



How the interactions with humic acids affect the mobility of ionic dyes in hydrogels – Results from diffusion cells



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ABSTRACT

The complexation of charged compounds by humic acids represents the process of exceptional environmental importance. Nevertheless, traditional methods utilized in the complexation studies do not address the way, how these interactions affect the transport of ions in humic-rich environments. To overcome this dilemma, the diffusion cells technique is proposed as an innovative reactivity mapping technique. Using this method, the diffusion of methylene blue was studied in aqueous solutions and in agarose gels with and without the addition of humic acids. Experimental results clearly illustrate the immobilizing effects of humic acids on the transport of methylene blue in gels. The partitioning of methylene blue at the solution-gel interface and the specific interactions between methylene blue and humic acids is discussed on the basis of experimental data. Effective structural parameters of hydrogels (effective porosity, tortuosity factor) were calculated, as well as some standard diffusion and interaction parameters (diffusion and partition coefficients and apparent equilibrium constants).

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1. Introduction

Humic acids (HA) represent the crucial component of many non-living parts of nature, such as soils, waters and sediments, where they – in diverse colloidal forms – play numerous irreplaceable environmental roles. In soils and sediments, precipitated humic acids impact the porosity and act as sorbents and reservoirs of water and different kinds of chemicals [1], while, in water aquifers, dissolved HA serve as important colloidal carriers of solutes [2,3]. HA also represent a promising raw material. Many potential applications of HA in agriculture, industry, environmental engineering and even in medicine are proposed [4–6]. Exact structure of humic acids is still unknown – controversy lasts on whether HA are of macromolecular or supramolecular (i.e. aggregate) nature [7] – anyway, high content of diverse functional groups (e.g. carboxyls, phenols, aromatic rings) gives to these compounds an outstanding ability to bind solutes of various chemical nature.

It is generally accepted, that the mobility of ionic compounds in soils and waters is affected by their interaction with negatively charged dissolved or precipitated humic acids (HA) [4,8,9]. Ion–HA interactions are thus essentially of an electrostatic origin, but due to diverse degree of structural complexity of HA, it is not possible to explain or predict the destiny of ions in humic matrices

universally. For the experimental study of ion–HA interaction, the inspiration can be drawn from the studies on ion binding by standard polyelectrolytes (e.g. charged biopolymers like chitosan, hyaluronan or others). Many works were published on theoretical modeling of interaction between low-molecular ions and such compounds on the molecular scale [10–12], nevertheless, to our best knowledge, there is no standard experimental methodology utilized routinely in the observation and quantification of ion–polyelectrolyte matrices and their influence on the rate of transport in these systems. The most widespread experimental approaches are still based on simple adsorption experiments [13–16], nevertheless, the batch sorption approach brings several serious drawbacks as far as humic substances are utilized. For example, the size of colloidal humic particles is of a great importance; the homogenous distribution of particle sizes in such colloidal forms as sols or suspensions is always questionable and the interactions/sorption in such systems can be limited just to the surface of the particle. The actual experimental conditions – e.g. the rate of agitation of the mixture – play a crucial role as well.

Simple experimental techniques for the study on solutediffusion in hydrogels prepared from humic acids put forward an interesting experimental alternative, as was discussed in details in our previous works [17–20]. Such diffusion processes are easily realizable; the mathematical apparatus for the data evaluation is well explained [21] and provides some reasonable parameters – e.g. apparent diffusion coefficients – the values of which involve the interactions in the system. A comprehensive handlist of several simple laboratory methods is presented in [22,23] for the

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Nomenclature

α	rock capacity factor (-)	K_{app}	apparent equilibrium constant (-)
β	cell constant (m^{-2})	L	sample thickness (m)
ε_{eff}	effective porosity (-)	L_e	actual distance traveled by diffusant (m)
Φ	partition coefficient (-)	n	total solute mass absorbed in gel (mol)
Φ_{app}	apparent partition coefficient (-)	r	Stokes–Einstein radius of solute (m)
η	dynamic viscosity (Pa s)	R	ideal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
A	pre-exponential factor for diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)	t	time (s) (for better comprehensibility, the time unit is changed from seconds (s) to hours (h) in the figures and tables)
c	molar concentration (subscript D refers to the donor solution, subscript A to the acceptor solution and subscript “gel” represents the concentration inside hydrogel) (mol m^{-3})	t_L	time lag (s) (for better comprehensibility, the time unit is changed from seconds (s) to hours (h) in the figures and tables)
D_0	free solution diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)	t	temperature ($^{\circ}\text{C}$)
D_e	effective diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)	T	absolute temperature (K)
D_a	apparent diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)	T_m	tortuosity factor (-)
E_A	activation energy of diffusion (J mol^{-1})	w	weight concentration (wt.%)
f	oscillation frequency (Hz)	x	direction of diffusion (m)
$ G^* $	complex modulus magnitude (Pa)		
J_d	steady-state diffusion flux ($\text{mol m}^{-2} \text{s}^{-1}$)		
k	Boltzmann constant (J K^{-1})		

experimental arrangement of the diffusion experiment. For the routine determination of diffusion coefficients in semi-solid samples (like hydrogels), the method of the diffusion cells (alternatively called the diaphragm, Stokes or Franz cells) represents the method of choice [24–27].

The main objective of this work was to test the applicability of the method of diffusion cells to study the interactions between humic acids (HA) and the model organic dye – methylene blue. In our previous works, several laboratory techniques were used in order to study the diffusion of ions in gel prepared from controlled coagulation of alkaline humic acids solutions simply by the decrease of their pH [17–20]. This humic gel reasonably modeled natural environments with homogeneously distributed, partially dissolved, partially highly swelled solid humic substances. On the other hand, this hydrogel form was not suitable for the in-depth studies on the interactions between the humic content of gel and a diffusing solute, because such elementary properties of gels as the inner pH or relative content of HA were difficult to control. The preparation of interpenetrating polymer network (IPN) gels [28] from humic acids in a supporting gel-forming polymer is proposed to overcome these difficulties. Agarose (linear polysaccharide of red algae, made up of the repeating monomeric unit of agarobiose) was used as a supporting polymer in the experiments presented in this paper. The network of agarose chains is interpenetrated by molecules of HA at higher temperatures where both compounds are dissolved ($>60^{\circ}\text{C}$) and the mixture is then easily gelled by cooling to normal temperature ($\sim 20^{\circ}\text{C}$). The mechanical and textural properties of agarose hydrogels as well as the gelation mechanism are well understood [29–31]. In the IPN hydrogels used in the presented paper, HA are immobilized and their reactive groups are homogeneously distributed in the supporting agarose matrix.

The diffusion in agarose gels has already been subjected to a vast concern. Golmohamadi et al. [32] studied the self- and mutual-diffusion of Cd^{2+} and organic cations in agarose hydrogel by means of fluorescence correlation spectroscopy and the diffusion cell method, respectively. The gel's Donnan potential was measured and used for the explanation of discrepancy between the results of the mutual and self-diffusion measurements and of the pronounced enhancement of cation concentrations in hydrogel. For agarose hydrogels, the diffusion cells were utilized in determining the diffusion coefficient of e.g. humic acids [33], proteins

[34] or ethanol [35]. Other authors subjected agarose gels to other techniques for determining the diffusion coefficients such as the refractive index measurement [36], electronic speckle pattern interferometry [37], fluorescence correlation spectroscopy [38] or fluorescence recovery after photobleaching [39].

Methylene blue (MB) is well-known cationic organic dye, commonly used for dyeing cotton, wood and silk. As can be generalized for all organic dyes, its transport in nature is the matter of concern from both toxicological and aesthetical point of view. Many works focused on the sorption of methylene blue and other cationic dyes on humics and humic-rich materials in last decades. Guy et al. in their study on organocation speciation in natural waters [40] determined the sorption isotherms for MB on humic acids at different solution pH values and KNO_3 concentrations. The variation of pH was not found to play an important role during the sorption process. In the desorption studies it was found, that more than 50 wt.% of MB remains bound to HA at pH = 1 on contrary to other sorbates (paraquat, Cu^{2+}). Sheng et al. introduced a new photometric method which evaluates the adsorption capability of humic acids for another cationic dye – toluidine blue – from the difference between visible spectra of dye and dye-HA complex [41]. Contrary to previous authors, they found the pH and ionic strength to strongly influence the dye sorption on humics. Zhou et al. [42] presented a considerable enhancement of both the adsorption rate and the capacity of Fe_3O_4 nanoparticles for the MB sorption by coating these particles with humic acids. Moreover, the MB desorption ability and the reused performance of $\text{Fe}_3\text{O}_4/\text{HA}$ nanoparticles were also excellent. Janoš [43] proposed iron humate as a cost-effective sorbent of basic dyes. Experimental data on sorption of several dyes including MB were evaluated by the multisite Langmuir isotherm model and gave the sorption capacities ranging from 0.01 to 0.09 mmol/g for individual dyes (0.03 mmol/g for MB). The leachability of dye from the loaded sorbent was found to be very low, especially in water. The sorption of methylene blue was only slightly affected by pH and the presence of inorganic salts, the presence of anionic surfactant (sodium dodecyl sulfate), however, dramatically enhanced the sorption of MB. In other works [44,45], the author studied the sorption of cationic and anionic dyes on oxihumolite – kind of oxidatively altered young brown coal that originated on the surface of lignite deposits by post-sedimentary oxidation. This material is composed of up to

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