

TRANSPORT AND IMMOBILIZATION PROPERTIES OF HUMIC HYDROGELS

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Abstract

Reactivity and transport properties of metal ions are important both for evaluating and understanding role of humic acids in natural systems and human-driven applications as solving their structural questions. This paper focuses on metal ions diffusion and immobilization in humic hydrogels. Humic acids were purchased from International Humic Substances Society (isolated from different matrices - peat, soil, leonardite, water) and extracted from lignite mined in Czech Republic. Copper(II) ions were chosen as a model example of reactive metal for the diffusion experiments. Previous works showed that transport of metal ions in humic gels were strongly influenced by reactivity of humic acids. Therefore samples isolated from different sources resulted in changes in the content of acidic functional groups and different diffusivity metal ions in prepared hydrogels. The diffusion coefficients of copper(II) ions, determined in this work, showed the significant dependence on reaction ability of humic hydrogels. Lower amounts of the acidic functional groups caused the increase of the effective diffusion coefficient. In general, diffusion experiments seem to provide valuable method for reactivity mapping studies on humic substances.

Keywords: Humic acids, diffusion, reactivity, immobilization, copper

1. INTRODUCTION

Humic acids are recognized as a component of natural organic matter that plays a key role in such issues as global warming, carbon cycle in the nature or self-detoxification of soils and sediments. The ability of soils and sediments to reduce the mobility of chemical pollutants or even to immobilize them represents their important natural feature. They affect biological uptake and bioaccumulation of toxic chemicals in plants as well as the pollution of the underground water supplies [1]-[5]. In natural systems, humic acids can bind contaminating metal ions and in this way they influence the effectiveness of the regeneration and purification processes in these systems. The reactivity and transport properties of metal ions in humic systems are important for understanding the role of humic substances in both natural systems and human-driven applications [6]-[9].

Our previous works [9]-[11] has demonstrated the effectiveness of the simple "tubing" method in diffusion studies. It was shown that transport of metal ions in humic gels is strongly influenced by reactivity of humic acids, therefore changes in the content of functional groups result in changes of diffusivity [5]. 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 natural system can be assigned to its complex nature. Different natural constituents have a different ability to reduce mobility or even to immobilize metal ions.

In this work, the method was further developed to the level of the diffusion instantaneous planar source method [3], [5], [8]. Copper is a traditional model ion that is used to study metal-humic interactions because of its strong affinity for humic acid binding sites [1]-[3], [12].

2. MATERIALS AND METHODS

Six different humic acids were used in this work. One sample of humic acids was extracted from lignite mined in the Czech Republic (Mikulčice in South Moravia) and the other samples of humic acids were purchased from International Humic Substances Society (IHSS).

Lignitic humic acids (in this work designated as LGHA) isolated by means of the same procedure was used in our previous research [2], [3], [6], [7] (for more details of chemical structure and the isolation procedure see previous works [[2], [3], [6], [7] and [13]).

Humic samples purchased from IHSS were: Nordic Lake Humic Acids 1R105H (NLHA), Elliot Soil Humic Acids 1S102H (ESHA), Suwannee River Humic Acids 2S101H (SRHA), Pahokee Peat Humic Acids 1S103H and Leonardite Humic Acids 1S104H (LEHA). Humic acids were purchased from International Humic Substances Society (isolated from different matrices - peat, soil, leonardite, water) and extracted from lignite mined in Czech Republic (LGHA).

All hydrogels, utilized in diffusion experiments, were prepared via the method of thermoreversible gelation of aqueous solution of agarose described in previous work [14]. Agarose hydrogels gelatinized from the solution of agarose in water or aqueous solutions of humic acids. Dry agarose content in gel was 1 wt. %, dry content of humic acids was 0.01 wt. %.

Cu(II) ions were chosen as an example of reactive metal for the diffusion experiments. The environment for the diffusion experiment was prepared from the hydrogel form of humic acids. The hydrogels (prepared by the process described above) were pressed gently in glass tubes and used for diffusion experiments (method of instantaneous planar source). After the diffusions the hydrogel from the tubes was sliced and Cu(II) ions were extracted separately from the slices of hydrogels by the 1 M HCl. The concentration of copper(II) ions in extractants was determined by means of ultraviolet/visible spectrometry [6], [7].

3. RESULTS AND DISCUSSION

Mathematical apparatus utilized in description of any nonstationary diffusion process comes from an appropriate analytical solution of general Fick's equation, which characterize time-spatial distribution of the diffusing matter. For the simplest case of one-dimensional diffusion, the Fick's equation can be written in following form:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (1)$$

where c represents the concentration of the diffusing compound in the time t and the position x (the coordinate parallel to the direction of diffusion movement). Diffusion coefficient D is the main parameter characterizing rate of the diffusion process. While solving this partial differential equation, appropriate initial and boundary conditions must be applied according to the particular experimental settings [7], [9], [15], [16].

In Eq. (1), strictly one-dimensional diffusion in an "inert" medium is considered ("inert" means that the medium does not chemically interact with the diffusing particles). When studying diffusion in such complex media as reactive hydrogels (such as in this work), where the movement of the diffusing particles gets tortuous because of the porous character of the gel and some interactions between the diffusing matter and the gel network can be assumed, mathematical apparatus becomes much more complicated. Theoretically, all the reaction rate components must be added to the right side of Eq. (1) and an analytical solution of the equation becomes hardly accessible. Nevertheless, a simplification is often applied: it presumes that all the mentioned interactions between diffusing compound and the surrounding medium do not destroy the fickian character of the diffusion process, but the value of diffusion coefficient is altered. Mathematically, this presumption is expressed by the modified form of Eq. (1):

$$\frac{\partial c}{\partial t} = D_{\text{eff}} \frac{\partial^2 c}{\partial x^2} \quad (2)$$

where D_{eff} is the so called “effective diffusion coefficient” in which two main effects (tortuous movement of the diffusing matter, chemical interactions in the system) are involved. For experimental settings presented in this paper, mathematical concept of unsteady diffusion from instantaneous planar source of the diffusing matter can be adopted. This concept represents a solution of the Fick’s equation for the case of diffusion from initial concentration pulse of infinitesimally small width. For this presumption and for the zero initial concentration of diffusing matter in surrounding media, following mathematical solution can be found:

$$c = \frac{n}{S\sqrt{\pi D_{\text{eff}} t}} \exp\left(-\frac{x^2}{4D_{\text{eff}} t}\right) \quad (3)$$

where n stands for the total mass of diffusing compound applied in the form of a narrow pulse and S is the cross-section area available for the transport of the compound. For calculation of effective diffusivity directly from the experimental concentration profiles (concentrations of the diffusing compound at different positions), the linearization of Eq. (3) is usually applied in the form

$$\ln c = \ln \frac{n}{S\sqrt{\pi D_{\text{eff}} t}} - \frac{x^2}{4D_{\text{eff}} t} \quad (4)$$

The effective diffusion coefficient D_{eff} can then be determined from the slope of linear regression using Eq. (4) [3], [7], [9], [15], [16].

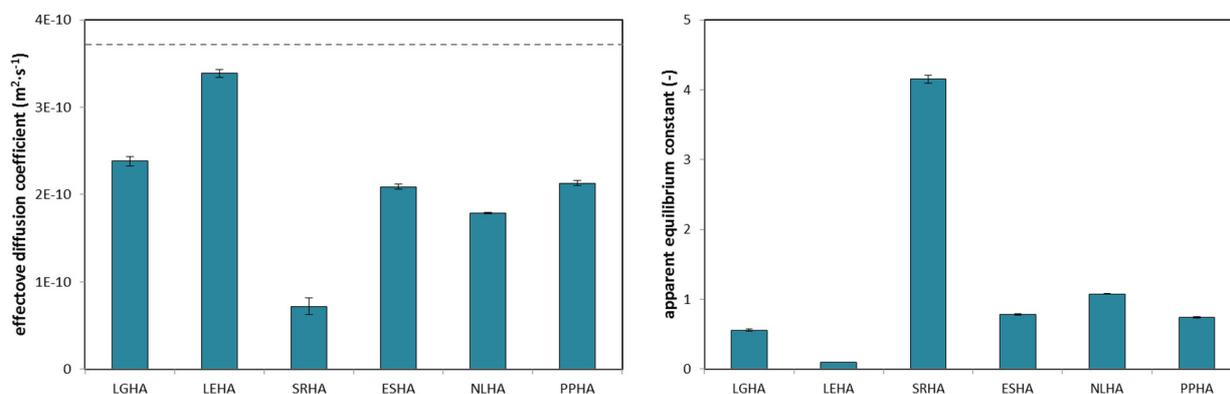


Figure 1 Values of effective diffusion coefficient and apparent equilibrium constant characterizing transport processes in hydrogels containing different humic acids

Figure 1 shows values of effective diffusion coefficient using Eq. (4). As we can see, all hydrogels containing humic acids had lower diffusivity in comparison with the pure agarose hydrogel. The decrease was caused by the high affinity of copper to humic acids and its partial immobilization in hydrogel structure. It is well known, that metal ions are bound in humic acids mainly via acidic functional groups [4]-[8]. Previous works showed that transport of metal ions in humic gels is strongly influenced by reactivity of humic acids, therefore changes in the content of acidic functional groups result in changes of diffusivity [7], [8]. The inverse proportionality between the effective diffusion coefficients and the content of acidic functional groups was obtained in **Figure 2**. The increase of the content of acidic functional groups was connected with the decrease of the mobility of copper in hydrogels.

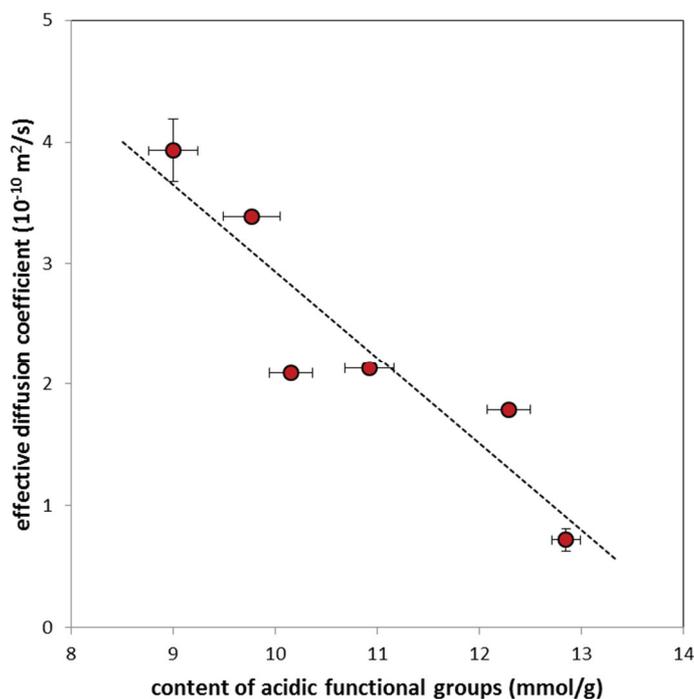


Figure 2 The dependence of effective diffusion coefficient on the content of acidic groups in humic acids

As mentioned above, the tortuous movement of the diffusing matter and chemical interactions in the system are involved in the value of D_{eff} , which can be expressed as:

$$D_{\text{eff}} = D \frac{\varphi}{\tau(K+1)} = D \frac{\mu}{K+1} \quad (5)$$

where D is the diffusion coefficient for free mobile copper(II) ions in water. The parameter φ is the ratio of the effective diffusive cross section, which is available for transport, to the bulk cross section. The available cross section is smaller than in case of a homogenous material because the diffusion takes place only through the fluid-filled pores and voids of humic hydrogels. Because the pores are not straight, the diffusion effectively takes place over a longer distance than it would in a homogenous material. The tortuosity τ is a value characterizing the longer distance traversed in the pores. The parameter μ represents the influences of the structure of humic hydrogel and its local geometry in the diffusion [7], [9]. D can be substituted by diffusivity in an aqueous solution, because of the high water content in the hydrogel. Its value for copper(II) ions is $1.43 \times 10^{-9} \text{ m}^2/\text{s}$ [17]. If we compare this value with the value of D_{eff} obtained for pure agarose hydrogel ($3.71 \times 10^{-10} \text{ m}^2/\text{s}$), we can determine the parameter μ as 0.26 in this case.

Symbol K in Eq. (5) represents the influence of interactions of humic acids with copper(II) ions. It is the ratio between immobilized and free Cu(II) ions in humic hydrogel and it can be considered as an equilibrium constant of local interactions between humic acids and copper (II) ions in hydrogel [1], [10], [11], [15]. If we use the value of structural parameter m obtained for pure agarose hydrogel and assume a negligible influence of low content of humic acids in hydrogels (0.01 wt.%), we can calculate the apparent equilibrium constant K by means of Eq. (5). Its values are shown in **Figure 1**. We can see that the highest values were determined for river humic acids SRHA and lake humic acids NLHA. These aqueous humic acids had also the highest contents of acidic functional groups able to immobilize metal ions in their structure. The lowest values were determined for coal humic acids (LGHA and LEHA) with the lowest content of acidic functional groups.

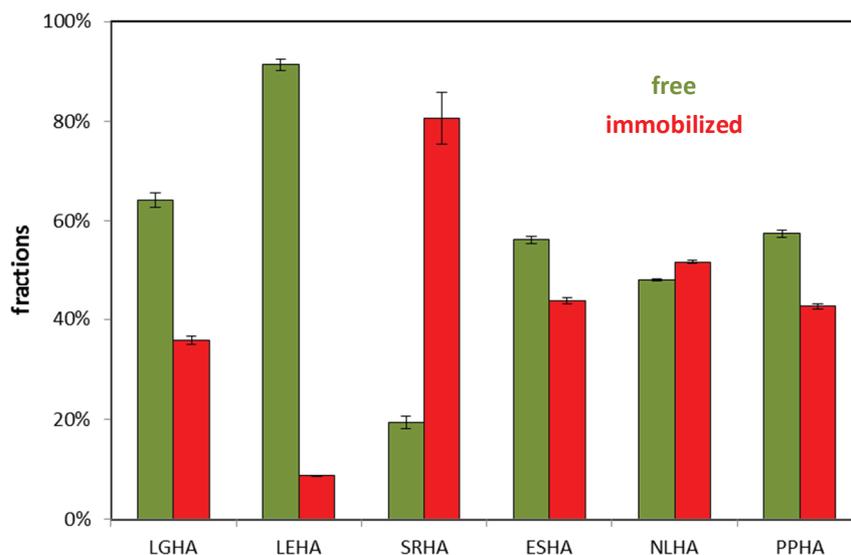


Figure 3 The content of free mobile fraction and immobilized fractions of copper(II) ions in hydrogels containing different humic acids

Percentage portions of free mobile and immobilized fractions of copper(II) ions in humic hydrogels are compared in **Figure 3**. We can see that free mobile copper(II) ions predominated in hydrogels containing the most aromatic coal humic acids (LEHA and LGHA) with the lowest content of acidic functional groups. In contrast, aquatic humic acids (SRHA and NLHA) can immobilize higher portion of metal ions.

4. CONCLUSION

Structural complexity of humic acids was manifested in kinetic behavior of their interactions with copper(II) ions, knowledge of which is important for various applications of these materials. In general, diffusion experiments seem to provide valuable method for reactivity mapping studies on humic substances. Obtained parameters such as effective diffusion coefficients and apparent equilibrium constants can be used in order to discuss the quality of humic acids from different origin and with different structures and contents of reactive functional groups. To summarize, the comparison of the results of diffusion experiments clearly showed that the transport of metal ions in hydrogels was strongly affected by structure and properties of humic acids. Although the content of humic acids in hydrogel was very low, effective diffusion coefficients as well as apparent equilibrium constants differed significantly as a result of the content and bond strength of acidic functional groups. Structure of humic acids, their aromaticity and content of other functional groups played also relatively important role.

ACKNOWLEDGEMENTS

Materials Research Centre at FCH BUT-Sustainability and Development, REG LO1211, with financial support from National Programme for Sustainability I (Ministry of Education, Youth and Sports).

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