Sorption kinetics of diuron on volcanic ash derived soils

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HIGHLIGHTS

- A two-stage mechanism for DI sorption on volcanic soils is proposed.
- The mechanism explains the mass transfer and intraparticle diffusion of DI on volcanic soils.
- OM content and minerals composition of volcanic soils impact the sorption kinetic of DI.
- The TSNE model explained the full behavior kinetic of DI.

ABSTRACT

Diuron sorption kinetic was studied in Andisols, Inceptisol and Ultisols soils in view of their distinctive physical and chemical properties: acidic pH and variable surface charge. Two types of kinetic models were used to fit the experimental dates: those that allow to establish principal kinetic parameters and modeling of sorption process (*pseudo-first-order*, *pseudo-second-order*), and some ones frequently used to describe solute transport mechanisms of organic compounds on different sorbents intended for remediation purposes (*Elovich* equation, *intraparticle diffusion*, *Boyd*, and *two-site nonequilibrium* models). The best fit was obtained with the *pseudo-second-order* model. The rate constant and *the initial rate constant* values obtained through this model demonstrated the behavior of Diuron in each soil, in Andisols were observed the highest values for both parameters. The application of the models to describe solute transport mechanisms allowed establishing that in all soils the mass transfer controls the sorption kinetic across the boundary layer and intraparticle diffusion into macropores and micropores. The slowest sorption rate was observed on Ultisols, behavior which must be taken into account when the leaching potential of Diuron is considered.

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1. Introduction

Sorption reactions have been investigated in many heterogeneous and homogeneous systems [1–5]. These reactions are known to be important because they are time-dependent processes, which control transport and availability of organic pollutants in soils. The herbicides contamination of surface and groundwater is a major concern due to the intensive and widespread use of these chemicals in agricultural and urban areas. Adsorption of herbicides from soil solution to soil particle active sites is one of the most important chemical processes, which limit transport in soils by reducing their concentration in the soil solution and consequently leaching potential. Therefore, if herbicides adsorption increases with time, their availability and transport to running and ground waters decreases.

The sorption process occurs within the boundary layer around the sorbent and is described as a complex process involving a number of sequential mechanisms which determine the rate of adsorption: (i) bulk solution diffusion (liquid film diffusion controlled); (ii) surface diffusion (particle diffusion controlled); (iii) sorption and desorption on the solid surface (as a chemical reaction); (iv) interactions between herbicide and surface functional groups. Sorption occurs in the liquid-filled pores (external mass transfer) and along the walls of the pores (internal mass transfer) of the soil [6]. The efficiency of the sorption process will depend on the accessible surface area of the soil and the adsorption characteristics, e.g. chemical adsorption involving ligand exchange and/or physical adsorption controlled by van der Waals physical forces.

Adsorption kinetic is important to describe the time dependence of sorption of pesticides in soil solution, on the soil. Non-ideal

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sorption, time-dependent or non-equilibrium sorption, resulting from physical and chemical non-equilibrium, and intra organic matter diffusion have been suggested to be the two predominant factors responsible for the non-ideal sorption of nonionic or hydrophobic compounds. In general, non-equilibrium sorption has been attributed to several factors, such as diffusive mass-transfer resistances, rate-limited sorption reactions, nonlinearity in sorption isotherms, and sorption–desorption non-singularity [7].

Non-equilibrium sorption occurs during the transport of pesticides in soils. Rate-limited diffusion of the sorbate from bulk solution to the external surface of the sorbent, and rate-limited diffusion within mesopores and micropores of the soil matrix, will occur before the equilibrium is reached [3].

Volcanic ash-derived soils have great importance in the agricultural economy of countries of Asia, Africa, Oceania and America. They are abundant and widespread in Central-Southern Chile (from 19° to 56° S latitude), accounting for approximately 69% of the arable land. Among them Andisols and Ultisols are the most significant. Andisols characterized by their high organic matter (OM), high specific surface area, and a mineralogy dominated by short-range ordered minerals such as allophane ($Al_2O_3SiO_2 \times nH_2O$). Ultisols have lower OM than Andisols but higher total iron oxide content, presenting both an acidic pH (4.5–5.5). Andisols present variable surface charge, originated in both, inorganic and organic constituents. Inorganic minerals as goethite, ferrihydrite, gibbsite, imogolite and allophane, contribute through the dissociation of Fe-OH and Al-OH active surface groups; while OM through the dissociation of its functional groups (mainly carboxylic and phenolic), and humus-Al and Fe complexes with amphoteric characteristics, contributes too. For the other side Ultisols present little or no variable surface charge, because more crystalline minerals such as halloysite and/or kaolinite dominate their mineralogy.

Diuron (DI) [3-(3,4-dichlorophenyl)-1,1-dimethylurea] classified, as a phenylurea is a nonionic herbicide currently used as a pre-emergence herbicide. It is primarily released on the soil surface, where runoff may occur. It is used to control broad-leaved weeds in different agricultural setting, e.g., cotton, wheat, olive trees, and sugar cane, but it is also used in urban areas [8]. This herbicide is highly persistent, with low water solubility (42 mg L^{-1} at 25 °C). When applied to soil it has a mean half-life of approximately 330 days and will not leach below 5–10 cm from surface [8].

Taking into account the limited literature reports on the kinetic behavior of DI in volcanic ash-derived soils, and the widespread and increasing use of urea based herbicides in world agriculture, the aim of present paper is to establish the sorption kinetic of DI in volcanic ash derived soils, as well as to determine the best kinetic model to describe the process. Seven different kinetic models will be used and discussed, considering models restrictions and soil characteristics.

Sorption characteristics and model description are necessary to model DI transport in a porous media as volcanic soils, and to prevent potential contamination of water resources.

2. Materials and methods

2.1. Chemicals

Analytical reference standard DI (98%, purity) was obtained from Sigma–Aldrich. Water solubility is 35.6 and 42 mg L^{-1} at 20 °C and 25 °C, respectively. All reagents used were analytical or *HPLC* grade. The stock solution for all purposes was 1 mg mL^{-1} DI in acetonitrile (AcN).

2.2. Soil samples

The ten volcanic soils used in this study were taken from the 0 to 15-cm layer in the agricultural regions of the southern-central Chile. Two Ultisols: Collipulli (COLL) (*Fine*, *Mesic*, *Xeric*, *Paleumult*) (36°58′ S; 72°09′ W) and Metrenco (MET) (*Fine*, *Mesic*, *Paleumult*) (38°34′ S; 72°22′ W), One Inceptisol: Diguillin (DIG) (*Medial*, *Thermic*, *Typic*, *Dytrandept*) (36°53′ S; 72°10′ W), and seven Andisols: Freire (FRE) (*Medial*, *Mesic*, *Xeric*, *Placandept*) (38°57′ S; 72°36′ W), Santa Barbara (STB) (*Ashy*, *Medial*, *Mesic*, *Typic*, *Dystrandept*) (36°50′ S; 71°55′ W), Osorno (OSN) (*Medial*, *Mesic*, *Typic*, *Dystrandept*) (40°32′ S; 73°05′ W), Temuco (TCO) (Medial, Mesic, Entic Dystrandep) (38°56′ S; 72°36′ W), Ralun (RAL) (*Mesic*, *Umbric*, *Vitrandept*) (41°32′ S; 73°05′ W), Nueva Braunau (NBR) (*Ashy*, *Mesic*, *Hydric*, *Dystrandept*) (41°19′ S; 73°06′ W), and Frutillar (FRU) (*Medial*, *Isomesic*, *Typic*, *Placandept*) (41°06′ S; 73°07′ W) were collected.

2.3. Soil characterization

The soil organic carbon (OC) content was determined by the *Walkley–Black method* [9]. The pH was measured in soil suspensions with a soil to water ratio of 1:2.5 (w/v). Cation exchange capacity (CEC) was determined by the method outlined by Blake [10], corresponding to the sum of Na, K, Mg, and Ca concentration in the ammonium acetate extracts. Samples were suspended in 0.01 M KCl to perform electrophoretic measurements in a *Zeta meter* (*ZM-77*) to establish the isoelectric point (*IEP*). The zeta potential (ZP) was calculated using the *Helmholtz Smoluchowski equation* [11]. Soils mineralogy and chemical composition have been previously described [12].

2.4. Kinetic sorption experiments

Kinetic experiments were carried out at 30 ± 1 °C. Duplicate samples of 2 g of air-dried soils were mixed with a 10 mL aliquot of an aqueous solution of 5 µg mL^{-1} DI (in 0.01 M CaCl$_2$) in 50 mL centrifuge tubes. The tubes were shaken "end over end" at the natural pH of soils during 5, 15, 30, 45, 60, 90, 120, and 180 min and then centrifuged at 3250 rpm for 20 min; each supernatant was filtered through a 0.22 µm pore-size Millipore filter. The concentration of DI in solutions was determined by *HPLC-DAD* (*SHI-MADZU*), provided with a *MultoHigh 100 RP C$_{18}$* (150 mm × 4.6 mm ID, 5 µm) column. No degradation products were detected after 16 h of shaking in a soil solution extracted from the most complex matrix (NBR). Mobile phase was 75:25 (V/V) = AcN:water at 1.1 mL min^{-1} flow rate was used as mobile phase, at constant oven temperature (35 °C). Injection volume was 25 µL and the detector wavelength was setting at 212 nm. Interferences from soils were discarded through the corresponding purity and matching tests. Quality parameters for the chromatographic analysis were previously established. Analytical sensitivity, detection and quantification limits were 0.002, 0.006 and 0.019 µg mL^{-1} respectively. These values were calculated from a calibration curve carried out at eight concentration levels, 0.025, 0.050, 0.075, 0.100, 0.250, 0.500 0.750 and 1.000 µg mL^{-1}. The chromatographic response was found to be linear in this concentration range with an R^2 value of 0.999.

2.5. Sorption kinetic models

2.5.1. Hyperbolic model

This empirical model has been previously applied to study sorption process of several pesticides in soils [3,13,14]. This model in its