

TRANSPORT OF ORGANIC COMPOUNDS THROUGH POROUS SYSTEMS CONTAINING HUMIC ACIDS

SMILEK J.¹, KLUCAKOVA M.¹ and SEDLACEK P.¹

¹ Brno University of Technology, Faculty of Chemistry, Materials Research Centre, Purkynova
118/464, 61200 Brno, Czech Republic
E-mail: xcsmilek@fch.vutbr.cz

ABSTRACT

Humic acids are natural supramolecular compounds which play a key role in several essential processes in the nature environment. They have an extraordinary position in controlling of the pollutant transport because of their outstanding capacity towards to compounds of diverse chemical nature (i.e. heavy metal ions, organic dyes, etc.). Chemical properties of these valuable materials are known quite well. Major gaps in knowledge of humic research are still found on their reactivity and barrier properties at natural dynamic conditions. New universal reactivity-mapping tool is required to overcome this problem with studies on the reactivity of humic acids.

The original combination of simple diffusion techniques with the advantages of hydrogel porous media (simple preparation of hydrogels, the diffusion is undisturbed by convection, etc.) provides very valuable information about the reactivity of humic acids. The transport and barrier properties of supramolecular humic acids are studied by diffusion of simple organic dyes through the hydrogel material where humic acids are homogeneously distributed. Humic acids reactivity is evaluated by determination of fundamental diffusion parameters such as effective diffusion coefficients, sorption capacity, break-through time (time needed for through-penetration of selected organic dye) or concentration of organic dye on the interface hydrogel-solution.

Barrier and transport properties of humic acids were studied by two diffusion methods (non-stationary and stationary diffusion experiments in the diffusion cell). The linear polysaccharide agarose was used for preparation of porous hydrogel media in both cases. The influence of changes in physical-chemical properties of the system can be studied very easily (i.e. pH, ionic strength, temperature, concentration of active substances, modification of humic acids, etc.).

Systems based on hydrogels used for study on the reactivity of humic acids are dynamic, therefore the conditions of studying humic systems in the laboratory are very similar to the real humic acids environment. The unique combination of diffusion experiments with hydrogels provides us valuable information about the reactivity of humic-like systems in their natural environment. Developed methods for determination of the diffusivity of organic dyes through hydrogels with humic acids together with classical sorption experiments could be the universal tool for the studies on the reactivity of not only humic acids but also for other natural biopolymers or supramolecular compounds. The universality of developed methods was tested also on systems with natural biopolymers (i.e. chitosan, sodium alginate). The influence of basic physical-chemical conditions of the systems containing natural substances can be studied easily in laboratory conditions and this is one of the greatest advantages of developed methods.

Keywords: humic acids, reactivity, diffusion, hydrogel

1. Introduction

Humic acids are complex substances which are a crucial compartment of the soil. Their role in the nature environment system is indisputable especially in the case of pollutant binding. The most important function of humic acids in the natural environment (soil) is the ability of pollutant

complexation. Humic acids have a relatively high affinity towards to common pollutants (i.e. heavy metal ions, pesticides etc.). This ability has been reported in several publications (Tipping, 2002; Schnitzer and Khan, 1972; Kördel *et al.*, 1997). The interaction of humic acids and pollutants is mostly given by carboxylic and phenolic functional groups. The complex structure of humic acids, the presence of diverse functional groups such as carboxylic groups and phenolic groups has been widely reported (Ritchie and Perdue, 2003; Fukushima *et al.*, 1995).

From the other side of view the positive affinity and sorption ability of humic acids towards to common pollutants is given by the presence of hydrophobic centres (De Paolis and Kukkonen, 1997; 7. Ran *et al.*, 2007), which have the major responsibility for these interactions while the presence of acidic functional groups has minor influence. The verification of the role of acidic functional groups in comparison with hydrophobic interactions of humic acids with pollutants is one of the main goals of this research article.

Humic acids belong among a wide group of natural biocolloids. The chemistry of humic acids is relatively known and very detailed described in literature (Stevenson, 1994). One of the most important gaps in the humic acids (generally biocolloids) knowledge is their reactivity. The reactivity of humic acids is mostly studied by classical sorption experiments (Martyniuk and Wieckowska, 2003; Bradl and Acikel, 2004) but these experiments have several deficiencies. First of all, the sorption experiments are mostly realized in solid form of humic acids, but in the natural environment, humic acids are mostly in the colloid or hydrogel form. Therefore, the simple diffusion techniques for the study on the reactivity of humic acids were developed. These methods are based on the assumption, that humic acids are homogeneously distributed in the agarose hydrogel which is used for diffusion experiments. In our recent works (Klucakova and Pekar, 2003; 2006; Klucakova *et al.*, 2013) the reactivity of humic acids was studied by interaction with heavy metal ions (Cu^{2+}) and the effective diffusion coefficients and sorption capacity of humic-like hydrogels were determined as the main transport parameters of diffusion processes. Developed methods for the study on the reactivity of humic acids (diffusion cell technique and non-stationary diffusion technique) were published in our previous publications (Sedlacek *et al.*, 2013; 2014). In these publications the influence of the concentration of lignite humic acids and the influence of temperature has been studied.

2. Experimental

Agarose (routine use class, < 10 wt. % moisture content) and Methylene Blue hydrate (MB, CI Basic Blue 9, dye content, \geq 95 wt. %) were purchased from Sigma-Aldrich and were used without further purification.

Lignite humic acids were isolated by alkali extraction from South-Moravian lignite. The exact procedure of isolation can be found in literature (Ghabbour *et al.*, 1994). Modified humic acids were prepared via methylation using trimethylsilyl-diazomethan. The procedure of modification is detailed described in literature (Klucakova *et al.*, 2013). By the modification procedure, the amount of acidic carboxylic groups is adjusted. Carboxylic groups are covered by methyl-groups during the modification therefore the influence of carboxylic groups on the reactivity of humic acids is eliminated. The presence of carboxylic groups in the structure of humic acids was tested by FTIR.

2.1. Preparation of hydrogels

The diffusion experiments mentioned in this paper were realized in supporting hydrogel matrix based on linear polysaccharide agarose. The preparation of interpenetrating polymer network (IPN) from humic acids in a supporting hydrogel-forming polymer based on agarose was done via thermoreversible processes. The network of agarose chains is interpenetrated by molecules of humic acids at higher temperature – the mixture dissolved at 85 °C and the mixture was then filled up in pre-heated mould. The solution of agarose with/without humic acids was poured into the pre-heated PTFE mould and the glass slides (also pre-heated) were placed on the opposite

sides of mould. The mixture of agarose with humic acids gradually solidified into the cylindrical hydrogel plate sample (40 mm in diameter and 5 mm thick).

2.2. Realization of diffusion experiments – diffusion cell

The hydrogel in PTFE mould was placed between two chambers of diffusion cell. First chamber of diffusion cell was filled by $0.01 \text{ g}\cdot\text{dm}^{-3}$ Methylene Blue and the second chamber was filled with deionized water. Both chambers of diffusion cell were filled by 60 cm^3 of solutions simultaneously. The change of concentration of diffusion probe was determined by ultraviolet-visible fibre spectrometer USB 2000+ (Ocean Optics, Inc.) in the receiving part of diffusion cell as the time function. The ultraviolet-visible spectra were collected continuously at given time intervals. After the termination of the diffusion experiments, the absorbance in the source part of diffusion cell was measured. The water-jacketed side-by-side diffusion cell purchased from Permegear Inc.

3. Results

The diffusion process in diffusion cell can be divided into two different steps: (i) sorption, (ii) steady state flux. During the first stage, the concentration of diffusing probe is not changing in the acceptor compartment of diffusion cell. Diffusing probe (simple organic dye) may interact with the structure of humic acids, till all functional groups (or hydrophobic centres) are occupied by molecules of dyes. After that, the concentration of diffusing probe will begin to change in the acceptor compartment of diffusion cell and the steady state stage will begin. Steady state flux can be determined by fitting the linear part of break-through curve (steady-state stage), while the break-through time (lag time) is calculated from the x-axis intercept (Figure 1).

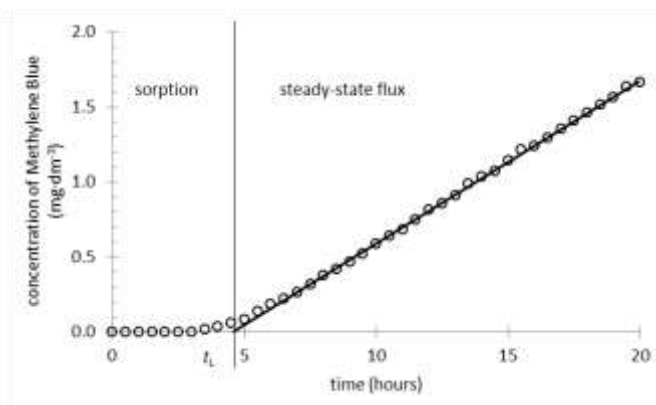


Figure 1: The change of concentration as time function for 1 wt. % agarose hydrogel.

It is obvious, that the increasing concentration of humic acids in agarose hydrogel sample slows down the rate of diffusion. This fact is supported by the increasing value of lag time (time needed for penetration of dye through the hydrogel sample) and decreasing the slope of linear part of the curve. The effective diffusion coefficients were calculated from the linear part of the breakthrough curve (Figure 1). The calculated values of effective diffusion coefficients and break through time (lag time) of agarose hydrogels with/without the addition of humic acids for all ranges of measured concentration are shown in Figure 2 (left).

The rate of interaction of humic acids with cationic organic dye is dependent on the amount of carboxylic groups in the structure of humic acids. The amount of carboxylic groups in the structure can be influenced by methylation, because of this fact; the interactions between humic acids and basic organic dye are limited in the case of modified (methylated) humic acids.

Diffusion coefficients, calculated from the linearly increasing concentration of Methylene Blue in the acceptor cell, are one of the most important parameter calculated from the dependences, which illustrate the interaction between MB and humic content in the studied hydrogels. Other important parameter providing useful information about the reactivity of humic acids is the lag

time (time needed by first molecule of Methylene Blue to penetrate through the hydrogel into the acceptor cell). From the Figure 2 (right), it is evident how the content of humic acids slows down the dye breaking through the hydrogel. In comparison with pure agarose hydrogel without addition of humic acids. In the case of addition of 0.010 wt. % of humic acids (without modification) to the same agarose hydrogel gives increase in penetration time of more than 20 hours and more than 12 hours for methylated humic acids.

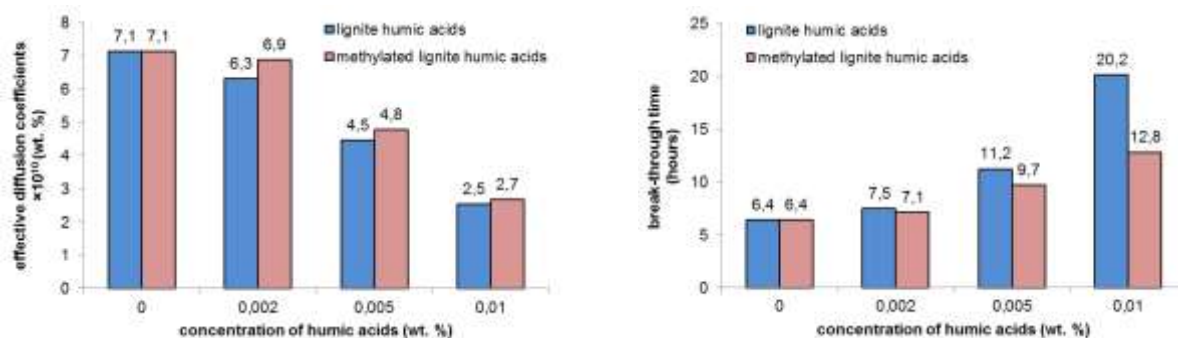


Figure 2: The effective diffusion coefficients (left) for 1 wt. % hydrogels with different concentration of humic acids (non-modified vs. methylated) and break-through time (lag time) for 1 wt. % hydrogels (right).

4. Conclusions

Unconventional diffusion techniques, presented in this paper represent a very interesting and useful tool for mapping of biopolymers reactivity. Innovative diffusion approaches seem to give much more information about the reactivity of HAs at their natural environment than classical sorption experiments, because the results obtained from sorption experiments are strongly dependent on the particle size of the HAs and level of homogeneity. These disadvantages are eliminated, when the experiments are realized in hydrogel media. Hydrogel contains a high percentage of water; it is able to simulate a real environment of HAs. From an experimental point of view, hydrogel is easy to prepare in the exact shape and thickness and acquaintance of these parameters is necessary for the description of diffusion processes from a mathematical point of view. These methods seem to be also suitable for experiments at different conditions (e.g. temperature dependence, influence of ionic strength, influence of pH, etc.) because these parameters are easily variable. Diffusion experiments based on presenting diffusion techniques should also become a universal method applicable for study on the reactivity of different compounds.

REFERENCES

1. Tipping E. (2002), Cation Binding by Humic Substances, Cambridge University Press, Cambridge.
2. Schnitzer M. and Khan S.U. (1972), Humic Substances in the Environment, Marcel Dekker, Inc., New York.
3. Kördel W., Dassenakis M., Lintemann J. and Padberg S. (1997), The importance of natural organic material for environmental processes in waters and soils (Technical Report), Pure. Appl. Chem., **69**, 1571-1600.
4. Ritchie J.D. and Perdue E.M. (2003), Proton-binding study of standard and reference fulvic acids, humic acids, and natural organic matter, Geochim. Cosmochim. Ac., **67**, 85-88.
5. Fukushima M., Nakayasu K., Tanaka S. and Nakamura H. (1995), Chromium(III) binding abilities of humic acids, Anal. Chim. Ac., **317**, 195-206.
6. De Paolis F. and Kukkonen J. (1997), Binding of organic pollutants to humic and fulvic acids: Influence of pH and the structure of humic material, Chemosphere., **34**, 1693-1704.
7. Ran Y., Sun K., Yang Y., Xing B. and Zeng E. (2007), Strong sorption of phenanthrene by condensed organic matter in soils and sediments. Environ. Sci. Technol. **41**, 3952-3958.
8. Stevenson F. (1994), humus chemistry: genesis, composition, reactions, John Wiley and Sons, New York.

9. Martyniuk H. and Wieckowska J. (2003), Adsorption of metal ions on humic acids extracted from brown coals, *Fuel. Proces. Technol.* **84**, 23-36.
10. Bradl H.B. and Acikel Y.S. (2004), Adsorption of heavy metal ions on soils and soils constituents, *J. Colloid. Interf. Sci.* **277**, 183-223.
11. Klucakova M. and Pekar M. (2006), New model for equilibrium sorption of metal ions on solid humic acids, *Colloid. Surface. A.* **286**, 126-133.
12. Klucakova M. and Pekar M. (2003), Study of structure and properties of humic and fulvic acids. IV. Study of interactions of Cu²⁺ ions with humic gels and final comparison. *J. Polym. Mater.* **20**, 155-162.
13. Klucakova M., Kalina M., Sedlacek P. and Grasset L. (2013), Reactivity and transport of Cu(II) ions in humic hydrogels. *J. Soils. Sediments.* **14**, 579-583.
14. Sedlacek P., Smilek J. and Klucakova M. (2014), How the interactions with humic acids affect the mobility of ionic dyes in hydrogels – 2. Non-stationary diffusion experiments. *React. Funct. Polym.* **75**, 41-50.
15. Sedlacek P., Smilek J. and Klucakova M. (2013), How the interactions with humic acids affect the mobility of ionic dyes in hydrogels – 1. Results from diffusion cells. *React. Funct. Polym.* **73**, 1500-1509.
16. Ghabbour E.A., Khairy A.H., Cheney D.P., Gross V., Davies G., Gilbert T.R., Zhang X.Y. (1994), Isolation of humic-acid from brown alga *pilayella-littoralis*. *J. Appl. Phycol.* **6**, 459-468.