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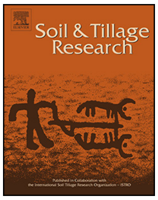

The Elovich equation as a predictor of lead and cadmium sorption rates on contaminant barrier minerals

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ABSTRACT

Contaminant sorption reactions in soils are generally heterogeneous, multi-steps solid–liquid reactions that compliment transport processes. For contaminant barrier materials, reaction heterogeneity is promoted by variability in the mineralogy and grain size distribution of materials required in mix proportions to satisfy various design functions. The adsorption/desorption of contaminants in barrier systems is necessary for performance assessments. In this paper, the sorption/desorption rates of Pb^{2+} and Cd^{2+} on Na-montmorillonite ($(OH)_4Si_8Al_4O_{20}nH_2ONa$) and kaolinite ($(OH)_8Si_4Al_4O_{10}$) were investigated by varying nature of aqueous contaminants and clay. Heavy metals including Pb^{2+} and Cd^{2+} were adsorbed/desorbed on the clays at pH levels of 2, 3, 4, and 7 for 48 h. Sorption/desorption of these heavy metals was found to be influenced by point of zero charge, cation exchange capacity, particle size, pH of the system, complexation of metals, and hydrated ionic radius of metals. As a result, Elovich equation was found to adequately explain the kinetics of Pb^{2+} and Cd^{2+} on two clay minerals with the squared correlation coefficients (R^2) that range from 0.70 to 0.99. At pH 2, removal rate were 36.3% for Pb^{2+} and 64.5% for Cd^{2+} from Na-montmorillonite while 67.1% for Pb^{2+} and 75.0% Cd^{2+} from kaolinite, respectively. The results obtained from the Elovich equation could be useful for assessing the sorption equilibrium for the metals potentially attained in soil barrier systems.

1. Introduction

Contaminant barriers are usually installed across the flow path of contaminant plumes in the subsurface. They are most commonly clayey soil mixes that are compacted to densities that establish balance among hydraulic conductivity, sorption capacity, and other desirable characteristics. Such barriers have been used to retard the movement of contaminant plumes that contain heavy metals. The mechanism of retardation of the heavy metals by clayey materials is mostly adsorption.

Adsorption of ions can be described as the accumulation of ions at the surface of a solid from a solution. Usually, a surface complex model is used to describe adsorption behavior (Sposito, 1989). Surface complexes form between the metal ion and surface of the clay mineral. Adsorption processes control the amount of contaminants that are retained on the surfaces of clay minerals. Both chemical and physical parameters may be involved. Often, metal ions are surrounded by hydration water molecules that provide a boundary between the clay surface and the metal ions in solution, leading to outer-sphere bonding. The reactions involved in this bonding are weak and the adsorbed metal ions can easily be removed from the clay surface. When the metal ion is directly attached to the surface with no hydration water molecules existing between the clay surfaces and the metal ions, the reaction can be described as an inner-sphere complex (Sparks, 1989). This involves ionic and/or covalent bonding between the surface and the metal ion and is usually an irreversible process because of strong bonding between the surface and the metal ion. Metal ions that are in an outer-sphere complex are surrounded by hydration water molecules, which are not directly bonded to the soil surface. Relevant reactions are usually rapid and reversible due to indirect contact between the ions and particle surfaces. When the metal ion is directly bonded to a particle surface, inner-sphere complexation is involved and in most cases, these reactions are slow. The type of interaction in the soil matrix determines the kinetics of the predominant mechanisms during sorption processes in barrier systems.

Haas and Horowitz (1986) studied the adsorption of cadmium by kaolinite in the presence of organic materials. It was discovered that Cd complexation with organic matter might enhance Cd

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adsorption on kaolinite. The effects of ionic strength, complex formation and exchangeable cations on Cd adsorption by montmorillonite were investigated by Garcia-Miragaya and Page (1977). They found that increase in ionic strength reduced the amount of Cd adsorption. Lim et al. (1997) investigated the sorption of lead, copper, cadmium, zinc and chromium from fly ash on marine clay. The mobility of the metals was in the order: Cd > Zn > Cu > Pb > Cr.

Many methods have been developed to obtain and analyze experimental data that adequately describe the process responsible for the time-dependent sorption observed in barrier minerals. For several heavy metals, retention/release reactions in soils have been observed to be strongly time-dependent. Several kinetics models exist for describing both adsorption and desorption of metals to and from clay. Sparks (1989) and Sposito (1994) have described different kinetics models such as the first order, second order, Elovich equation, and others for use in the analyses of the behavior of metals in soil systems. In Table 1, some kinetic studies are listed that were executed by various investigators.

Elkhatib and Hern (1988) used first order kinetics to describe desorption of potassium from some soils. Kuo and Mikkelsen (1980) investigated the kinetics involved in desorption of zinc from soils. Vaslow and Boyd (1952) also expressed the distribution of ions between a homogeneous solid solution and its equilibrium saturated aqueous solution with the first order kinetics. Eick et al. (1999) stated that the second order equation is best utilized by optimizing the ranges of time to obtain the best fit.

The Elovich equation is one of the most commonly used equations for describing the kinetics of heterogeneous chemisorption of gases on solid surfaces. It has been used in soil kinetics to analyze both sorption and desorption processes. This relationship can be expressed as shown in Eq. (1).

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \left(\frac{1}{\beta}\right)\ln(t) \tag{1}$$

The parameters α and β are constants, α is the initial sorption rate of Elovich equation ($\mathrm{g\,g^{-1}\,min^{-1}}$), β is adsorption constant ($\mathrm{g\,g^{-1}}$) and q_t is the amount of metal adsorbed/desorbed at time t (g/g), and t is the reaction time (min). A plot of q_t versus $\ln(t)$ shows a linear relationship with a slope of $(1/\beta)$ and intercept $(1/\beta)\ln(\alpha\beta)$. Aharoni and Ungarish (1977) found that the Elovich equation requires accurate data at short reaction times.

Several investigators have used the Elovich equation to analyze the kinetics of contaminant sorption reactants. Often the correlations obtained are compared to those of other kinetics models. Bao et al. (2010) found that the rates of tetracycline sorption onto Alfisol and Ultisol samples that they tested could best be described by the Elovich equation. For all soil/solution ratios, the correlation coefficients exceeded 0.80. Huang et al. (2012) evaluated four adsorption kinetics models for copper on β-cyclodextrin-based adsorbent (CAM). The results indicated that the Elovich model was more suitable for estimation of copper at higher concentration levels as confirmed by correlation coefficients that range from 0.910 at copper concentration of 25 mg/L to 0.956 at 150 mg/L. Correlation coefficients that average about 0.99 have been obtained by Dou et al. (2011) in their experiments on $\mathrm{Hg^{2+}}$ sorption by $\mathrm{TiO_2}$ nanoparticles. Wu and Tseng (2008) used the Elovich model to describe the rate of sorption of dyes by NaOH-activated carbon and obtained correlation coefficients greater than 0.99.

While the results cited above pertain mostly to manufactured or amended sorbents, the kinetics of sorption of chemical substances by natural sorbents such as soils has also been modeled with the Elovich equation (Shariatmadari et al., 2006; Reyhanitabar and Gilkes, 2010; Fuentes et al., 2014). Vistoso et al. (2009) obtained a correlation coefficient of 0.93 with their best-fit Elovich equation for experimental data on molybdate and phosphate sorption on Chilean Andisols. With respect to desorption kinetics, experimental studies of potassium release from weathered soil to a sodium tetraphenyl boron solution at periods up to 168 h (Darunsontaya et al., 2010) have shown that the Elovich equation may not be inferior to other models in predicting desorption rates.

In spite of the utility of the Elovich equation in estimation of reaction kinetics, it should be noted that other kinetics models may at times, exhibit albeit marginally superior correlation coefficients for sorption and desorption kinetics of chemical substances. An example was idealized by Yang et al. (2012) who investigated the kinetics of perchlorate adsorption by calcined iron-based layered

Table 1
Summary of literature review on kinetic models and isotherms used by investigators.

Investigator	Adsorbate	Isotherms	Kinetic models
Griffin and Jurinak (1974)	Boron	Langmuir	Pseudo first order
Kuo and Lotse (1974)	Phosphate	Langmuir, Freundlich	NA
Griffin and Au (1977)	Lead	Langmuir	NA
Benjamin and Leckie (1981)	Cadmium, lead, copper, zinc	Langmuir	NA
Biddappa et al. (1981)	Lead, cadmium, zinc, copper, nickel	Langmuir	NA
Elkhatib and Hern (1988)	Potassium	NA	Elovich, first order, parabolic
Aharoni et al. (1992)	Cesium	NA	First order
Peters and Shem (1992)	Lead	Langmuir, Freundlich	NA
Bereket et al. (1997)	Lead, copper, cadmium, zinc	Freundlich, Langmuir	First order
Eick et al. (1999)	Lead	NA	First order, parabolic diffusion
Wu and Tseng (2008)	Dyes	Langmuir	Elovich
Vistoso et al. (2009)	Molybdate, phosphate	NA	Zero order, first order, second order, parabolic, Elovich
Bao et al. (2010)	Tetracycline	Freundlich	Elovich, Exponential
Darunsontaya et al. (2010)	Potassium	NA	Parabolic diffusion, power-function, Elovich
Dou et al. (2011)	Mercury(II)	Langmuir	Elovich
Seifi et al. (2011)	Benzene, toluene, ethyl benzene, xylenes	NA	Pseudo-first order, pseudo-second order, Elovich
Huang et al. (2012)	Copper(II)	Langmuir, Freundlich, Temkin	Quasi-first order, quasi-second order, Elovich, interparticle diffusion
Yang et al. (2012)	Perchlorate	NA	Pseudo-second order, interparticle diffusion, Elovich

NA, not available.