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Studies of hexavalent chromium attenuation in redox variable soils obtained from a sandy to sub-wetland groundwater environment

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Abstract

Laboratory experiments were conducted to characterize and quantify the capacity and kinetics of the combined effects of natural attenuation processes, such as adsorption, reduction, and precipitation, for hexavalent chromium [Cr(VI)] in a variable geochemical (i.e. fraction of organic carbon [foc], redox) environment of glaciated soils. Equilibrium attenuation terms: linear sorption (K_d), estimated capacity, and non-linear Langmuir (K_L, Q) sorption parameters; varied over several orders of magnitude. The pseudo-first-order rate of disappearance of Cr(VI) from aqueous:soil slurries ranged from $\sim 10^{-5}$ to $\sim 10^{-1}$/min. An operationally defined kinetic attenuation term, attenuation capacity (AC), describing the quantity of Cr(VI) disappearing from the slurries, ranged from 1.1 to ~12 μg Cr(VI)/g soil/7 days. The linear K_d's and estimated attenuation capacities were indirectly and directly related to increasing soil pH and foc, respectively. The AC values decreased and increased as a function of increasing soil pH and foc, respectively. The parameters determined in this work were used to evaluate the kinetics, capacity, and stability of chromium attenuation in the sub-wetland saturated soils in Hellerich (2004. A field, laboratory, and modeling study of natural attenuation processes affecting the fate and transport of hexavalent chromium in a redox variable groundwater environment. Ph.D. Dissertation, Department of Civil and Environmental Engineering, University of Connecticut-Storrs) using a statistical simulation framework.

Keywords: Hexavalent; Chromium; Natural; Attenuation; Groundwater; Redox

1. Introduction

Chromium is among the most common groundwater contaminants at industrial contaminated sites (NRC, 1994). In groundwater, the predominant form of chromium is the oxidized form, hexavalent chromium [Cr(VI)], present as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$). Cr(VI) is toxic and mobile, while trivalent chromium [Cr(III)], the reduced form, is less toxic and less mobile (NRC, 1994) because it precipitates out of solution at pH's above 5. Chromium is susceptible to redox, sorption, precipitation, and complexation reactions and is pH sensitive, resulting in a range of chemical speciation (Richard and Bourg, 1991).

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Nomenclature

C_{sorbed}	mass of sorbed Cr(VI) per mass of soil (μg/g)
K_d	linear sorption coefficient (mL/g)
C_{aqueous}	concentration of aqueous Cr(VI) (μg/L)
EAC	estimated attenuation capacity (μg Cr(VI)/g soil)
K_L	Langmuir sorption coefficient (mL/g)
Q_L	Langmuir capacity parameter (μg/g)
$\bar{C}$	average concentration of the duplicate set of measurements at time t (μg/L)
$\bar{C}_0$	the average initial concentration (μg/L)
t	time (min)
k_1	pseudo-first-order bulk disappearance rate constant (1/min)
AC_t	Cr(VI) specific attenuation capacity for a given time point (μg Cr(VI)/g soil/time (days or hours))
C_{k_1}	simulated Cr(VI) from Eq. (1) for a given time point (μg/L)
$\bar{V}_{\text{AQ}}$	the average aqueous volume (mL)
$\bar{M}_\text{S}$	the average soil mass (g)
Cr(VI)	hexavalent chromium
[Cr(VI)]	concentration of Cr(VI)
Cr(III)	trivalent chromium
foc	fraction of organic carbon
MNA	monitored natural attenuation
NA	natural attenuation
SOM	soil organic matter
RDC	reduction capacity (meq/g)
OXC	oxidation capacity (meq/g)
EPA	United States Environmental Protection Agency
NLLS	non-linear least-squares
μ	mean
σ	standard deviation
β	buffering capacity
R^2	correlation coefficient
RMSE	root mean square error
n	porosity (dimensionless)

Several in situ and ex situ remediation approaches are available to address chromium-contaminated groundwater (Fruchter, 2002). Palmer and Puls (1994) have suggested that monitored natural attenuation (MNA) of Cr(VI) may be viable under certain geochemical conditions. Palmer and Puls (1994) state the following with respect to successfully implementing natural attenuation (NA) of Cr(VI) as a remedy at a particular site: "If natural attenuation is to be considered a viable option, then ideally it must be demonstrated that: there are natural reductants present in the aquifer; the amount of Cr(VI) and other reactive constituents does not exceed the capacity of the aquifer to reduce them; the time scale required to achieve the reduction of Cr(VI) to the target concentration is less than the time scale for the transport of the aqueous Cr(VI) from source area to point of compliance; the Cr(III) will remain immobile; and there is no net oxidation of Cr(III) to Cr(VI)."

Several researchers have attempted to evaluate the specific processes responsible for the NA of Cr(VI) at sites of varying geochemistries. Henderson (1994) studied the geochemical reduction of Cr(VI) in the Trinity sand aquifer at the Odessa I Chromium site in Texas. The author postulated that reduction of Cr(VI) to Cr(III), followed by precipitation, was the primary attenuation process. Nikolaidis et al. (1994) evaluated the sorption of Cr in a glacial fluvial aquifer located at an electroplating facility with Cr contaminated groundwater, and postulated (with experimental evidence) that a combination of binding with organic matter, adsorption onto iron oxide coatings, and diffusion into the soil matrix might account for the high sorption coefficients and attenuation of Cr(VI) observed at the site. Mattuck and Nikolaidis (1996) conducted a study of Cr attenuation at the same site and observed that chromium strongly sorbed to wetland sediments; however, no mechanism for Cr immobilization was clearly defined. Masscheleyn et al. (1992) conducted experiments to identify and quantify processes controlling chromium redox chemistry in a seasonally flooded Lower Mississippi Valley forested wetland located in Louisiana. The authors surmised that in the floodwater column, Cr chemistry was regulated by a combination of Cr(VI) diffusion into the soil, Cr(III) precipitation, complexation by organic ligands, sorption onto suspended solids, and reduction of Cr(VI) to Cr(III).

In the chromium NA studies related literature reviewed above, the attenuation processes (reduction, adsorption, surface precipitation) were not definitively separated to the extent necessary to develop a robust mechanistic-based NA predictive approach for Cr(VI). It is possible to identify and quantify specific Cr(VI) attenuation processes or factors in pure or simple systems, such as: the reduction of Cr(VI) to Cr(III) by Fe(II) in the presence of known mineral surfaces (Buerge and Hug, 1997), green rust (Lee and Batchelor, 2003), amorphous Fe(S) (Patterson and Fendorf, 1997), and soil humic substances (Wittbrodt and Palmer, 1996); adsorption of Cr(VI) to model mineral adsorbents (Fendorf et al., 1997); or precipitation with well-characterized Fe(III) (Olazabal et al., 1997). However, Cr(VI) attenuation-related process studies in complicated natural soil systems have not been adequately separated to allow for the development of a mechan-