2.1. Testing materials

The clay was obtained from the Maoyingzi zone in Dalian city. The clay was never in contact with Cr(VI). The chemical composition of the clay measured by X-ray fluorescence spectrometry was 60.7% SiO_2, 23.8% AL_2O_3, 0.3% Fe_2O_3, 0.2% CaO, 0.1% MgO, 4.0% K_2O, 2.0% Na_2O and 0.1% TiO_2. The bentonite was obtained from Weifang Huawei Bentonite Co., Ltd. The chemical composition was 61.2% SiO_2, 18.4% AL_2O_3, 7.4% Fe_2O_3, 2.5% CaO, 2.4% MgO, 1.7% K_2O and 0.5% Na_2O. GAC was obtained from Shenyang Pengtai Active Charcoal Co., Ltd. The improved soil was composed either of 97% or 94% clay plus 3% or 6% acid-activated bentonite, or of 97% or 94% clay plus 3% or 6% GAC (Table 1). The grain size distribution of the raw clay is given in Fig. 1. Potassium dichromate solution was used in the batch tests as a source of Cr(VI).

2.2. Permeability tests

Permeability tests were performed on conventional compacted clay liner and the improved clay liner containing GAC or acid-activated bentonite. The hydraulic conductivity was measured with a changing-head permeability test using flexible-wall permeameters (Nanjing Soil Instrument Factory) following the procedure in SL237-1999. The specimens containing various amounts of water were compacted in the permeameter molds. The liquid used for the tests was a leachate from the Maoyingzi landfill of Dalian city. The tests were repeated three times.

2.3. Batch tests

The dry soil samples (12.5 g) were dispersed in 50 ml aqueous solutions of various concentrations of Cr(VI). Landfill leachates had pH values of 4.5–9, so pH of the test solutions was adjusted to approximately 7.00 with dilute HNO_3 or NaOH (He et al., 2006; Christensen et al., 2001). The dispersions were shaken at 30 °C. The stirring speed was 120 rot/min The concentration of Cr(VI) in the supernatant solution after centrifugation was measured by spectrophotometry (Shanghai Third Analytical Instruments Factory) according to GB 7467-87 DPC. The error of the colorimetric measurements was <4%. Each batch test was repeated three times. The amount of Cr(VI) adsorbed on the soil particles was calculated from the mass balance.

2.4. Column tests

The column tests were carried out with a large tank-shaped column of 10 cm in diameter and 18 cm in height (Fig. 2). To reduce the “wall effect” during the column tests, the inner wall of the column was covered with a layer of rubber mold. The compacted soil layer, 10 cm thick, was formed at the maximum dry density in the column. A constant pressure head of deionized water, 250 cm in height, was applied to the soil layer surface at the beginning. After establishing a steady drainage rate at saturation, the deionized water was replaced by Cr(VI) solution. These experiments were performed at room temperature (Table 2).

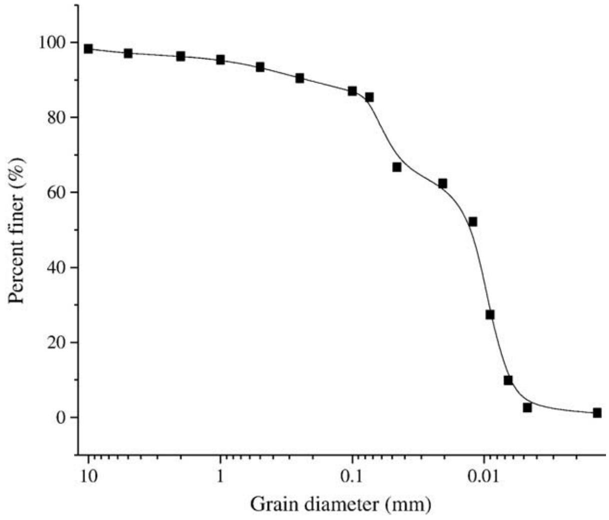

Fig. 1. Grain size distribution of the raw clay.

At the completion of the column tests, the soil specimens were extruded using steel tubes. The extruded specimens were sliced into ten sublayers using a stainless steel thread. The pore water in each sublayer was obtained by squeezing the soil at a pressure of about 10.0 kPa for approximately 12 h. The concentration of Cr(VI) in the pore water was measured spectrophotometrically.

3. Results and discussion

3.1. Theory

The adsorption on all soil samples was described by the Langmuir isotherm model (Bartelt-Hunt et al., 2005),

$$C_s = \frac{q_m b C_e}{1 + b C_e} \tag{1}$$

where C_s is the adsorbed amount, C_e is the equilibrium concentration, q_m is the monolayer capacity and b is the Langmuir parameter.

A one-dimensional solute transport equation was used to simulate the transport of Cr(VI) through the landfill liner (Zhang et al., 2006),

$$\left(1 + \frac{\rho q_m b}{n_e (1 + bC)^2}\right) \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} \tag{2}$$

Table 1
Soil samples.

Soil samples	Liquid limit/(%)	Plastic limit/(%)	Plasticity index/(%)	Maximum dry density/(g/cm^3)	Optimum water content/(%)	Porosity ratio	Specific density
Raw clay	29.9	14.2	15.7	1.72	18.8	0.35	2.66
Clay containing 3% activated bentonite	33.7	14.8	18.9	1.67	21.3	0.32	2.60
Clay containing 6% activated bentonite	35.6	15.2	20.4	1.63	24.5	0.34	2.62
Clay containing 3% GAC	34.6	13.5	21.1	1.62	18.4	0.36	2.57
Clay containing 6% GAC	32.4	14.8	17.6	1.56	17.4	0.32	2.59