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Utilization of fractional extraction for characterization of the interactions between humic acids and metals

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ABSTRACT

Diffusion experiments in humic hydrogels provide valuable findings on reactivity of humic matrices. This article concentrates on the study of interactions between humic acids and copper(II) ions in diffusion experiments. The diffusion experiments were supplemented with selective extraction of the diffused copper(II) ions. For this purpose, the leaching agents with increasing affinity towards copper(II) ions were used. The presented results showed that several different forms of the diffused ions exist in the humic gel, which is given by the strength of bonds towards humic acids. Distribution of copper into these forms becomes constant after some initial period, which indicates local equilibration of interactions between the ions and the humic content of the gel during the transport process. The proposed experimental method seems promising in order to shed new light on the effects of humic acids reactivity on mobility of important compounds in nature.

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1. Introduction

Humic substances are currently assumed to be the most widely distributed organic material on the earth's surface. They are formed through the biological activity of microorganisms and through the biochemical changes of organic residues. According to their solubility, humic substances are classified into three main fractions: fulvic acids are soluble in aqueous media, humic acids (HA) are insoluble under acidic conditions and humins stay insoluble throughout the whole range of pH-values. Humic materials are present in soils, waters, sediments and coals (Stevenson, 1982). Humic acids, as the major fraction of humic substances, were even extracted from a living plant (Ghabbour et al., 1994). The main sources of HA are peat and coal, from which they can be extracted by well-known chemical methods (Stevenson, 1982). HA represent material of outstanding biological and environmental impact. The main function of HA in soils and sediments is to impact the porosity and to act as a sorbent and reservoir of water and different kinds of chemicals (Jansen et al., 1996). Many potential applications of HA in agriculture, industry, environmental engineering and medicine are listed in Schnitzer and Khan (1972) and Peña-Méndez et al. (2005). For many decades, HA have been substantially investigated in light of their remarkable affinity towards heavy metals and they have frequently been proposed for utilization in decontamination of areas loaded with toxic metals (Tipping and Hurley, 1992).

Heavy metals naturally exist in different chemical forms and can be bound to various matrices with different bond strength. Determination

of different metal binding modes can give us the information on their mobility, (bio)availability or toxicity. This can be essential for description of their effects on nature, especially on the living organisms. Diversity in metal-binding ability of a soil can be assigned to its complex nature; different soil constituents have a different ability to reduce mobility or even to immobilize metal ions. Among these constituents, organic matter and especially humic substances play the key role. In Kyziol et al. (2006), sorption of chromium on different fractions of natural organic matter was studied. The results indicate that most Cr(III) ions were immobilized in a stable complex, only a small fraction was bound by ion exchange mainly to aliphatic carboxylic acids.

The widely used method for determination of the mobility of metals in soils is leaching by chemical extractants (Main et al., 2000). Using the method of sequential extraction, the whole amount of metals, originally sorbed on organic matter, is divided into different fractions by sequential addition of various extractant agents. The leached amount of the metal is then given by the strength of the extraction agent (and thus the strength of metal-soil interaction). The first studies proposing sequential extraction for this purpose were designed by Tessier et al. (1979). Tessier et al. (1979) distinguished five different groups of metal ions according to their bond strengths towards soil: exchangeable, bound to soils carbonates, bound to iron and manganese oxides, bound to organic matter and the residual fraction. Zeien and Bruemer (1991) came with an even more selective technique for sequential extraction of metals from soil samples. Following their procedure, the metal content is fractionated into seven fractions. Other works (Slavek et al., 1982; Rauret, 1998; Groenflaten and Steinnes, 2005) submit modifications of Tessier's extraction technique. These studies indicate chelating agents (EDTA, DTPA and their salts) and acid solutions (e.g. HCl, HNO_3, HAc) to be the most efficient substances for

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total extraction of the whole metal content. Further, the extraction yields decrease in following order: buffered salt solutions (e.g. NH_4OAc, $NaOAc$), salt solutions (e.g. $MgCl_2$, $CaCl_2$, $NaNO_3$, $BaCl_2$, $AlCl_3$, NH_4NO_3) and water. Copper is often used as a model heavy metal mainly because of its renowned affinity to humic acids (Stevenson, 1982). In Siqueria et al. (1989), the total extractability of copper(II) ions, previously sorbed on humic acids was verified, when 0.5 M HCl or 1 M HNO_3 was applied. To summarize, most of numerous extraction procedures proposed so far utilize ionic salt solutions (e.g. $MgCl_2$ or NH_4NO_3) as extraction agents for ion-exchangeable fractions of metals. The strong acids or chelating agents are utilized in order to leach the organic-bound fraction of metal ions.

Humic acids can be found as solids, colloidal solutions and also as swollen hydrogels in the nature. Simple laboratory procedures were proposed for preparation of model humic hydrogels (Martyniuk and Wieckovska, 2003; Sedláček and Klučáková, 2009a, 2009b). A hydrogel form of humic acids enables not only modeling the material's natural occurrence, but also brings some experimental benefits. It simplifies the manipulation with humic samples and allows their preparation in precise size and shape. As far as interactions between HA and other compounds are concerned, the gel form can be considered a system allowing fixation of humic matrix in aqueous medium while retaining its binding ability in the whole volume. Consequently, not only physico-chemical interactions of the studied compound with the humic content but also its simultaneous transport within the volume of the humic matrix are observed experimentally and the exact effect of the interactions on the transport are monitored. In such experiments, disturbance coming from mechanical and thermal convection of a liquid is markedly suppressed in the gel matrix compared to the above phenomena in liquid state. All the above mentioned advantages represent an outstanding support for the idea of studying transport (i.e. diffusion) processes in humic hydrogels. Such diffusion processes are (under appropriate experimental conditions) easily observed; moreover, the mathematical apparatus used for data evaluation is well explained (Crank, 1956) and provides some standard parameters – diffusion coefficients – that involve all interactions in the system.

1.1. Diffusion experiments

In previous works (Klučáková and Pekař, 2004; Sedláček and Klučáková, 2009a, 2009b), diffusion experiments in humic hydrogels were proposed and confirmed as suitable tools for the innovative study of reactivity of HA. The main object of this paper is to supplement the classical diffusion experiment in humic hydrogels with a subsequent selective extraction of individual ion fractions from humic matrices.

First part of the experimental procedure presented in the paper deals with the transport of copper(II) ions from aqueous solutions into humic gel samples. Numerous undemanding methods of choice for the study of diffusion in solid and semi-solid samples can be proposed; for example, the article by García-Gutiérrez et al. (2006) gives in-depth summary of such methods. Pros and cons of individual methods are exemplified by diffusion of both neutral (tritium) and ionic (Cl^-, I^-, SO_4^{2-}, Na^+, Ca^{2+}...) substances in compacted bentonite.

In experiments presented in this paper, diffusion proceeded from an aqueous solution of a copper(II) salt into cylindrical gel samples through both circular ends of the gel cylinder. Mathematically, the concept of unsteady diffusion with chemical reaction in a semi-infinite media was adopted concerning diffusion from time-variable source. Mathematical description of such non-stationary transport phenomena arises from the solution of Fick's law in the following form

$$\frac{\partial c_g}{\partial t} = D^0 \frac{\partial^2 c_g}{\partial x^2} + \dot{r}, \tag{1}$$

where c_g is the concentration of copper(II) ions at time t and distance x in a humic gel, D^0 is the value of diffusion coefficient of the ions in a gel matrix without assuming any chemical interaction between the diffusing compound and the environment (in other words, D^0 represents diffusion coefficient of ions in a hypothetical hydrogel with the same structural properties – e.g. porosity – as the real one, but without any ability to bind diffusing compound) and $\dot{r}$ represents the rate of chemical reaction between the ions and the humic matter in the gel.

If the Fickian character of the transport is preserved in the system, Eq. (1) can be simplified as follows:

$$\frac{\partial c_g}{\partial t} = D_g \frac{\partial^2 c_g}{\partial x^2}. \tag{2}$$

In this case, D_g stands for an "effective" value of diffusivity, a value in which the effect of chemical reaction between copper(II) ions and HA is already involved.

From the analytical solution of Eq. (2), mathematical expressions for the concentration profiles in the gel and for the total amount of diffusing ions can be derived considering the conditions of the particular experimental design (for more details see Ref. Crank (1956) and Cussler (1984)). In particular experiments, the time variation of concentration of the solution is caused by the diffusion process, and the concentration profile of diffusing substance in the gel can be expressed by equation

$$c_g = \frac{\varepsilon \, c_0}{(1 + \varepsilon \sqrt{D_g/D}} \, erfc \frac{x}{\sqrt{4 \, D_g \, t}} \tag{3}$$

where ε is the ratio of concentration of copper(II) ions in the gel and in the solution at the interface between both media, c_0 is the initial concentration in the solution and D is the diffusion coefficient of copper(II) ions in aqueous solution. The dependence of cumulative diffusion flux (total amount of the transported ions) on time can be obtained in a similar way in the following form

$$m = \frac{2\varepsilon c_0}{1 + \varepsilon \sqrt{D_g/D}} \sqrt{\frac{D_g t}{\pi}}. \tag{4}$$

The second term of the general Eq. (1) represents the rate of chemical reaction between copper(II) ions and HA and its exact mathematical formulation arises from the particular kinetic model of the interaction. For the first approximation, we can consider fast immobilization with the existence of local equilibrium between mobile and immobilized copper(II) ions. It is described by equilibrium constant K, which represents mathematically the proportionality constant between immobilized and mobile copper(II) ions. The higher is K, the more pronounced is the immobilization of copper(II) ions. Eq. (1) then turns to the following form

$$\frac{\partial c_g}{\partial t} = D^0 \frac{\partial^2 c_g}{\partial x^2} - K \frac{\partial c_g}{\partial t} \tag{5}$$

and consequently

$$\frac{\partial c_g}{\partial t} = \frac{D^0}{1 + K} \frac{\partial^2 c_g}{\partial x^2} = D_g \frac{\partial^2 c_g}{\partial x^2}, \tag{6}$$

$$D_g = \frac{D^0}{1 + K}. \tag{7}$$

Eq. (7) then defines mathematically, how the simple immobilization of the ions affects the value of their effective diffusion coefficient.