

Modelling of metal pollutant transport in natural humic environments

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Abstract

This contribution introduces newly developed method for metal ions diffusion study in humic gel. The main aim was to check the applicability of used experimentation (designed apparatus, mathematical model) in diffusion experiments. The experimental part focused mainly on determination of Cu^{2+} ions diffusion coefficient in humic gel and on the influences of copper(II) solution concentration and diffusion time on the total diffusion flux across the solution–gel interface. In none of all experiments any Cu^{2+} presence in side-water was determined, which confirms high capacity of humic gel for metal ions immobilization. Results of FT–IR measurement confirmed participation of carboxylic and phenolic groups of humic acids on the complexation of Cu^{2+} ions.

Keywords: humic, transport, diffusion, remediation

1. Introduction

Humic acids (HA) are ubiquitous organic material, which forms chemically most important fraction of soils and sediments, peat, young coals etc. Long term study of this matter has been interested mainly in chemical structure and sorption processes on humic substances. High sorption and complexation ability of HA towards various groups of chemicals makes them responsible for natural soil detoxification and also very promising in potential production of soil remediation agents. For this application, cheap methods of extraction from their rich natural sources have been developed.

It is well known that sorption ability depends strongly on size of humic particles. One important reason is transport of adsorbed ions (or molecules) into humic particles to bind with active centre. Many works concerning sorption abilities of solid humic acid and/or humic sols have been published. This contribution focuses on the study of HA in a form of gel.

In general, gel form of sorbent is suitable for the exploration of transport phenomena. Sample can be prepared in defined size and shape, which is necessary for mathematical modelling of observed processes and the suppression of convective and thermal mixing is advantageous, too. In the case of humic acids, other advantages appear: easy preparation of humic gel and mainly good simulation of natural conditions, because HA are usually found in highly humid environments (water sediments, peat etc.) and thus in the swollen form.

Among common groups of chemical pollutants, heavy metals play important role in soil and water chemistry. Copper is used as model metal in this work because of its high affinity for humic substances; HA–Cu(II) binding is among the highest strengths. Besides this, content of Cu^{2+} ions can be also easily spectroscopically quantified.

Diffusion of metal ions into the humic gel is affected by reduced mobility of ions in the gel phase and by complexation of ions by functional groups of humic acids. Thus, the mathematical apparatus, applied on the description of diffusion processes is quite complicated. Basic diffusion theory, used in this work, is listed in detail in Crank (1956). Mathematically, the concept of unsteady diffusion with chemical reaction in semiinfinite slab is adopted in two variations: diffusion from the constant source and diffusion from the time-variable source. For cylindrical gel sample stationary diffusion of ions only through two circular planes at both ends of gel cylinder is assumed. For these conditions, following equations for total ion diffusion flux (m) have been derived:

$$m = 2 c_s \sqrt{\frac{D_g t}{\pi}} \quad [1]$$

$$m = \frac{2 \varepsilon c_0}{1 + \varepsilon \sqrt{D_g / D}} \sqrt{\frac{D_g t}{\pi}} \quad [2]$$

Relation Eq. [1] describes diffusion from the constant source while relation Eq. [2] is derived for the diffusion from time-variable source. In this formula, ε stands for the ratio of the ion concentration in the gel and in the solution at final equilibrium, c_s is concentration of diffusion ions at gel/solution interface, c_0 is the initial solution concentration, D_g is the effective value (i. e. value in which the chemical reaction between ions and HA is involved) of Cu^{2+} diffusion coefficient in the humic gel and D is the diffusion coefficient of ions in aqueous solution.

Similarly, relations for the theoretical concentration profiles of diffusing ions in humic gel can be derived; Eq. [3] for diffusion from the constant source and Eq. [4] for diffusion from the time-variable source:

$$c_g = c_s \operatorname{erfc} \frac{x}{\sqrt{4 D_g t}} \quad [3]$$

$$c_g = \frac{\varepsilon c_0}{(1 + \varepsilon \sqrt{D_g / D})} \operatorname{erfc} \frac{x}{\sqrt{4 D_g t}} \quad [4]$$

2. Materials and methods

2.1. Isolation of HA

HA were extracted from South-Moravia lignite by means of the alkaline extraction. Lignite was stirred with extractant ($0.5 \text{ mol.dm}^{-3} \text{ NaOH} + 0.1 \text{ mol.dm}^{-3} \text{ Na}_4\text{P}_2\text{O}_7$) in the 20 g per 1 dm^3 ratio for 12 hours. Formed suspension was kept overnight and next day the solution was separated from solid phase, than acidified by 20 % hydrochloric acid up to pH below 1. Solid residue was put into another 1 dm^3 of extractant and after 1 hour of stirring, extract was separated and acidified in the same way. Acid extracts were kept in the refrigerator overnight.

Precipitated HA were separated by means of centrifugation (4000 min^{-1}), washed in deionized water several times and centrifuged until Cl^- ions removal and dried at $50 \text{ }^\circ\text{C}$. Before humic gel preparation HA were washed in water, centrifuged and dried one more time.

2.2. Preparation of humic gel

For the preparation of humic gel, solid HA were dissolved in 0.5 M NaOH . The gel was then acquired by precipitation of sodium humate by acidification with HCl up to pH below 1. The mixture was centrifuged, supernatant was discarded and gel was repeatedly washed by deionized water and centrifuged. Resulting gel contained about 86% of water.

2.3. Diffusion experiments

Diffusion experiments were divided into two parts according to Cu^{2+} ions source. As a constant source super-saturated solution of cupric chloride was used. Humic gel was packed into plastic tube as 5 cm long cylinder and all tubes were put separately into 50 ml of saturated CuCl_2 solution in which one spoon of crystalline CuCl_2 were added. Different time durations of diffusion were applied and for each one the experiment was triplicated. After the end of an experiment, each gel sample was sliced and each slice was separately extracted by $0.025 \text{ M NH}_4\text{-EDTA}$ (100% effectivity of extraction had been previously experimentally verified). By the UV-VIS quantification of copper(II) ions content in each extract, the concentration profile of the gel cylinder and the total diffusion flux across the solution-gel interface were determined.

In all remaining parts diffusion from time-variable source of copper(II) ions was studied. The experiments took place in apparatus presented on Figure 1. Humic gel was packed into plastic tube again and 2 ml of both copper ions solution and deionized water were filled into side containers.

First of all diffusion dependency on Cu^{2+} solution initial concentration was monitored by changing the initial concentration of CuCl_2 solution placed in the apparatus container, while the duration of experiment was maintained at 24 hours . Next part focused on the influence of time duration of diffusion experiment. The 1 day , 3 days and 5 days periods had been chosen. The experiment was repeated for three Cu(II) initial concentration values: 100 mol.m^{-3} , 300 mol.m^{-3} and 600 mol.m^{-3} . Following experimentation was adopted from previous experiment without changes.

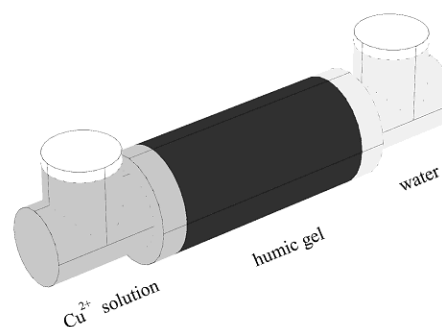


Figure 1 Scheme of the apparatus used in experiments on diffusion from time-variable source

3. Results and Discussion

3.1. Diffusion experiments

3.1.1. Diffusion from constant source

Experimentally explored dependency of copper(II) ions total diffusion flux from super-saturated solution on time allows determination of diffusion coefficient of ions in humic gel. As the permanency of the metal ions concentration at solution/gel interface is assumed, the total diffusion flux is theoretically linear function of the square root of time. As can be seen on Figure 2, agreement between this theory and experimental results is satisfactory. From the slope of the linear regression of this dependency, the value of copper(II) ion diffusion coefficient in humic gel was calculated using Eq. [1]. This value together with the one published for diffusion in water is shown in Table 1.

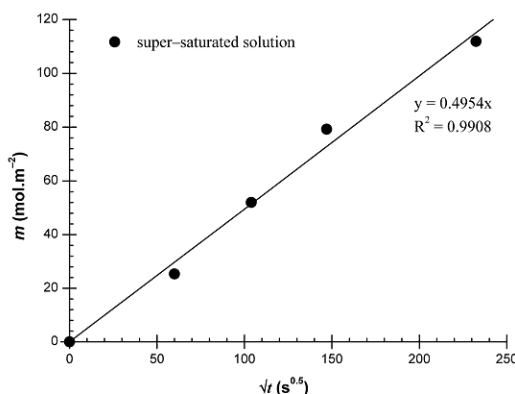


Figure 2 The total diffusion flux dependency on the square root of time (constant source)

Table 1 Comparison of calculated value of diffusion coefficient in humic gel (D_g) and that published for diffusion in water^b (D)

D_g	$7.92 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$
D	$1.43 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$

^b cited from Lide D.R. (1995)

3.1.2. Diffusion from time-variable source

Next part of the work focused on copper(II) ions diffusion from solutions with time-variable copper(II) concentration applying different time duration and different initial concentration of copper(II) salt solution. In such cases, constant ratio of copper concentration in the gel and in the solution in final equilibrium is usually assumed. As can be seen on relation Eq. [2], the total diffusion flux over the interface is then linear function of initial Cu^{2+} concentration in the solution and of the square root of time.

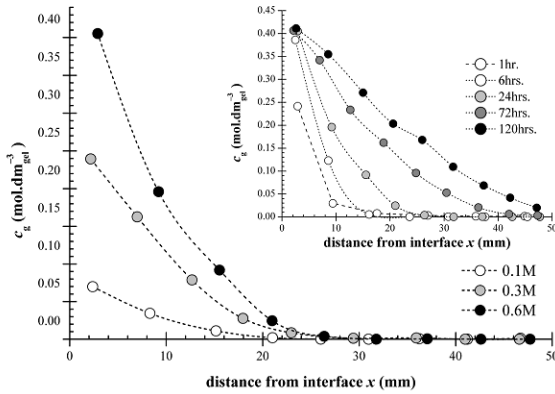


Figure 3 Concentration profiles of Cu^{2+} in gel cylinders (time-variable source) corresponding different initial concentration of solution (larger figure; example for time duration 24 hrs) and different time (smaller figure; example for initial concentration of solution 0.6 M)

All presented diffusion flux values have been calculated as the sum of copper(II) ions detected in gel slices and verified by spectroscopically measured decrease of the solution concentration (in average, 98 % agreement was found between these two methods). Figure 4 shows linear dependency of experimental diffusion flux values on the initial solution concentration for all measured time durations. The slope of this dependency increases with the time of diffusion experiment. In this case, the agreement between experiment and the theory is very good.

On the other hand, disagreement between theoretical and experimentally measured time dependencies of total diffusion flux was found. In the region of very short times, experimental total flux rises linearly with the square root of the time duration according theoretical relation Eq. [2]. The slope of this line (solid lines in Figure 5) linearly increases with the initial copper(II) concentration of the solution. Somewhere around 6 hours this linear function deflects to lower values. The divergence proportionally rises with the square root of the time so the following tendency of the time dependency is approximately linear with nonzero m -intercept. Discussed deflection of the diffusion flux time dependency indicates some changes in system occurring in later time which make the velocity of diffusion become slower than that corresponds the simple mathematical model.

On the other hand, disagreement between theoretical and experimentally measured time dependencies of total diffusion flux was found.

Explanation of this behavior is not easy. The main reason lies probably in predictions used to deduce mathematical description (the system of diffusion of metal ions in humic gel including complexation reactions is very complex and resulting model is not solvable analytically). We used model of semi-infinite medium. Although no copper(II) ions were detected for $x \rightarrow 5$ cm (length of tube), obtained results could be influenced by interaction of humic gel with deionized water, if diffusion experiment is prolonged, in this case. Besides this, while

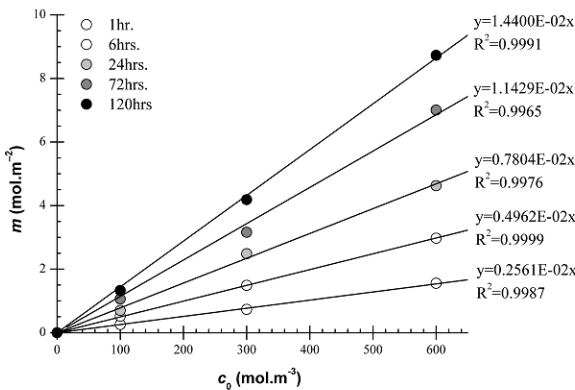


Figure 4 The total diffusion flux dependency on the initial ion concentration in the solution (time-variable source)

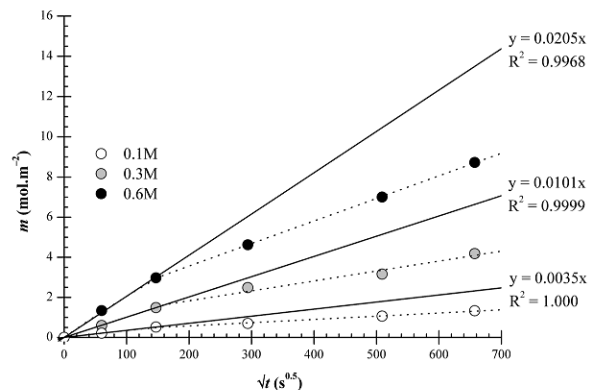


Figure 5 The total diffusion flux dependency on the square root of time (time-variable source)

deriving whole mathematical apparatus the diffusion coefficients were supposed to be constant. The possible dependency of copper(II) ions diffusion coefficient in humic gel on solution concentration should be experimentally examined to be able to discuss its participation on mentioned abnormalities.

Nevertheless, the most probable reason for this disagreement between theoretical relation and experimental data lies in the preconditions linked with chemical reaction between HA and Cu^{2+} ions. We used relatively simple equations based on Fick laws, which so-called effective diffusion coefficient is considered in. Its value embraces ever diffusion transport or chemical reaction on condition that concentration of immobilized ions is directly proportional to concentration of free (movable) copper(II) ions in humic gel. The advantage of this model is its simplicity and possibility of relatively wide utilization. However, the real situation in diffusion in humic gel is more complex. This complexity affects the equilibrium on the solution/gel interface. The equilibrium is described by ratio of the ion concentration in the gel and in the solution – ε . While deriving Eqs. [2] and [4] we presumed its permanency. If we neglect other possible influences (such as non-permanency of diffusion coefficient) and calculate ε from experimental diffusion flux values following Eq. [2], we will see that while changing initial concentration of ions in the solution, ε really stays constant, but there is a dependency of ε on the diffusion time which can be seen in Figure 6. This fall of ε could be caused by formation of some stable chemical or structural complexes between gel and ions, not involved in immobilizing reaction assumed while deriving D_g (i.e. this reaction does not fulfil proportionality between mobile and immobilized fraction of diffusing ions). This binding depresses the actual concentration of mobile ions in the gel side of interface and thus the velocity of the diffusion through gel cylinder.

The knowledge of the ε value allows the calculation of theoretical concentration profiles of the copper(II) ions in the humic gel for different experiment conditions (initial concentration and time duration). The examples on Figure 7 show good agreement between calculated and measured concentration profiles. This agreement supports consideration presented in previous paragraph.

3.2. FT – IR analysis

The FT–IR spectroscopy was used to find the way of copper(II) ions binding in the gel (see Figure 8). The result for humic acids used in the gel preparation shows typical transmission

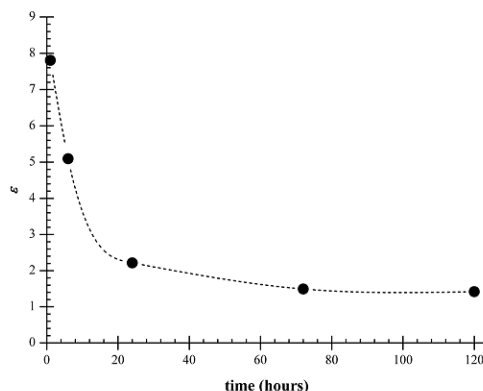


Figure 6 Time shift of calculated ε

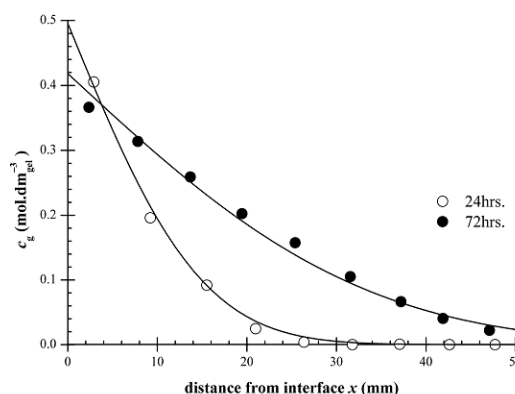


Figure 7 The comparison of experimental concentration profiles (points) with those calculated ($c_0 = 0.6 \text{ M}$)

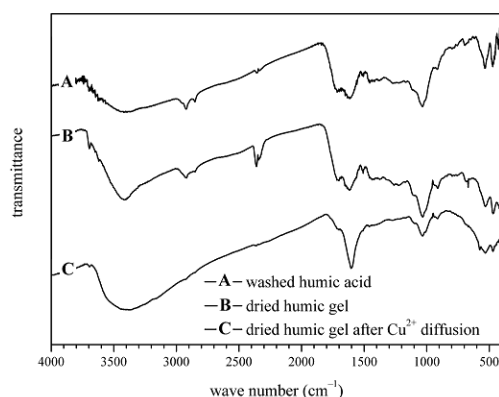


Figure 8 IR characterization of used HA, humic gel and humic gel with diffused Cu²⁺ ions

spectrum of highly humified organic matter. As far as there is no important difference between IR spectra of HA and humic gel made up of them, no chemical or structural changes of HA occur while gelation followed by gel drying.

On the other hand, several differences can be found in the IR spectrum of humic gel with diffused Cu²⁺: wide absorption band around 3400 cm⁻¹ stands for the moisture – HA are known to form hydrocomplexes with copper(II) ions – and disables detail interpretation of the spectrum in the range from 3500 cm⁻¹ to 3000 cm⁻¹. The complexation of Cu²⁺ affects markedly absorption bands of the carboxylic groups. In the area of 1700 cm⁻¹, where the absorption of carboxylic –OH takes place, strong decrease of the band can be seen comparing spectra of HA and the raw gel. On the other hand, new band appears around 1610 cm⁻¹, demonstrating the presence of dissociated –COO⁻. Small band standing for the absorption of phenolic –OH groups, which can be found in the spectra of HA and raw humic gel, after the diffusion of Cu²⁺ disappears. These results verify published participation of carboxylic and phenolic groups of HA on the complexation of metal ions. The complexation occurring on dissociated acid groups releases H⁺ ions which increase the acidity of side water solutions. This fact was also experimentally proved (pH values of side water samples after diffusion experiments decreased with increasing time duration as well as with increasing initial concentration of Cu²⁺ solution).

4. Conclusions

The main aim of this contribution is to present experimentation (designed apparatus, mathematical model) developed for diffusion studies in humic gel. The experimental part focused mainly on determination of Cu²⁺ ions diffusion coefficient in humic gel and on the effects of copper(II) solution concentration and diffusion time on the total diffusion flux across the solution–gel interface.

Although the applied apparatus was very simple and could be improved for following experiments (the higher solution volumes should be used) experimental data are fitted well by the theoretical calculations, so it can be said that this method presented itself suitable for the wide spectrum of diffusion experiments using humic gel as a very useful natural–like model.

Discovered disagreements between theoretical and measured dependencies, such as the deflection of the total diffusion flux dependency on the square root of time, will be taken as subjects of the following research.

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