DIFFUSION EXPERIMENTS AS A NEW APPROACH TO THE EVALUATION OF COPPER TRANSPORT IN HUMICS-CONTAINING SYSTEMS

Petr SEDLÁČEK[1,*] and Martina KLUČÁKOVÁ[2]

Institute of Physical and Applied Chemistry, Faculty of Chemistry, Brno University of Technology, Purkyňova 118, 612 00 Brno, Czech Republic; e-mail: [1] sedlacek-p@fch.vutbr.cz, [2] klucakova@fch.vutbr.cz

Received March 13, 2009
Accepted July 14, 2009
Published online September 3, 2009

Diffusion measurements seem to provide a valuable approach to mapping studies on heavy metal transport in systems containing humic substances. The paper deals with the diffusion of cupric ions in a humic hydrogel. The diffusion coefficients of Cu^{2+} in this medium were determined using in-diffusion from the constant source, diffusion couple and instantaneous planar source. The applicability of the experimental arrangements and mathematical description of metal ion transport are discussed in terms of the influence of complexation of Cu^{2+} with humic acids. All determined diffusion coefficients of Cu^{2+} in humic gel were lower but of the same order of magnitude compared with that obtained in water.

Keywords: Diffusion; Heavy metals; Humic acids; Immobilization; Hydrogels; Copper transport.

Because of their complex nature, humic substances face an identification dilemma. A part of scientific community (mainly environmental scientists) recognizes humic acids (HA) as a component of natural organic matter (NOM) that plays a key role in such issues as global warming, carbon cycle in the nature or self-detoxification of soils and sediments, while the others consider this material one of the greatest sources of organic carbon for industry. Industrial applications of humic substances are encouraged by rich alternative natural sources – peat, young coal etc. – from which they can be obtained by simple and cheap methods of extraction and purification[1]. Humics are also chemically reactive. They contain a wide range of functionalities that could change when structural modifications are made to acquire desired properties[2].

Due to a diffuse nature and diverse functionalities of humic substances, fundamental knowledge regarding their chemistry and properties is still

© 2009 Institute of Organic Chemistry and Biochemistry
doi:10.1135/cccc2009035

missing. These substances are not well understood with regard to exact structure; it is hence necessary to develop an appropriate methodology in order to compare applicable properties of humic substances from different sources and to confront them with other materials (e.g. synthetic polymers and biopolymers). Therefore, systematic reactivity and biological activity mapping studies are needed.

Humic acids provide the outstanding ability to sorb common groups of pollutants such as metallic cations. Many works focused on sorption of different toxic chemicals on solid humic acid and/or humic sols[3–9] have been published. But it is also well known that the sorption ability depends strongly on the mobility and the transport of adsorbed ions (or molecules) into humic particles. Involvement of diffusion transport of a sorbate in a specific form of humic material is therefore necessary for modeling sorption on HA in their natural environments. It is necessary to study and understand both complex behavior of this natural system and the role of its constituents. Published studies of diffusion in humic systems are relatively scarce. Wang et al.[10] investigated the effect of HA on Eu^{3+} diffusion in compacted bentonite. They found that HA hinder the Eu^{3+} diffusion and migration because of a formation of Eu–HA complexes which precipitate at the surface of compacted bentonite. Consequently, only a small part of Eu exists as a free ion in the humics-containing system. Wold and Eriksen[11] carried out similar experiments with diffusion of Eu^{3+}, Co^{2+} and humic colloids through compacted bentonite. Humic colloids diffused through the bentonite regardless its compaction. The apparent diffusivities of both metals increased significantly in the presence of humic colloids. Chang et al.[12] investigated the sorption kinetics of volatile organic compounds in dry, pressed humic acid disks by tracking the weight change of the sorbent with a microbalance. Kinetics of sorption and desorption are successfully described by a diffusion model.

Masaro et al.[13] present a detailed overview of diffusion in polymer solutions, gels and solids. Various theoretical descriptions of the diffusion processes are proposed. The theoretical models are based on different physical concepts such as obstruction effects, free volume effects and hydrodynamic interactions. References therein illustrate an applicability of these models in treatment of diffusion data for various systems.

Our previous results confirmed that kinetics of metal–humic interactions are generally dependent on the colloidal state of HA[14,15]. In natural state, HA are usually found in wet environments (water sediments, peat etc.) in swollen form, hence recent contributions focus on the study of HA in the hydrogel form[15,16]. Besides good simulation of natural humic environment,

the gel form of HA provides some additional benefits. The most valuable one is preparation of HA with defined size and shape, which is necessary for the evaluation of transport parameters by means of a mathematical model. Besides, the gel form of HA can be considered as a system which allows fixation of humic material while enabling interactions in its bulk. Consequently, not only these physicochemical interactions but also transport within the humic matrix can be studied. Humic hydrogels can also be prepared in a simple and cheap way using a method of controlled coagulation[9].

The diffusion studies on humics could be utilized in easy characterization of the material. Parameters such as effective diffusion coefficients of common pollutants in hydrogel forms of humic acids can be used in discussing the quality of humic substances of different origin in comparison with other synthetic or natural materials regarding desired applications. Determination of diffusion coefficient of various substances in polymer gels is taken as a topic for numerous works[17–29]. Seki and Suzuki[17] prepared composite adsorbents containing humic acids entrapped in an alginate gel and carried out a kinetic study of lead adsorption on this gel. The shrinking core model was used to determine apparent lead diffusion coefficients in the gels. Scally et al.[18] derived diffusion coefficients of metal ions and metal–ligand complexes in polyacrylamide hydrogels at different ionic strengths using a diffusion cell. Effects of humic and fulvic acids as ligands were also studied.

Although the accurate measurement of diffusion coefficients usually needs expensive and sophisticated equipment, e.g. nuclear methods such as NMR, Rutherford backscattering spectrometry (RBS) or elastic recoil detection analysis (ERDA), simple laboratory techniques exist for determination with standard error below 10%[19]. In general, measurement in diffusion cells is the method used most frequently in gel[20–25]. Besides, several other simple methods for determination of diffusivity in solids and gels have been developed, such as a method of instantaneous planar source[26,27] which differs from others by the fact that diffusion coefficient is calculated from a linearized concentration profile in the gel sample instead of using a time dependence of total diffusion flux. García-Guttieréz[29] provides in-depth summary of methods for the determination of diffusion coefficients in solids. Pros and cons of each method are discussed on the example of diffusion of both neutral (tritium) and ionic (Cl^-, I^-, SO_4^{2-}, Na^+, Ca^{2+}, ...) substances in compacted bentonite.

The cupric ion is well known for its high affinity to humic substances[1,9] and the ability to form one of the strongest bonds with them. Due to the

above and also because of easy quantification of Cu^{2+} content (e.g. by means of UV-Vis spectroscopy), cupric ions have been chosen as a model of heavy metal sorbate. The diffusivity of cupric ions in the humic gel is determined by their reduced mobility in a porous gel phase and by their interactions with HA. Mathematically, these effects are described by the following equation derived from conservation of mass

$$\frac{\partial c_1}{\partial t} = D^0_{\text{eff}} \frac{\partial^2 c_1}{\partial x^2} - \dot{r} \tag{1}$$

where c_1 is the concentration of Cu^{2+} in time t and distance x in a humic gel. D^0_{eff} is the value of the diffusion coefficient that embraces the influence of the porous phase. This coefficient is usually defined by the relation[19]

$$D^0_{\text{eff}} = \phi \frac{D}{\tau} \tag{2}$$

where D is the diffusivity in dispersion medium (water in the case of hydrogel), ϕ represents the porosity of the porous medium and τ stands for its tortuosity. Tortuosity is related to longer diffusion pathway in three-dimensional network as compared with diffusion in an aqueous solution. For highly porous media, its value lies between 2 and 6, usually it is close to 3 as the substance diffuses in 3 directions instead of 1 and the pathway is consequently approximately three times longer. The second term of Eq. (*1*) represents the rate of chemical reaction between Cu^{2+} and HA and it is defined as

$$\frac{\partial c_2}{\partial t} = \dot{r} \,. \tag{3}$$

This balance describes distribution of the fixed Cu^{2+} ions in time and space.

If fast immobilization with the presence of local equilibrium between mobile and immobilized Cu^{2+} is presumed, Eq. (*1*) is written now as

$$\frac{\partial c_1}{\partial t} = D^0_{\text{eff}} \frac{\partial^2 c_1}{\partial x^2} - K \frac{\partial c_1}{\partial t} \tag{4}$$

and, consequently,

$$\frac{\partial c_1}{\partial t} = \frac{D^0_{\text{eff}}}{1 + K} \frac{\partial^2 c_1}{\partial x^2} = D_{\text{eff}} \frac{\partial c_1}{\partial x^2} \tag{5}$$

where K is the proportionality constant between mobile (c_1) and immobilized (c_2) Cu^{2+} ions defined as

$$c_2 = Kc_1 . \quad (6)$$

Equation (*5*) defines a new effective diffusion coefficient

$$D_{\text{eff}} = \frac{D^0_{\text{eff}}}{1+K} . \quad (7)$$

In this case, "the effective value" means the value in which effects of both chemical reaction and porous character of the gel are involved. From the analytical solution of Eq. (*5*), mathematical expressions for the concentration profiles of diffusing ions in the gel can be designed for corresponding experimental conditions (for more details, see ref.[14]). The aforementioned simplification is often used wherever an interaction between a diffusing substance and a medium can be assumed fast enough in comparison with the diffusion itself. In practice, this condition is usually fulfilled if the macroscopic diffusion characteristics obey rules for the Fick's diffusion (i.e. cumulative diffusion flux is directly proportional to square root of time).

EXPERIMENTAL

Isolation of Humic Acids

HA were extracted from South-Moravian lignite by alkaline extraction. Lignite was stirred with the extractant (0.5 M NaOH and 0.1 M $Na_4P_2O_7$) in the 20 g per 1 dm^3 ratio for 12 h. The formed suspension was kept standing overnight and the next day the solution was separated from the solid phase and acidified with 20% hydrochloric acid to pH below 1. The solid residue was put into another 1 dm^3 of the extractant and after 1-h stirring the extract was separated and acidified in the same way. The acid extracts were kept in refrigerator overnight. Precipitated HA were separated by centrifugation (4 000 rpm), washed by deionized water several times and centrifuged again (until Cl^- ions were removed) and dried at 50 °C. Before humic gel preparation, HA were washed by deionized water, centrifuged and dried once more.

Characterization of HA

Obtained HA were characterized by elemental analysis (CHNSO Microanalyser Flash 1112, Carlo Erba) and UV-Vis (Hitachi U 3300). For UV-Vis spectroscopic characterization, dry HA (7 mg) were diluted with 0.1 M NaOH and absorbance at wavelengths 200–900 nm was measured.

Preparation of Humic Gel

For the preparation of the humic gel, solid HA were dissolved in 0.5 M NaOH. The hydrogel was then obtained by precipitation of sodium humate after acidification with HCl to pH below 1. The formed mixture was kept overnight and the next day the mixture was centrifuged, the supernatant was discarded and the gel (labeled as 'gel A') was repeatedly washed with deionized water and centrifuged. About 86% of total weight of the resulting hydrogel is represented by water content.

Diffusion Experiments

The paper compares three simple experimental methods for determination of D_{eff}. In all of them, non-stationary (transient) diffusion of Cu^{2+} is assumed. Each of the following experiments was done in triplicate; the individual diffusion flux was calculated as the arithmetic mean of the three corresponding values with determination of the standard error.

In-diffusion from constant source. The first diffusion experiment was focused on the diffusion from constant source of Cu^{2+}. This method is often used in determining diffusion coefficients in various solid samples[29–31]. The humic gel (gel A) was packed into cylinders (1 cm internal diameter and 5 cm length). These cylindrical samples were put separately into 50 ml of saturated $CuCl_2$ solution with ca. 2 g of crystalline $CuCl_2$ added before. As the rate of dissolution of the crystalline salt is assumed to be higher in comparison with the rate of diffusion, we can suppose that the concentration of Cu^{2+} in solution is maintained at a constant value during diffusion experiments. In given times, gel samples were sliced and the slices were extracted separately with 0.025 M NH_4EDTA solution. Previous extraction experiments had confirmed the 100% effectiveness of the leaching of Cu^{2+} ions from humic gel to 1 M HCl up to the 1 mol l^{-1} content in the gel. Acid extraction is advantageous because dissolved humic acids do not interfere with the UV-Vis signal of Cu^{2+} in extracts. Nevertheless, higher Cu^{2+} concentrations require the use of NH_4EDTA as the leaching agent. The Cu^{2+} content in each extract was quantified by UV-Vis spectrophotometry (Hitachi U3300). Consequently, the concentration profile was determined by assessing the concentration of Cu^{2+} determined from a slice from a corresponding position in the gel cylinder. Simultaneously, the cumulative diffusion flux was calculated from the sum of the Cu^{2+} contents over the whole cylinder.

Diffusion pair. Diffusion pair (also called Half-plugs method) is often used for determination of diffusivity in solids[29,32,33]. The measurement is carried out by connecting two samples (usually tubes filled with a studied material) which differ only in concentration of diffusing matter. This approach was implemented as follows. The humic gel with incorporated Cu^{2+} ions (gel B) was prepared by diffusing the ions into the humic gel described in the previous chapter (gel A). The gel A was gently pressed into a silicone tube (inner diameter 1 cm and length 3 cm) and placed into 1 M $CuCl_2$ solution (30 ml). Cu^{2+} ions were diffusing into the gel for 8 days, until a constant concentration in the tube was achieved. The diffusion pair was then realized by connecting two silicone tubes, one filled with the humic gel containing Cu^{2+} ions (gel B) and the other filled with the humic gel without metal ions (gel A, tube length 5 cm). In a given time, the samples were disconnected and the concentration of diffusing substance was found in different positions. For this purpose, gel-slicing was used again, determining the concentration of Cu^{2+} ions in a separate slice after extraction with 1 M HCl by UV-Vis spectrophotometry. Satisfactory effectiveness of this extraction in the particular region of Cu^{2+} concentrations in the gel was confirmed again. From the

dependence of cumulative diffusion flux (total mass of substance transported through the interface of the diffusion pair) on time or from the shape of concentration profile of the diffusing substance in the sample, diffusion coefficient is then calculated.

Instantaneous planar source. For an instantaneous planar source of the diffusing matter, an infinitesimally small width of the initial concentration pulse is presumed[26–29]. This can be considered, e.g., when a filter paper tagged with a highly soluble substance is located at the end of a tube filled with the studied hydrogel. In the particular experiment, a circular slice of filter paper (1 cm in diameter) was immersed into 1 M $CuCl_2$ solution for 1 min. The humic gel (gel A) was packed into a plastic tube (1 cm inner diameter and 5 cm length) with the immersed filter paper placed at one end. At given times, gel samples were sliced and both paper and gel slices were extracted separately with 1 M HCl. Concentrations of Cu^{2+} ions in separate slices were determined using UV-Vis spectrophotometry.

RESULTS AND DISCUSSION

Characterization of HA

Results of the HA elementary analysis illustrate the major content of H (42.12 mole %) and C (41.16 mole %); high content of O (15.64 mole %) and the minor amount of N and S (0.91 and 0.17 mole %, respectively). All values are normalized on dry ash-free HA. These results are in accordance with previous elementary analysis published for lignitic humic acids[1,7]. From the UV-Vis spectrum of sodium humate, standard optical characteristics were calculated. They are very useful for the determination of the chemical structure of HA[1]. The absorption ratio A_{280}/A_{465}, which corresponds to the ratio between resistant lignin structures and HA with the low degree of humification[34], was 3.75. A_{465}/A_{665} ratio ($E4/6$) indicates the humification index and decreases with increasing molecular weight or degree of dispersion. Low $E4/6$ (3.35) hence indicates high molecular weight of the applied HA. Kumada[35] connected the value of $\Delta \log K$ ($\Delta \log K = \log A_{400} - \log A_{600}$) with the degree of humification of HA. According to this value, the author distinguishes three basic types of the material: A-type ($\Delta \log K$ up to 0.6), B-type (0.6–0.8) and R_p-type (0.8–1.1); the lower the $\Delta \log K$ value the higher humification degree. The used HA belong to A-type ($\Delta \log K = 0.57$) which indicates high degree of humification. Particular FT-IR, UV-Vis, elemental, ^1H and solid-state ^{13}C NMR characterization of used HA can be found in more details in Peuravuori et al.[36].

Diffusion Experiments

Schematic representations of all methods described in the following section are shown in Fig. 1. Corresponding initial conditions are also implied.

In-Diffusion from Constant Source

Prior to the start of the experiment, homogeneous distribution of concentration of a diffusing substance is required. In our experiment, the diffusing species of interest are Cu^{2+} ions and the homogeneous concentration in the gel in time $t = 0$ s is zero. When the phase boundary (a circular surface at the end of the gel cylinder) is kept at a constant concentration ($x = 0$ m: $c_1 = c_{x=0}$ for $t > 0$ s), Eq. (*5*) can be easily processed by Laplace transformation. The time development of the concentration profile of diffusing substance in the gel can be calculated from the following equation[19,29,37]

$$c_1 = c_{x=0} \operatorname{erfc} \frac{x}{\sqrt{4D_{\text{eff}} t}} . \qquad (8)$$

A diffusion flux J can be expressed by Eq. (*9*)

$$J = -D_{\text{eff}} \left(\frac{\partial c_1}{\partial x} \right)_{x=0} . \qquad (9)$$

The derivative of the concentration profile incorporated in Eq. (*9*) gives the expression for the total amount of substance transported through the solution/gel interface (cumulative diffusion flux). From this flux, D_{eff} can be calculated

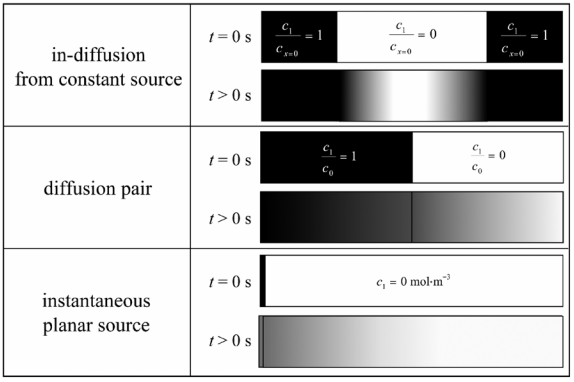

FIG. 1
Schematic representation of the used diffusion methods

$$m = 2c_{x=0}\sqrt{\frac{D_{\text{eff}}t}{\pi}}\,. \qquad (10)$$

In nonstationary diffusion of ions through two circular planes at both ends of the gel cylinder, concentration profiles of Cu^{2+} in the gel show a typical symmetrical shape with a minimum in the middle of the gel sample, as was verified experimentally (concentration profiles are not listed here). For constant concentration of Cu^{2+} at solution/gel interface, the total diffusion flux dependence on the square root of time is assumed to be linear. As can be seen in Fig. 2, the agreement between this theory and experimental results is good. From the slope of the linear regression of this dependence, the value of diffusion coefficient of cupric ion in the humic gel was calculated using Eq. (*10*). Values of $c_{x=0}$ are determined by extrapolation of concentration profiles. The resulting value of diffusion coefficient together with all the values determined by the following methods and the value published for diffusion in water are shown in Table I.

Diffusion Pair

An example of the experimental concentration profile obtained for gel B in the diffusion pair with gel A is given in Fig. 3. It shows that concentrations at both sides of the A–B interface are equal or, in other words, no concentration jump is observed. The reason is clear; both gels are of the same material origin. First step of their preparation is the same; they differ just in

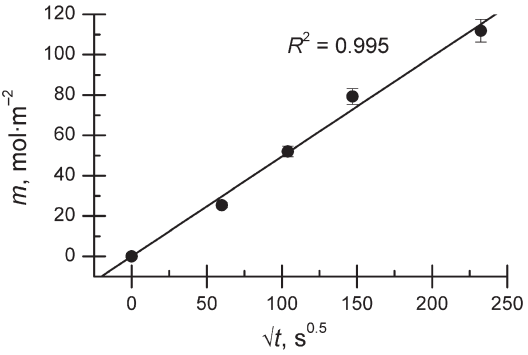

FIG. 2
Dependence of the total diffusion flux on the square root of time (in-diffusion from constant source)

the presence of Cu^{2+} in one of them when starting the experiment. These ions enter the final complete gel structure and can be consequently trapped only by functional groups of HA, not involved in the formation of primary gel structure. The nature, structure and properties of gel B are in this respect similar to those of the gel A.

A mathematical description of the diffusion in this diffusion pair is simple. When the diffusion starts, gel B has a constant concentration of Cu^{2+} ions along the whole tube length ($x < 0$ m: $c_1 = c_0$ for $t = 0$ s), whereas their concentration in the gel A is zero ($x > 0$ m: $c_1 = 0$ mol m^{-3} for $t = 0$ s). These initial conditions were verified experimentally. The solution of second Fick's law is the same as in the previous case and leads to the concentration profile of Cu^{2+} in diffusion pair in the following form[19,29,37]

TABLE I
Diffusion coefficients D_{eff} determined by different diffusion methods (with a 95% confidence interval)

Method	D_{eff}, m^2 s^{-1}
In diffusion method	$(7.9 \pm 0.6) \times 10^{-10}$
Half-plugs method	$(7.1 \pm 0.2) \times 10^{-10}$
Instantaneous planar source (slopes)	$(4.8 \pm 0.4) \times 10^{-10}$
Instantaneous planar source (intersection points)	$(5.0 \pm 1.4) \times 10^{-10}$
Diffusion in water[a]	14.3×10^{-10}

[a] Cited from Lide et al.[38]

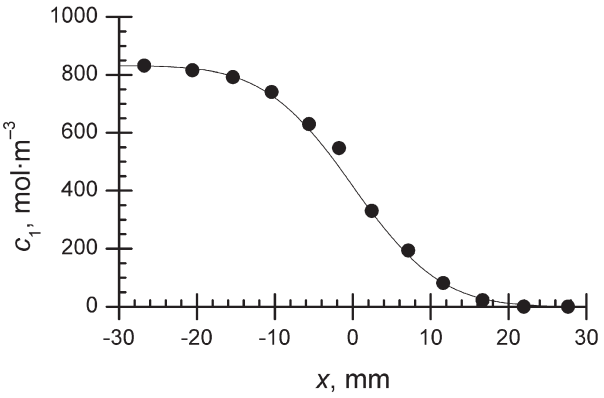

FIG. 3
Comparison of calculated (line) and measured concentration profile in diffusion pair after 16 h

$$c_1 = \frac{1}{2} c_0 \operatorname{erfc} \frac{x}{\sqrt{4D_{\text{eff}} t}} . \qquad (11)$$

From Eq. (*11*), it can be seen that concentration of diffused component on the interface is time-independent and equal to $c_0/2$.

The total diffusion flux m which goes through the interface between gel B and the gel A ($x = 0$) in time t can be calculated as

$$m = c_0 \sqrt{\frac{D_{\text{eff}} t}{\pi}} . \qquad (12)$$

A comparison of Eqs (*9*) and (*10*) with Eqs (*11*) and (*12*) indicates that, in fact, diffusion in diffusion pair corresponds to that from constant source; the outer part of the pair serves as a source which ensures constant concentration of diffusing substance (equal to $c_0/2$) at the interface with the "in" part.

Again, the dependence of experimentally determined m on $\sqrt{t}$ is strongly linear (Fig. 4). Therefore, Eq. (*12*) can be used for calculation of diffusion coefficient. The value of D_{eff} obtained for the Cu^{2+} diffusion from gel B into gel A is slightly lower than the value determined by diffusion from constant source (Table I) but the confidence interval is markedly more narrow.

To test the validity of calculated D_{eff}, Eq. (*11*) was used in order to calculate theoretical concentration profiles for different times. As it can be seen in Fig. 3, there is a good agreement between experimentally measured profile and the calculated one.

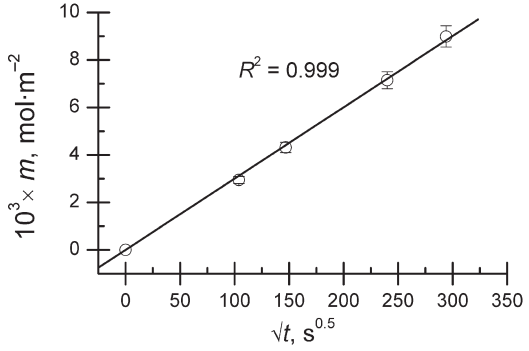

FIG. 4
Dependence of the total diffusion flux on the square root of time (diffusion pair)

Instantaneous Planar Source

The method of instantaneous planar source differs from the other methods mainly because that diffusion coefficient is primarily determined from the shape of measured concentration profiles of diffusing matter instead from the dependence of the total diffusion flux on time.

Instantaneous planar source involves an initial concentration pulse of infinitesimally small width. For this presumption and for the zero initial concentration of Cu^{2+} in the gel, the solution of the second Fick's law gives the following relationship for concentration profile[19,29,37]

$$c_1 = \frac{n_{Cu}}{S\sqrt{\pi D_{eff} t}} \exp\left(-\frac{x^2}{4D_{eff} t}\right) \qquad (13)$$

where n_{Cu} stands for total Cu^{2+} content in sample, x is the distance from the intercept between the gel and the paper filter and S is the cross-section area.

Linearization of this equation provides Eq. (*14*)

$$\ln c_1 = \ln \frac{n_{Cu}}{S\sqrt{\pi D_{eff} t}} - \frac{x^2}{4D_{eff} t} \qquad (14)$$

where it can be seen that while the linear regression of $\ln c_1 = f(x^2)$ is found in the form $\ln c_1 = B - Ax^2$, the effective diffusion coefficient influences both slope A and intersection point B

$$A = \frac{1}{4D_{eff} t}, \qquad B = \ln \frac{n_{Cu}}{S\sqrt{\pi D_{eff} t}}. \qquad (15)$$

For a better readability, the linear regressions for all three times are listed starting from 0 in Fig. 5. As mentioned before, the effective diffusivity can be derived from both A and B. In Fig. 6, the value of D_{eff} is shown as a slope of time-dependence of $1/(4A)$. For the calculation of D_{eff} from intersection point B, the following substitution can be used

$$Y = \frac{1}{\pi}\left(\frac{n_{Cu}}{S}\right)^2 \exp(2B). \qquad (16)$$

If compared with Eq. (*15*), it can be easily found, that $Y = D_{\text{eff}}\, t$. D_{eff} can be therefore calculated as the slope of time-dependence of Y (see Fig. 6).

Using the calculated diffusivity, the theoretical concentration profiles can be found. Figure 5 shows the agreement between measured and theoretical profiles, calculated using the value of D_{eff} derived from slopes of the linearized profiles.

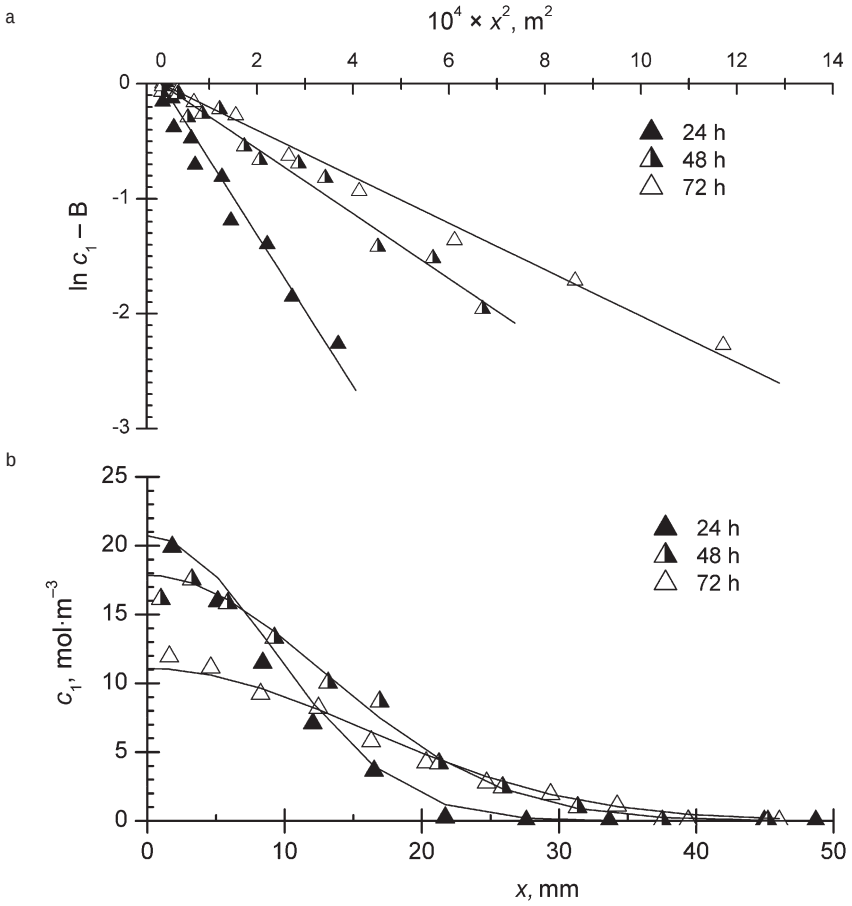

FIG. 5
Linearized concentration profiles of Cu^{2+} in humic gel (a) and a comparison of measured profiles (b) with those calculated (b, lines) using subsequently determined diffusion coefficient

Calculated Diffusion Coefficients

All calculated values of the diffusivities are listed in Table I. It can be seen that all values are of the same order of magnitude as that published for diffusion of Cu^{2+} in water[38]. This finding is common for diffusion in hydrogels. These values are also in good agreement with published diffusivities of Cu^{2+} in various hydrogels. Already in 1930's, diffusion coefficient of Cu^{2+} was measured in silica gel (ca. 4×10^{-10} m^2 s^{-1})[39] and in 2% agar gel (2.9×10^{-10} m^2 s^{-1})[40]. Much more recently, Garmo et al.[41] determined diffusion

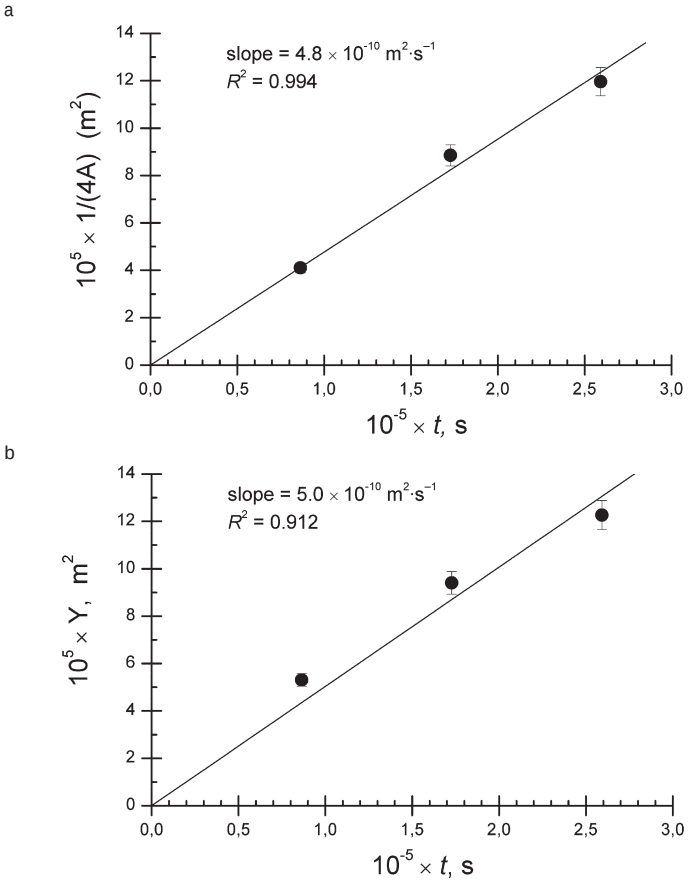

FIG. 6
Time dependence of the substituted slopes (a) and intersection points (b) of linearized concentration profiles

coefficients of 55 elements in DGT (diffusive gradients in thin films) equipment which consisted of diffusive agarose polyacrylamide gel and iminodiacetate chelating resin. Effective coefficient of Cu^{2+} in this complex medium was in the range 5.5–6.6 × 10^{-10} m^2 s^{-1} for pH 4.7–5.9. Scally et al.[18] studied transport of Cu^{2+} in the gels used for DGT method as well. They obtained values 6.30–6.45 × 10^{-10} m^2 s^{-1} for agarose cross-linked polyacrylamide and 4.18–4.81 × 10^{-10} m^2 s^{-1} for restricted polyacrylamide gel. The solid contents of both gels were very close to those of humic gel (~15%). The range of diffusivity corresponds to various $NaNO_3$ amounts added to source solutions of Cu^{2+}.

Table I shows a good agreement between D_{eff} values determined by the methods of in-diffusion and diffusion pair. The relative difference between the highest and the lowest mean values is slightly above 10%. These values correspond to about 50% of diffusivity of Cu^{2+} in water. As expected, Cu^{2+} ion movement in the gel matrix is slower than in water regardless of a high content of the aqueous phase in the gel. The reaction of Cu^{2+} with the active sites of HA in combination with a tortuous pathway decelerates the transport of Cu^{2+} through the phase interface. In other words, the driving force for the diffusion may be the same but the resistance to ion movement is higher when diffusing in the gel.

Both values of D_{eff} determined experimentally with an instantaneous planar source are noticeably lower. This can be caused by a dependence of a diffusion coefficient on concentration of diffusing substance as is often published[19]. In the former experiments, considerably higher amounts of diffusing substance were used and the concentration of Cu^{2+} in humic gel was always at least one order higher there and therefore an influence of the chemical reaction on the transport can be more pronounced. Because the value of D_{eff} is governed by the shapes of concentration profiles, the standard error of D_{eff}, characterized by the 95% confidence interval, is higher here. Nevertheless, this method possesses many advantages including low demands on supply of diffusing matter.

CONCLUSIONS

For the various applications of humic acids utilizing the natural sorption ability, it is necessary to combine classical sorption experiments with modeling of the sorbate transport in humic material which simulates the natural forms of HA. For this reason, basic diffusion experiments were performed. They were focused on the Cu^{2+} transport in the humic gel and the main goal was to test the applicability of theoretical mathematical apparatus and

simple laboratory methods to the study of the pollutant transport in materials that model natural humic environments.

In general, these diffusion measurements seem to provide a valuable method for reactivity and permeability mapping studies on materials containing humic substances. All methods proved themselves suitable for easy and quick description of transport phenomena. All experimental data fit theoretical calculations well. Specific parameters of each method (e.g. concentration of diffusing substance) must be taken into account when choosing an appropriate method for defined conditions. Consequently, either in-diffusion from a constant source or a diffusion pair can be utilized wherever the amount of the diffusing substance is not a limiting factor. In opposite cases, instantaneous planar source represents the method of choice.

As compared to diffusion of Cu^{2+} in water, the experimentally determined values of diffusion coefficient of Cu^{2+} in the humic gel were lower but of the same order of magnitude. This finding agrees with an increase in resistance to transport, which is well known for the reactive gels. The investigation of the diffusion behavior of typical pollutants in the gel forms of humic acids (from various sources or methods of extraction and purification) can serve as an important tool for the evaluation and standardization of their usability in a large range of applications.

SYMBOLS

c_0	initial concentration of diffusing substance in source gel (diffusion pair), mol m^{-3}
c_1	concentration of a diffusing substance, mol m^{-3}
c_2	concentration of an immobilized diffusing substance, mol m^{-3}
$c_{x=0}$	constant concentration at the phase interface (constant source), mol m^{-3}
D	diffusion coefficient in dispersion medium (water for hydrogels), m^2 s^{-1}
D_{eff}^0	effective value of diffusion coefficient excluding any reaction effect, m^2 s^{-1}
D_{eff}	effective value of diffusion coefficient including a reaction effect, m^2 s^{-1}
erfc	complimentary error function
J	intensity of diffusion flux, mol m^{-2} s^{-1}
K	proportionality constant between mobile and immobilized form of diffusing substance (dimensionless)
m	cumulative diffusion flux, mol m^{-2}
n_{Cu}	total amount of Cu applied in experiment (instantaneous source), mol
S	cross-section area, m^2
t	time, s
x	distance, dimension, m
ϕ	porosity of a porous medium (dimensionless)
τ	tortuosity of a porous medium (dimensionless)

This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic (project MSM 0021630501).

REFERENCES

1. Stevenson F. J.: *Humus Chemistry: Genesis, Composition, Reactions*, 2nd ed. Wiley–Interscience, New York 1982.
2. Almendros G.: *Commun. Soil Sci. Plant Anal.* **1994**, *17*, 2711.
3. Klučáková M., Pelikán P., Lapčík L., Lapčíková B., Kučerík J., Kaláb M.: *J. Polym. Mater.* **2000**, *17*, 337.
4. Kerndorff H., Schnitzer M.: *Geochim. Cosmochim. Acta* **1980**, *44*, 1701.
5. Tipping E., Hurley M. A.: *Geochim. Cosmochim. Acta* **1992**, *56*, 3627.
6. Klučáková M., Kaláb M., Pekař M., Lapčík L.: *J. Polym. Mater.* **2002**, *19*, 287.
7. Klučáková M., Pekař M.: *Colloids Surf., A* **2006**, *286*, 126.
8. Klučáková M., Pekař M.: *J. Polym. Mater.* **2003**, *20*, 145.
9. Martyniuk H., Wieckovska A.: *Fuel Process. Technol.* **2003**, *84*, 23.
10. Wang X., Chen Y., Wu Y.: *Appl. Radiat. Isot.* **2004**, *60*, 963.
11. Wold S., Eriksen T.: *Phys. Chem. Earth* **2007**, *32*, 477.
12. Chang M. L., Wu S. C., Chen C. Y.: *Environ. Sci. Technol.* **1997**, *31*, 2307.
13. Masaro L., Zhu X. X.: *Prog. Polym. Sci.* **1999**, *24*, 731.
14. Klučáková M., Pekař M. in: *Humic Substances: Molecular Details and Applications in Land and Water Conservation* (E. A. Ghabbour and G. Davies, Eds), p. 167. Taylor & Francis, New York 2005.
15. Klučáková M., Pekař M.: *J. Polym. Mater.* **2003**, *20*, 155.
16. Klučáková M., Pekař M. in: *Humic Substances: Nature's Most Versatile Materials* (E. A. Ghabbour and G. Davies, Eds), p. 263. Taylor & Francis, New York 2004.
17. Seki H., Suzuki A.: *J. Colloid Interface Sci.* **1999**, *211*, 375.
18. Scally S., Davison W., Hao Zhang: *Anal. Chim. Acta* **2006**, *558*, 222.
19. Cussler E. L.: *Diffusion: Mass Transfer in Fluid Systems*. Cambridge University Press, Cambridge 1984.
20. Lakatos I., Lakatos-Szabó J.: *Colloids Surf., A* **1998**, *141*, 425.
21. Lakatos I., Lakatos-Szabó J.: *Colloids Surf., A* **2004**, *246*, 9.
22. Potter K., McFarland E. W.: *Solid State Nucl. Magn. Reson.* **1996**, *6*, 323.
23. Matsukawa S.: *Prog. Polym. Sci.* **1999**, *24*, 995.
24. Tamagawa H., Popovic S., Taya M.: *Polymer* **2000**, *41*, 7201.
25. Falk B., Garramone S., Shivkumar S.: *Mater. Lett.* **2004**, *58*, 3261.
26. Climent M. A., de Vera G., Lopez J. F., Viqueira E., Andrade C.: *Cem. Concr. Res.* **2002**, *32*, 1113.
27. de Vera G., Climent M. A., Viqueira E., Antón C., Andrade C.: *Cem. Concr. Res.* **2007**, *37*, 714.
28. Schantz E. J., Lauffer M. A.: *Biochemistry* **1962**, *1*, 658.
29. García-Gutiérrez M., Cormenzana J. L., Missana T., Mingarro M., Molinero J.: *J. Iberian Geol.* **2006**, *32*, 37.
30. Cave L., Al T., Yan Xiang, Vilks P.: *J. Contam. Hydrol.* **2009**, *103*, 1.
31. Suzuki K., Fukano T., Kataoka Y.: *J. Electrochem. Soc.* **1991**, *138*, 2201.
32. Balcone-Boissard H., Baker D. R., Villemant B., Boudon G.: *Chem. Geol.* **2009**, *263*, 89.

33. Paul A., Kodentsov A. A., van Loo F. J. J.: *J. Alloys Compd.* **2005**, 403, 147.
34. Chen Y., Senesi N., Schnitzer M.: *Soil Sci. Soc. Am. J.* **1977**, *41*, 352.
35. Kumada K.: *Food Fertilizat. Technol. Centre* **1975**, *22*, 10.
36. Peuravuori J., Žbánková P., Pihlaja K.: *Fuel Process. Technol.* **2006**, *87*, 829.
37. Crank J.: *The Mathematics of Diffusion*. Clarendon Press, Oxford 1956.
38. Lide D. R.: *Handbook of Chemistry and Physics*, 76th ed. CRC Press, New York 1995.
39. Eversole W. G., Doughty E. W.: *J. Phys. Chem.* **1936**, *40*, 55.
40. Ricketts V. L., Culbertson J. L.: *J. Am. Chem. Soc.* **1931**, *53*, 4002.
41. Garmo A., Røyset O., Steinnes E., Flaten T. P.: *Anal. Chem.* **2003**, *75*, 3573.