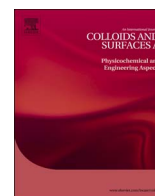




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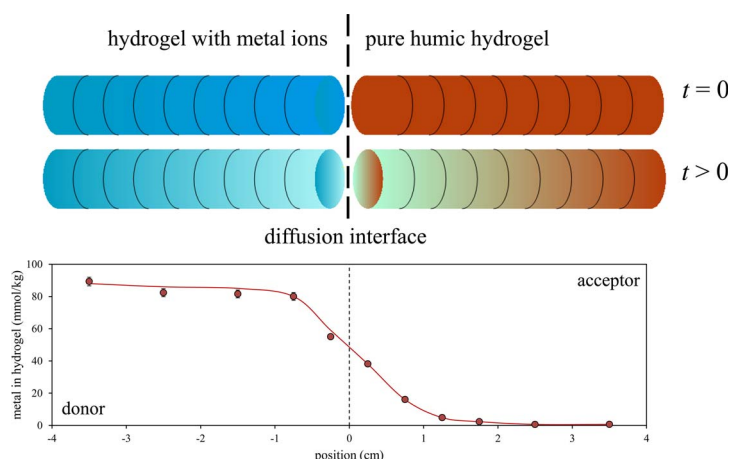
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The transport of metal ions in hydrogels containing humic acids as active complexation agent

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GRAPHICAL ABSTRACT



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ABSTRACT

The complexation and transport/immobilization abilities of humic acids are the most important environmental qualities of these substances. Therefore, the study of these properties is important for understanding their role both in natural systems and in human-driven applications. This contribution is focused on the diffusion of metal ions (Co, Cu and Ni) studied by means of a diffusion couple, and their immobilization in humic hydrogels. It was found that the diffusion characteristics of metal ions are strongly affected by their reactivity and their initial concentrations. The concentration dependence of Cu diffusivity exhibited a different trend when compared to Co and Ni, which the result of the high affinity of Cu to humic acids. When a metal ion is first complexed by humic acids it is bound in an exchangeable mode, which can be transferred to a nonexchangeable one. Our results indicate that the dynamic equilibrium established in the diffusion process includes mainly Cu ions in an exchangeable mode as a result of their high affinity and the high amount of bound Cu. Their transformation of bound Cu ions in strong Cu-humic complexes is very slow. In contrast, Co and Ni have much lower affinities to humic acids, thus their diffusivities are less affected by their reaction with humic acids.

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1. Introduction

The incorporation of potentially toxic metals into natural systems through industrial activities, such as metal mining, smelting and refining, fossil fuel combustion, atmospheric deposition, the land application of sewage sludge and industrial by-products, gasoline processing, and fertilization pose a great threat to the environment and human health. After combining with soil particles, heavy metals can persist in soils, resulting in harmful effects on biota. Such metals may be accumulated in the food chain, leach out of soils to pollute groundwater supplies or accumulate in plants, shrubs and trees [1–4]. A better understanding of soil and water pollution, as well as the factors controlling the retention and release of metal ions in nature is required. Many pollution problems involve such simultaneous processes as water flow, multicomponent solute transport, heat transport and biogeochemical processes and reactions. Models integrating various processes can be valuable tools for investigating the mobility of a wide range of inorganic and organic contaminants subject to different hydrologic and geochemical conditions [5]. The important process affecting the behavior of metal ions in natural systems is their complexation with soil components, which can involve the sorption of metal ions from the liquid phase (e.g. soil solution) onto solid particles, the immobilization of metals in the solid phase, and the complexation of metal ions with dissolved organic matter. The mobility of metal ions in soils is related to the partitioning between the soil solid phase and the solution phase, defined usually as the distribution coefficient [4,6]. Therefore, the sorption of metal ions on solid humic particles has been extensively studied by many authors (e.g. [7–10]).

Martyniuk and Wieckowska [7] compared the ion exchange capacities of solid and gel forms of humic acids. They showed that the binding of metal ions by the gel form was higher in comparison with the adsorption on solid humic particles. This finding was later supported by our previous results, which showed the presence of significant amounts of free mobile metal ions and weakly-bonded metal ions in ion-exchangeable mode, these contributing to an increase in the total amount of bonded metals [11–13]. In contrast, metal ions adsorbed on solid humic particles are mainly in form of stable metal-humic complexes and their amount is lower [14]. Similarly, Cao et al. [15] and Garcia-Mina [16] obtained a negative relationship between the stability constant of metal-humic complexes and the binding capacity of active sites and the metal humic ratio. Alvarez-Puebla et al. [8] studied the retention mechanism of Co(II), Cu(II) and Ni(II) ions. Their results showed that 2:1 complexes were formed at low concentrations. This structural coordination was energetically favored due to the chelate effect. The increase in metal concentrations caused an increase in the metal:humic ratio and metals occupied most of the surface active sites. In addition, the authors stated that high concentrations of metals preserved the 3D structure of humic acids. Our results confirmed that only a portion of metal ions are bonded with humic acids through carboxylic or phenolic groups and that other binding sites contributed to the total amounts of adsorbed metals [9]. Antonelli et al. [17] distinguished between specific binding sites (carboxylic and phenolic ones) and non-specific binding sites in humic substances. Baker and Khalili [18] identified four binding sites for chemical interactions between metal ions and humic acids. Shaker and Albishri [10] indicated three types of binding sites with different adsorption capacities. In contrast to other works, they presumed mainly the existence of physical adsorption which was diffusion controlled.

The mobility of metal ions in soils depends on the combination of several factors, including the nature of the metal, its concentration, environmental factors, and soil components. These factors determine the soil solution-solid phase equilibrium of metals through the mechanisms of sorption-desorption and dissolution-precipitation [19–21]. Bryan et al. [22] stated that metal ions in a non-exchangeable mode had a significantly higher mobility than those in an exchangeable mode. Metal ions in an exchangeable mode are strongly bound, but they may

dissociate from the humic substance and be immobilized by a stronger binding site on the surface. The sorption may significantly reduce the mobility. Lippold et al. [23] assessed the mobility of contaminant metals in transport systems with humic substances. They emphasized the influence of kinetic effects on stabilization processes leading to an increase in strongly humic-bonded metals. Chakraborty et al. [24] studied the dynamics of metal complexes and their diffusion in the presence of humic substances. They discovered that the interactions of Cu and Ni with humic acids are stronger than their interactions with fulvic acids and natural organic matter. They indicated that labile complexes were formed with different binding sites with diverse binding energies in humic substances. Labile Ni complexes were small [24,25] with very fast diffusion rates which corresponded with Ni bioavailability. The diffusion coefficients of labile Ni complexes were very similar to those of free Ni(II) ions. In contrast, the diffusion coefficients of Cu complexes were similar to those of humic substances or natural organic matter presented in studied systems and their diffusion rates were lower [24]. Comparing these findings with our previous work [26], we can see that the diffusion coefficient of Cu(II) ions in humic hydrogels was higher than the diffusion coefficients of Ni(II) and Co(II). Differences can be explained by the much higher content of diffusing metal ions in humic hydrogels (an excess concentration in relation to humic binding sites) resulting in high amount of free mobile ions. Kostic et al. [27] determined the binding strength of heavy metals bound to humic acids. Their results confirmed the high stability of metal humic complexes in the order Cu(II) > Ni(II) > Co(II), which indicated that in conditions of increased amounts of metal ions in the natural environment, these metal ions may be preferred and can thus indirectly increase the mobility and bioavailability of other metal ions. Furukawa and Takahashi [28] investigated the effect of complexation with humic substances on the diffusion of metal ions in aqueous solutions. Their results showed that the diffusion of each ion lost its characteristics by complexation with humic substances due to their large molecular weight. This is incompatible with results published in [24], which indicated that the diffusivities of Ni complexes were very similar to those of free Ni(II) ions.

The diffusion behavior of metal ions described above was studied by different authors using different methods. In general, diffusion can be sensitive to the concentration of diffusing particles, the properties of the diffusion medium, and (potential) chemical interactions. Therefore, the obtained discrepancies are not surprising. They are a result of differences in many factors concerning the realized diffusion experiments. We decided to study the transport of metal ions in humic hydrogels by means of the diffusion couple method [29–32]. In order to determine the concentration dependence of the diffusion coefficient, experiments were performed using three different initial contents of metal ions.

2. Material and methods

2.1. Humic acids

Humic acids were isolated from lignite mined in the Czech Republic (South Moravia). The sample was extracted in the ratio of 30 g of lignite to 1 dm³ of extraction agent - a mixture of 0.5 M NaOH and 0.1 M Na₄P₂O₇ (1:1). The obtained suspension was stirred at laboratory temperature (25 °C) overnight. The solid part was removed by centrifugation and extracted again for 60 min. Both leaches were mixed, acidified using concentrated HCl up to a pH value close to 1, and left in the refrigerator overnight. Precipitated humic acids were centrifuged (4000 rpm, 15 °C), washed repeatedly with deionized water until free of chlorides, and dried in an oven at 50 °C.

The ash and moisture contents of the prepared humic sample, measured by means of thermogravimetry (TGA Q5000), were equal to 11.0% wt. (ash) and 5.7% wt. (moisture).

The elemental composition of humic acids was determined by means of Euro EA CHNO Elemental analyser. The total acidity of the

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