Transport of Organic Dyes in Systems Containing Humic Acids

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http://doi.org/10.29227/IM-2019-01-30

Submission date: *11-07-2018* | Review date: *02-04-2019*

Abstract

This work is focused on transport organic dyes in systems containing humic acids as active reaction agent. Methylene blue was used as a model organic dye which can behave as pollutant and influence many processes in nature. Transport of pollutants in nature is strongly affected by interactions with humic acids or natural organic matter. Their influence is dependent on affinity of pollutant to content and strength of active binding sites. Two different humic samples are used in this study in order to compare their properties on transport of organic dye. Both humic acids are used in original extracted form as well as in the form of samples with selective blocked functional groups.

Keywords: humic substances, diffusion cells, methylene blue, ionic compound, diffusion

Introducion

Humic substances represent a wide range of organic compounds generated by gradual decomposition of plant residues and dead organisms in ecosystems. They are among the most widespread compounds in the world that contain a huge amount of carbon in its structure. Information and knowledge about them are still limited, thereby offering an opportunity for further research. Humic substances create an important part of soil organic matter, involved in soil self-cleaning, soil retention, buffer capacity soil and CO_2 binding in it. Industrial production, agriculture and other human activities bring a lot of pollution into nature. These pollutions are not only getting to the surface and ground water, but also to the soil and air. Therefore, it is important to understand the mechanisms of transport of pollutants, their interactions with soil organic matter and potential immobilization in nature.

Teams from all over the word deal with the binding of various pollutants to humic substances.

The interaction possibilities can be different: ion exchange, hydrogen bridge formation, coulombic interactions, hydrogen bridges, van der Waals interactions, hydrophobic interactions, etc. in Klučáková et al. (2014a) and Sedláček et al. (2013). These interactions and binding strength are strongly influenced by physical-chemical parameters such as pH, ionic strength, humectant concentration or temperature.

All these parameters can have important influence on the bioavailability of given pollutant and its further functioning in nature.

Main aim of this work is to study the transport of methylene blue through a membrane in a solution containing humic acids and their interactions. In order to investigate the interactions in detail, humic acids with selective blocked functional groups were used for the comparison. Due to methylation of carboxyl groups, which are mainly responsible for coulombic interactions between negatively charged carboxyl and cationic charged organic pollutant, was observed way of binding.

The methylene blue was chosen as a model organic dye due to its similar to many herbicides and pesticides commonly used in agriculture.

Material and Methods

Two different humic acids were used in this study. The first one, (HA1) was Leonardite standard of humic acids (1S104H) purchased from International Humic Substances Society (for its characterization see http://humic-substances.org). Other sample, (HA2) was extracted from lignite mined in the Czech Republic and characterized previously e.g. in Klučáková et al. (2014b) and Klučáková et al. (2016).

Sample HA1 was methylated with trimethylsilyldiazomethane by means of method described in Klučáková et al. (2014a, 2016). It was designated as mHA1. Methylated humic acids as well as original samples were characterized by means of FT-IR spectrometry (Nicolet iS50) and elemental analysis (EURO EA Elemental Analyzer).

Two different concentrations of humic acids (50 and 100 mg/L) and one concentration of methylene blue were used and all solutions were prepared in phosphate buffer (pH = 7).

The PrermeGear diffusion cells were used for the experiment. A dialysis membrane Spectra/Por® (Spectrum laboratories, Inc. MWCO: 3,500 kDa) was placed between diffusion cells to separate the solution of humic sample from the solution of methylene blue. A small magnetic stirrer was placed into the small space at the bottom of each dialysis cell the need to place in a small space at the bottom of the cells. Cell connection was secured by side clamps to ensure that cells are perfectly fixed. The absorbance at 665 nm (Hitachi U-3900H) was monitored during the experiment and concentration of methylene blue was calculated using calibration curve.

Results and Discussion

The basic characteristics of used humic samples are shown in Figure 1 and Table 1. It can be seen, the methyla-

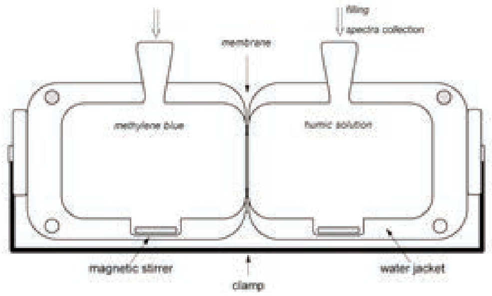

Fig. 1. Scheme of diffusion cells
Rys. 1. Schemat komórek dyfuzyjnych

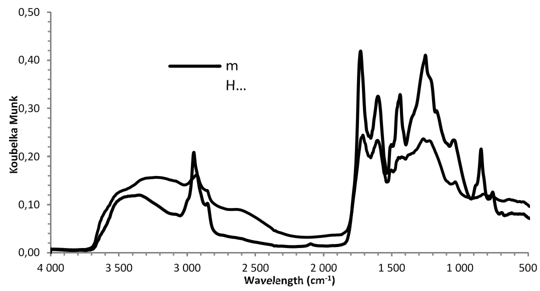

Fig. 2. FT-IR spectra of HA1 (full line) and mHA1 (dashed line) measured using DRIFT method
Rys. 2. Widma FT-IR HA1 (pełna linia) i mHA1 (linia przerywana) mierzone metodą DRIFT

tion of functional groups resulted in changes of FT-IR spectra characteristic for esters. The intensity of the broad peak at around 3500 cm^{-1} was decreased by methylation and the shallow band at 2580 cm^{-1} was completely absent. The absorption band corresponding to C=O stretching was shifted to higher wavenumbers after methylation (from ~1720 cm^{-1} to ~1735 cm^{-1}) and its intensity was increased. The observed changes in spectra caused by methylation corresponded with our results published previously Klučáková et al. (2014a, 2015).

The replacement of H+ ion by $–CH_3$ group in carboxylic functional groups was expressed in changes in the humic elemental composition. The ratio between carbon and hydrogen decreased and the ratio between carbon and oxygen increased as a consequence of the methylation. The contents of sulfur and nitrogen was very low, therefore their role in humic interactions can be neglected in this case.

In Figure 3, the example of experimental data is shown. The dye concentration decreased gradually in the donor cell as a result of its transport through membrane into the acceptor cell. Assuming that whole amount of dye transported through membrane interacts with humic acids, the decrease of its concentration should be equal to the amount of methylene blue bound to humic acids. The obtained decreases for all used humic samples are in the Table 2. The amount of methylene blue transported through membrane decreases with increasing initial concentration of humic acids in the acceptor cell. Simultaneously, this amount is lower in the case of humic acids with methylated carboxyl groups.

It can be seen can be seen, the concentration of methylene blue in the acceptor cell gradually increases (Figure 3). It means that some dye in the acceptor cell is unbound and mobile. As it was shown in our recent works Sedláček et al. (2013), Klučáková et al. (2014a,2015), the equilibrium between humic acids and reactant can establish and ions are bound in humic structure with different strength. Our experimental arrangement involves two equilibriums. At first, it is the equilibrium between donor and acceptor cells.

If we assuming that big humic molecules cannot be transported through membrane, so called Donnan equilibrium is established. Another equilibrium is established between free mobile and bound methylene blue. A general description or mathematical solution of our experiment is not easy. In addition, the situation can be more complex, e.g. equilibriums between dye particles bound to humic acids with different strengths can exist or some fractions of humic acids are able to move through the membrane. Many simplifying assumptions have to be accepted in order to make a mathematical model of the situation in our experimental arrangement.

On the other hand, our experiments can simulate some processes occuring in nature and our data from this experiment can improve our knowledge of interactions between natural organic matter and organic dyes. It was confirmed that the transport of pollutants in nature is strongly affected by the reactivity of humic substances. In general, leonardite humic standard contains much more carboxylic functional groups in comparison with the humic acids extracted from lignite (Klučáková et al., 2015). It caused positive influence on the concentration decrease of dye in the donor cell. The blocking of these binding sites caused a decrease of driving force of the dye transport through membrane as a result of the changes in experiment conditions (Figure 4). The blocked carboxylic groups cannot dissociate and bind dye ions but the interactions between hydrophobic humic structures and aromatic methylene blue can be more applied.

Tab. 1. Elemental composition of used humic samples (normalized on dry ash free mass)

Tab. 1. Skład pierwiastkowy badanych próbek humusowych (znormalizowany do suchej masy wolnej od popiołu)

sample	C (% at.)	H (% at.)	O (% at.)	N (% at.)	S (% at.)	C/H	C/O
HA1	48.1	33.2	17.7	0.8	0.2	1.45	2.72
mHA1	45.5	37.9	15.9	0.6	0.1	1.20	2.86
HA2	38.6	38.5	22	0.8	0.1	1.00	1.75

Tab. 2. Decrease of dye content in donor cell normalized on humic mass (number 1 means initial humic concentration 50 mg/L, number 2 100 mg/L)

Tab. 2. Zmniejszenie zawartości barwnika w komórce donora znormalizowanej (liczba 1 oznacza początkowe stężenie humusowe 50 mg/l, liczba 2 100 mg/l)

sample	decrease (g/g)	
	1	2
HA1	1.92 ± 0.01	0.99 ± 0.01
mHA1	1.63 ± 0.01	0.90 ± 0.01
HA2	1.60 ± 0.03	0.96 ± 0.02

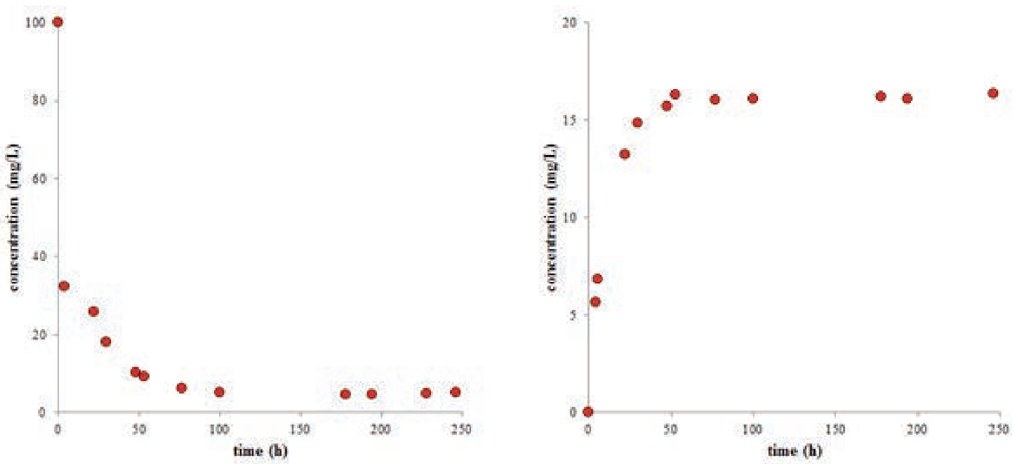

Fig. 3. Time development of concentration of methylene blue in donor (left) and acceptor (right) cell (HA2 with initial concentration 100 mg/L)

Ryc. 3. Zmiana w czasie stężenia błękitu metylenowego w komórce donora (po lewej) i akceptorze (po prawej) (HA2 o początkowym stężeniu 100 mg/l)

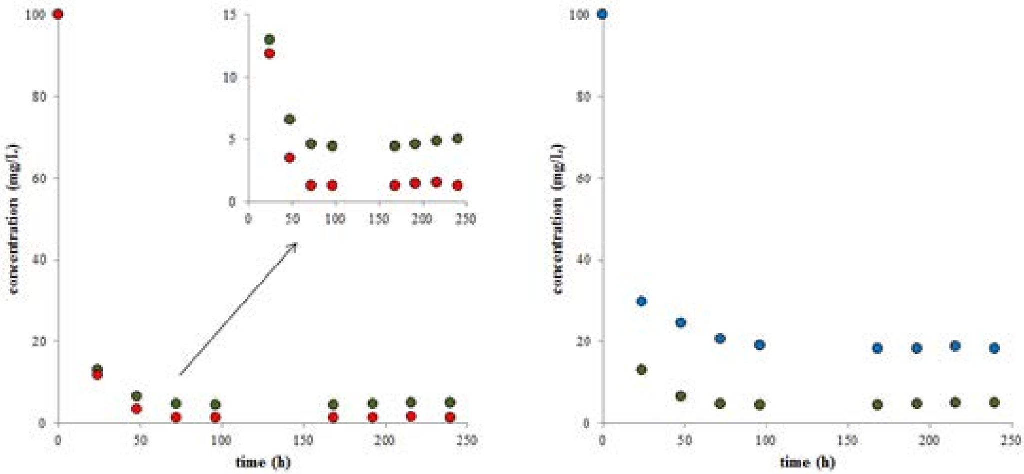

Fig. 4. Time development of concentration of methylene blue in donor cell: HA1 with initial concentration 50 mg/L (green), HA1 with initial concentration 100 mg/L (red), mHA1 with initial concentration 50 mg/L (blue)

Ryc. 4. Zmiana w czasie stężenia błękitu metylenowego w donorze: HA1 o początkowym stężeniu 50 mg/l (zielony), HA1 o początkowym stężeniu 100 mg/l (czerwony), mHA1 o początkowym stężeniu 50 mg/l (niebieski)

Conclusion

Main aim of this work was to study the transport of methylene blue through a membrane in a solution containing humic acids. Two different humic acids were used in this study. The first one, (HA1) was Leonardite standard of humic from International Humic Substances and sample (HA2) was extracted from lignite mined in the Czech Republic. Carboxyl groups are mainly responsible for coulombic interactions between negatively charged carboxyl and cationic charged organic dye (methylene blue). Due to methylation of carboxyl groups of humic acids were selectively blocked functional groups (mHA1).

The replacement of H+ ion by –CH3 group in carboxylic functional groups was expressed in changes in the humic elemental composition and the methylation of functional groups resulted in changes of FT-IR spectra characteristic for esters.

During experiments the concentration of methylene blue in the acceptor cell gradually increases and decrease of dye content in donor cell was measured. It means that some dye in the acceptor cell was unbound and mobile. There was the equilibrium between donor and acceptor cell if big humic molecules cannot be transported through membrane, so called Donnan equilibrium was established. There was equilibrium established between free mobile and bound methylene blue as well.

Leonardite humic standard (HA1) contains much more carboxylic functional groups in comparison with the humic acids extracted from lignite (HA2). It caused positive influence on the concentration decrease of dye in the donor cell. The blocked carboxylic groups (mHA1) cannot dissociate and bind dye ions but the interactions between hydrophobic humic structures and aromatic methylene blue can be more applied.

Acknowledgments

The Materials Research Centre at the Faculty of Chemistry, Brno University of Technology is supported by Project No. LO1211 from the Czech Ministry of Education, National Sustainability Program I.

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Transport barwników organicznych w układach zawierających kwasy huminowe

Niniejsza praca koncentruje się na transporcie barwników organicznych w systemach zawierających kwasy huminowe jako środek aktywny. Błękit metylenowy wykorzystano jako modelowy barwnik organiczny, który może zachowywać się jak substancja zanieczyszczająca i wpływać na wiele procesów w przyrodzie. Na transport zanieczyszczeń w przyrodzie silnie wpływają interakcje z kwasami huminowymi lub naturalną materią organiczną. Ich wpływ zależy od powinowactwa substancji zanieczyszczającej do zawartości i siły aktywnych miejsc wiązania. W badaniu tym zastosowano dwie różne próbki humusowe w celu porównania ich właściwości w transporcie barwnika organicznego. Oba kwasy humusowe stosuje się w oryginalnej postaci ekstrahowanej, jak również w postaci próbek z selektywnie zablokowanymi grupami funkcyjnymi.

Słowa kluczowe: substancje humusowe, komórki dyfuzyjne, błękit metylenowy, związek jonowy, dyfuzja