SORPTION OF SYNTHETIC DYES ONTO RIVER SEDIMENTS: A LABORATORY STUDY

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Abstract: This work deals with sorption of cationic synthetic dye thioflavine T (ThT) onto the river sediment obtained from the Váh River under conditions of batch and column system using spectrophotometric methods. We found that sorption of ThT onto river sediment was a rapid process with reaching of concentration equilibrium within 2 h of interaction. The values of distribution coefficient (*DC*) defined as concentration ratio $[\mathrm{ThT}]_{\mathrm{sediment}}$: $[\mathrm{ThT}]_{\mathrm{solution}}$ were linearly increased with increasing concentration of river sediment in solution within the range $C_{sediment}$ 1.25 – 10.0 g/dm^3 and minimally changed in the range of initial pH values 2 – 6. The increasing concentration of ThT in model solution caused exponentially decrease in the value of *DC*. The sorption processes characterized by dependence between equilibrium specific sorption Q_{eq} and ThT concentration C_{eq} in solution were better described by adsorption isotherm according to Freundlich (R^2 = 0.979) than according to Langmuir adsorption isotherm (R^2 = 0.914). From evaluation of ThT sorption onto river sediment in column system containing of 5 cm sediment layer with 30 cm of water column on the basis of ThT concentration changes in infiltrated water we found that these processes were significantly dependent on the rate of infiltrated water flow through the sediment layer R_{iw} as well as on qualitative and quantitative composition of water. The highest ThT desorption from the sediment layer was found in seepage of 50 % (v/v) ethanol (EtOH) solution through the sediment and efficiency of ThT desorption decreased in the order: 50 % (v/v) EtOH > 0.1 mol/dm^3 HCl > deionized water. Obtained data from the point of view of physico-chemical characteristics of the river sediment, such as pH, $\mathrm{pH}_{\mathrm{zpc}}$ (potentiometric titration), cation-exchange capacity (*CEC*) and elemental composition (X-ray fluorescence spectrometry), was also discussed.

Key words: thioflavine T, synthetic dyes, river sediments, sorption, desorption, column system

1. Introduction

Water pollution by organic or inorganic contaminants is one of the most common problems and has been of worldwide concern for many years. Besides organic compounds such as polychlorinated biphenyls, pesticides, polycyclic aromatic hydrocarbons, and halogenated aliphatic hydrocarbons in terms of environmental protection and remediation of contaminated localities the attention also focuses on synthetic dyes.

Synthetic dyes are widely used in various types of industry such as the textile, rubber, paper, plastic, leather, cosmetic, pharmaceuticals and food productions. Having a complex molecular structure and synthetic origin, making them biologically not degradable and resistant to environmental conditions, dyes are stable and difficult to treat (FORGACS *et al.*, 2004; RAI *et al.*, 2005). The use of dyes in expanding industries is accompanied by increasing volume of dyeing effluents. According to

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incomplete statistics, there are more than 10 000 types of dyes in commercial circulation (ALTINIŞIK *et al.*, 2010; SENTURK *et al.*, 2010). About 7.10^5 tons of dyes are manufactured worldwide each year, and 10 – 15 % is discharged into water bodies as effluents that seriously pollute the environment (TÜRGAY *et al.*, 2011; MOUSSAVI and KHOSRAVI, 2011). They significantly affect equally the human health and the aquatic ecosystem. Even in very small quantities dyes lead to changes in salinity and visible coloration of the water, reducing sunlight penetration and thus hinder photosynthetic activity of aquatic organisms, while some of them are moreover toxic and carcinogenic (ASGHER and BHATTI, 2012; FAN *et al.*, 2012; MAHMOUD *et al.*, 2012).

Synthetic dyes are classified according to their physico-chemical characteristics and their behaviour in solutions as follows: anionic – direct, acid and reactive dyes; cationic – basic dyes; non-ionic – disperse dyes (FU and VIRARAGHAVAN, 2001). According to EPA and OECD, basic dyes are considered one of the most toxic substances and the amounts of non-fixed basic dyes that may be discharged into the effluents were 1 % and 2 – 3 %, respectively (HESSEL *et al.*, 2007; WAWRZKIEWICZ, 2013). Basic (cationic) dyes are quaternary salts whose cations have the positive charge most often on the atom N (ammonium salts), rarely on C (carbonium), O (oxonium) and S (sulfone).

In the fate of organic pollutants in all compartments of the environment sorption processes play a decisive role. There are two main factors controlling sorption of organic pollutants: the content and the chemical structure of the soil or sedimentary organic mater (CHEFETZ *et al.*, 2004). However, sorption processes consist of at least two steps: forward (sorption) and reverse (desorption) processes. Thus, desorption processes have also significant environmental effects during the remediation of contaminated rivers, where the rate and level of sorbed pollutants which can be released into the water phase are determined mainly by these processes. Therefore, understanding the mechanisms that cause sorption-irreversibility is of interest from both a scientific and technological view-point (OREN and CHEFETZ, 2005).

Numerous papers have investigated dye sorption (affinity) to textiles and fibers (e.g. SALEEM *et al.*, 2005; SALEEM *et al.*, 2007) as well as attended to finding or evaluating new, inexpensive sorbents derived mainly from the waste biomass (e.g. ASGHER and BHATTI, 2012; PICCIN *et al.*, 2012), but few examined the affinity of dyes for natural components that are likely to impact the fate of dyes in the environment.

Our previous papers deal with sorption of radionuclides ^{137}Cs and ^{60}Co in components of freshwater system (HORNÍK *et al.*, 2007a) and bioaccumulation of mentioned radionuclides in freshwater plants (HORNÍK *et al.*, 2007b; HORNÍK *et al.*, 2008).

In this paper we characterize sorption and desorption processes of thioflavine T (ThT) binding, as model of benzothiazole cationic dye, onto river sediment obtained from the Váh River under batch conditions as well as conditions of laboratory column system in short-time experiments by using spectrophotometry. Also, in this work physico-chemical characterization of obtained river sediment as well as the study of environmental conditions effect on sorption processes were realized.

2. Materials and methods

2.1 River sediment

Samples of river bank sediment were taken from the Váh River − water reservoir Kráľová near the city of Šaľa (Slovak republic; N 48°12'35"; E 17°48'02") in spring period. The sampling depth was 0 – 10 cm from the surface of the sediment at least 1 m away from the riverbank. Subsequently, the river sediment was dried at laboratory temperature (23±2 °C), mixed thoroughly and homogenized by sieved through a 0.31 mm mesh. For the comparison treated river sediments by 3-times washing in deionized water or 0.1 mol/dm^3 HCl solution and laboratory chemically treated sea sand (fraction < 0.31 mm) as a model material were also used. The process of the sediment washing was carried out on rotary incubator shaker (250 min^{-1}) with concentration of the sediment 200 g/dm^3 within 2 h and at 25 ºC.

2.2 Physico-chemical characterization of river sediment

Potentiometric titration

To characterize the potential functional groups involved in the cationic dyes binding onto the surface of river sediment the potentiometric titration as described by the authors ZHANG *et al.* (2010) was used. The sediment (0.30 g) was transferred into Erlenmeyer flask containing a mixture of 100 cm^3 of 0.1 mol/dm^3 HCl and 0.1 mol/dm^3 NaCl, stirred on orbital incubator shaker (250 min^{-1}, 25 ºC) and after 2 h the sediment was centrifugated (3 500 rpm for 5 min). Subsequently, the sediment was transferred into 100 cm^3 of 0.1 mol/dm^3 NaCl solution and left to stir under identical conditions during 2 h. Potentiometric titration was carried out in Erlenmeyer flask by the successive addition of mixture 0.1 mol/dm^3 NaOH and 0.1 mol/dm^3 NaCl. After each addition of mentioned mixture and stabilization of the system the pH was measured using a glass electrode (three-point calibration with solution – pH 4.0; 7.0 and 10.0) in the range of pH values from 2.0 to 11.0 at 25 ºC. The relationship between the volume of added titrant 0.1 M NaOH (cm^3) and the measured pH values was analyzed by modelling program ProtoFit ver. 2.1 (TURNER and FEIN, 2006) with the aim to determine pKa values for individual functional groups and binding sites concentration C_{An}.

Cation-exchange capacity (CEC)

The determination of cation-exchange capacity (*CEC*) for studied river and treated sediment was carried out according to ISO standard method No. 11260. The sediment (0.25 g) was transferred into 3 cm^3 of 0.1 mol/dm^3 $BaCl_2$ solution and the suspension was allowed to shake on orbital incubator shaker (150 min^{-1}) for 1 h at 25 ºC. Subsequently, the sediment was centrifugated (3 500 rpm for 5 min) and the supernatant was decanted. The procedure of $BaCl_2$ solution addition, shaking, sediment centrifugation and decanting of supernatant was repeated two more times.

The solid sediment phase was then saturated by addition of 3 cm^3 0.025 mol/dm^3 $BaCl_2$ solution and the suspension was allowed to shake (150 min^{-1}) during 19 hours at 25 ºC. After this time, the sediment was centrifugated (3 500 rpm for 5 min) and the supernatant was decanted. Subsequently, 3 cm^3 of 0.02 mol/dm^3 $MgSO_4$ solution was added into the centrifugated sediment and the suspension was allowed to shake (150 min^{-1}) for the next 19 hours at 25 ºC. After the centrifugation, the concentration of Mg was determined in the decanted supernatant by chelatometric titration using 0.02 mol/dm^3 EDTA-Na_2 (standardization with $CaCO_3$ solution), Eriochrome black T indicator and ammonia buffer.

pH

The determination of the river and treated sediment pH value was carried out according to ISO standard method No. 10390 for the routine determination of pH using glass electrode in the soil suspension. The pH was measured in sediment suspension with distilled water, 1 mol/dm^3 KCl or 0.01 mol/dm^3 $CaCl_2$ at volume ratio V(sediment) : V(solution) = 1 : 5. Prepared suspension was stirred on orbital incubator shaker (150 min^{-1}) for 1 h at 25 ºC. Subsequently, the suspension was allowed to settle for at least 1 h and the pH was measured directly in the suspension at 25 º C.

X-ray fluorescence spectrometry

The elemental analysis of river and treated sediment was performed by X-ray fluorescence spectrometry using the high performance X-ray fluorescence spectrometer X-LAB 2000, SPECTRO (Germany). The content of As, Ba, Bi, Br, Ca, Cd, Ce, Cr, Cs, Cu, Fe, Ga, Ge, La, Mg, Mn, Mo, Nb, Ni, Pb, Rb, Sb, Se, Sn, Sr, Th, U, V, W, Y, Zn and Zr was analyzed in sediment samples treated to granularity < 0.063 mm.

2.3 Model of synthetic dye and synthetic freshwater

Stock solution of benzothiazole cationic dye thioflavine T (ThT; purity 75 %, CAS 2390-54-7; C.I. 49 005; Mr = 318.86; Fluka, USA) with the final concentration 200 mg/dm^3 was prepared in deionized water or synthetic freshwater. For experimental purposes, the stock solution was diluted with given type of solution for obtaining the desired concentrations. Chemical structure of ThT is shown in Fig. 1.

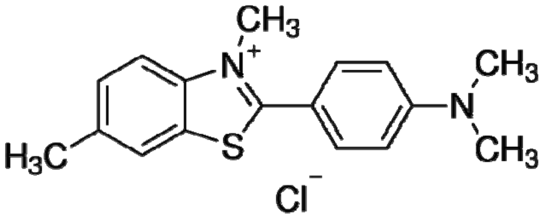

Fig. 1. Chemical structure of thioflavine T dye.

The preparation of synthetic freshwater was carried out according to work SMITH *et al.* (2002). Table 1 shows the composition of stock solutions for the preparation of synthetic model freshwater imitating the composition of water in lake Rostherne Mere (Lancashire) in the UK.

Table 1. Composition of stock solutions for preparation of synthetic freshwater imitating the water of lake Rostherne Mere (Lancashire) in the UK according to work SMITH *et al.* (2002).

Model of freshwater	Solution	Composition	Concentration [mg/dm^3]	Required volume*
Rostherne Mere (pH = 7.0; χ = 111 μS/cm)	**H1**	$CaCl_2$ $Ca(NO_3)_2.4H_2O$	7.49 1.18	10 cm^3
	H2	$CaCO_3$	0.092	910 cm^3
	H3	$KHCO_3$ KH_2PO_4	0.751 0.408	10 cm^3
	H4	$NaHCO_3$ Na_2SO_4	2.27 2.81	10 cm^3
	H5	$MgSO_4.7H_2O$	10.0	10 cm^3

* Required volume of individual stock solutions for the preparation of 1 dm^{3}of synthetic freshwater.

2.4 Spectrophotometric analysis

For the determination of the thioflavine T (ThT) amount in the analyzed samples of solution the UV-VIS spectrophotometer Varian, Cary 50 (AUS) was used. Calibration curve for determination of ThT was obtained by measuring the absorbance of standard ThT solutions at a wavelength λ_{max} = 412 nm.

2.5 Sorption of dye in batch system

Into a series of 100 cm^3 Erlenmeyer flasks containing 20 cm^3 of solution with known concentration of thioflavine T (ThT) and pH the defined amount of river sediment was added. Exposition was carried out on rotary incubator shaker (250 min^{-1}) at 25 ºC. The changes in concentration of ThT caused by evaporating of water were avoided by covering of flasks with parafilm. In time periods (10; 20; 40; 60; 120; 240; 360 and 1 440 minute) or in the end of experiments aliquot samples of solution were taken from flasks for spectrophotometric analysis at a wavelength λ_{max} = 412 nm and calculation of ThT dye concentration. The amount of ThT sorbed onto river sediment was calculated by the following equation (1):

$$Q = (C_0 - C_t)\frac{V}{S} \tag{1}$$

where:

Q – the amount of dye sorbed onto river sediment (mg/g; dry weight);

C_0 and C_t – the initial concentration of dye in solution at the time $t = 0$ min and at the time of solution sampling (mg/dm^3);
V and S – the volume of dye solution (dm^3) and the amount of river sediment in the experiment (g).

For characterization of environment effect on sorption processes at reaching of concentration equilibrium $[\mathrm{ThT}]_{\mathrm{solution}} : [\mathrm{ThT}]_{\mathrm{sediment}}$ distribution coefficient (DC) was calculated according to the following equation (2):

$$DC = \frac{Q}{C_{eq}} \tag{2}$$

where:
DC – the distribution coefficient (cm^3/g);
C_{eq} – the concentration of dye in solution at equilibrium reaching (mg/dm^3).

2.6 Sorption and desorption of dye in column system

Sorption of thioflavine T (ThT) onto river sediments was also realized in column system imitating conditions nearby shallow river bank using a glass chromatography column with inside diameter 0.8 cm and height 40 cm. In the bottom of the column the river sediment bed was arranged to height 5 cm (5.0±0.1 g; dry weight) and over sediment the model solution containing ThT was maintained with height 30 cm by periodic addition of fresh solution and infiltrated water samples taking. The changes in height of model solution column represented ± 5 % (± 1.5 cm). Samples of infiltrated water from the bottom of the column system were obtained in aliquot volumes (2 cm^3) and were analyzed in the term of ThT concentration in solution or pH values.

Desorption of ThT from river sediment was carried out by replacing of model solution containing ThT with deionized water, 0.1 mol/dm^3 HCl or 50 % (v/v) ethanol solutions. Sampling of infiltrated solution and determination of ThT concentration were realized identically as in the case of sorption experiments, except of the case of ThT determination in 0.1 mol/dm^3 HCl or 50 % (v/v) ethanol solutions, when changes in value of molar extinction coefficient ε were taken into account.

3. Results and discussion

3.1 Characterization of river sediment

It is generally known that xenobiotic binding into abiotic and biotic components of water bodies or water systems is affected by several primary factors mainly defined by physico-chemical characteristics of components themselves, xenobiotics and waters. This work is focused on characterization of cationic synthetic dye thioflavine T (ThT) sorption onto the river bank sediment obtained from the Váh River under laboratory conditions. Therefore in first step we carried out physico-chemical characterization of studied river sediment. In these analyses treated river sediments by washing in deionized water or in 0.1 mol/dm^3 HCl solution as well as laboratory chemically treated sea sand were included.

From the view of cationic dyes sorption, as well as xenobiotics molecules show cationic charge in solutions, the qualitative and quantitative occurrence of negatively charged functional groups on sorbent play an important role. For qualitative analysis of functional groups on different sorts of sorbents is wide and commonly used FT – IR analysis. However, in this work for qualitative characterization of functional groups as well as quantitative determination of binding sites concentration C_{An} for each predicted functional group the potentiometric titration with application of modelling program ProtoFit ver. 2.1 was used.

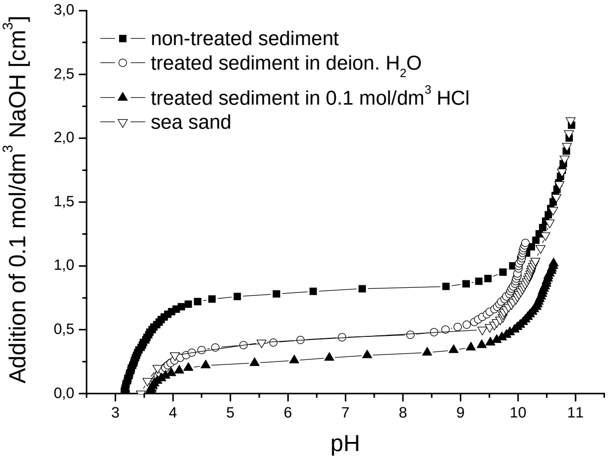

Fig. 2. Potentiometric titration curves for non-treated river sediment obtained from the Váh River, treated river sediment in deionized water or 0.1 mol/dm^3 HCl solution and chemically treated sea sand (3.0 g/dm^3). The titration was carried out with addition of 0.1 mol/dm^3 NaOH in the presence of background electrolyte 0.1 mol/dm^3 NaCl and at 25 °C.

The Fig. 2 shows potentiometric titration curves describing the dependence between added volume of 0.1 mol/dm^3 NaOH solution and measured value of pH in solution containing protonated non-treated or treated river sediment in HCl solution or deionized water as well as laboratory chemically treated sea sand. In generally, it can be expected that in sorption of cationic xenobiotics mainly negatively charged functional groups such as carboxyl (–COOH), hydroxyl (–OH), phosphate ($–PO_3H_2$) or amino ($–NH_2$) groups play an important role. In the case of river sediments content of organic matrix bond or involved on the surface of inorganic particles of sediments (mainly silica sands) can play a decisive role in this term.

We found that obtained data showed best-fit to the non-electrostatic model characterizing four binding sites. In the case of river sediment the qualitative analysis confirmed the presence of carboxyl (–COOH), hydroxyl (–OH), phosphate ($–PO_3H_2$) as well as amino ($–NH_2$) group, whereby hydroxyl and amino groups were presented in higher concentration C_{An}. In comparison, the laboratory sea sand did not showed the presence of carboxyl group (data not shown).

The abovementioned modelling program also allowed to determine the pH_{zpc} value (pH value of zero point of charge), which represents the pH value of environment when matrix shows zero surface charge. In the case, if $pH < pH_{zpc}$ then matrix has positively charged surface and if $pH > pH_{zpc}$ matrix shows negatively charged surface.

Among other important parameters, which characterize the ability of matrix to bind negatively charged organic compounds belong the pH value and cation-exchange capacity (*CEC*). Table 2 presents obtained values of *CEC*, pH_{zpc} as well as pH of studied river sediments and laboratory sea sand.

Table 2. Comparison of obtained values of pH (analyzed in distilled water − pH_{H2O}, 0.01 mol/dm^3 $CaCl_2$ − pH_{CaCl2}, 1 mol/dm^3 KCl − pH_{KCl}) determined according to ISO standard method No. 10390, cation-exchange capacity (*CEC*) determined according to ISO standard method No. 112 60 and pH_{zpc} predicted by the modelling program ProtoFit ver. 2.1 from potentiometric titration data according to authors ZHANG *et al.* (2010). Data characterize non-treated or treated river sediment obtained from the Váh River and chemically treated sea sand.

Sediment treatment	**pH_{H2O}**	**pH_{CaCl2}**	**pH_{KCl}**	***CEC* [meq/100g]**	**pH_{zpc}**
non-treated	7.91	7.55	8.56	12.6	9.78
deionized H_2O	8.06	7.38	8.44	7.60	10.2
0.1 mol/dm^3 HCl	7.24	7.10	7.37	4.00	10.8
sea sand	7.33	7.39	8.60	2.60	10.8

These values are routinely determined in the case of soil samples in terms of evaluation of bond and mobility of metal ions. In general, pH value suggests which type of substances or ions will significantly bind on analyzed matrix, respectively. From this it can be expected that if value of $pH << 7$ then bond of negatively charge ions will be dominant and if $pH >> 7$ then bond of positively charged ions will be dominant. *CEC* quantitatively indicates the ability of matrix to bind cations. In the case of clay or organic soils the *CEC* assumes values up to 20 meq/100 g. On the other hand, sandy soils with low ability to bind ions show values only 2 − 3 meq/100 g (PANSU and GAUTHEYROU, 2003).

As additional analysis, the determination of selected element content in studied river sediments by X-ray fluorescence spectrometry was realized (Table 3). United States Environmental Pollution Agency (US EPA) developed parameters the effects range low (ERL) and effects range median (ERM) as predictive tools for characterizing contamination in sediments. Both parameters have been widely applied and found to be effective predictive tools (ZAHARESCU *et al.,* 2009; YIN *et al.*, 2011). The ERL represents the tenth percentile of the effects database, below which harmful effects on aquatic biota are rarely observed. The ERM represents the fiftieth percentile of the effects data and is indicative of concentrations above which harmful effects are often observed (US EPA, 2002).

Table 3. The presence of selected elements in river sediments obtained from the Váh River determined by X-ray fluorescence spectrometry. A. – non-treated sediment; B. – sediment treated in deionized water; C. – sediment treated in 0.1 mol/dm^3 HCl.

Sample	Element															
	As	Ba	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Rb	Sr	V	Zn	Zr
A	–*	305 ppm	6.0 %	–*	37 ppm	9 ppm	0.9 %	1.6 %	0.03 %	14 ppm	13 ppm	41 ppm	200 ppm	31 ppm	29 ppm	134 ppm
B	–*	283 ppm	6.3 %	–*	38 ppm	7 ppm	0.9 %	1.6 %	0.03 %	14 ppm	16 ppm	39 ppm	198 ppm	27 ppm	49 ppm	132 ppm
C	–*	301 ppm	4.1 %	–*	36 ppm	9 ppm	0.9 %	1.4 %	0.02 %	15 ppm	13 ppm	43 ppm	165 ppm	26 ppm	29 ppm	151 ppm

* value below detection limits of X-ray fluorescence spectrometry (for As and Cd < 2 ppm).

We found that in obtained river sediment from the Váh River abovementioned limits were not exceed and determined values of metal content were minimally 2-times lower than ERL values. The influence of river sediment treatment by washing with deionized water or 0.1 mol/dm^3 HCl on metals presence in matrix was significantly observed only in the case of diluted solution of HCl and metals of alkaline earths (Mg, Ca and Sr). This fact indicates that metals weakly bound into sediment can be released at slightly acidic conditions. In the case of cationic synthetic dyes, it can be expected a similar effect, however more remarkable in the case of less polar solutions conditions (e.g. diluted solutions of alcohols or organic solvents).

3.2 Sorption of dye in batch system

In this part of the work we quantitatively characterize sorption of thioflavine T (ThT) onto river sediment obtained from the Váh River under batch non-equilibrium and equilibrium conditions. Experiments were realized in deionized water without addition of macro- and microelements or source of carbon, which could support the growth of microorganisms presented in sediments. To some extent batch experiments imitated a possible processes occurring during the movement of particles from upper layers of sediment caused by benthic organisms activity and bioturbation in rivers or lakes. It is generally known that these processes represent dominant mechanisms of sediment particles movement (see e.g. BENTLEY *et al.*, 2006).

On Fig. 3A is depict the kinetic of ThT binding onto river sediment at initial concentration of ThT C_0 = 40 mg/dm^3 and pH 7.0. We found that in ThT binding a rapid sorption processes play a decisive role when in exposition time 10 min nearly 40 % of ThT was bound onto sediment. After 2 h of interaction the concentration equilibrium $[\mathrm{ThT}]_{\mathrm{solution}}$: $[\mathrm{ThT}]_{\mathrm{sediment}}$ with maximal specific sorption Q = 4.5 mg/g was observed. Also, we found that kinetic of this process is characterized by two phases: first, rapid phase of dye molecules sorption from solution onto surface of sediment particles, and second, slow phase with concentration equilibrium reaching. BAUGHMAN (1995) in the work focused on adsorption of 9 acid and 5 direct dyes in sediments obtained from Oconee river (Greece) found that initial rapid dye removing from solution was followed by slow dye removing. From this result, he concluded that rapid sorption process was followed by intraparticle diffusion processes.

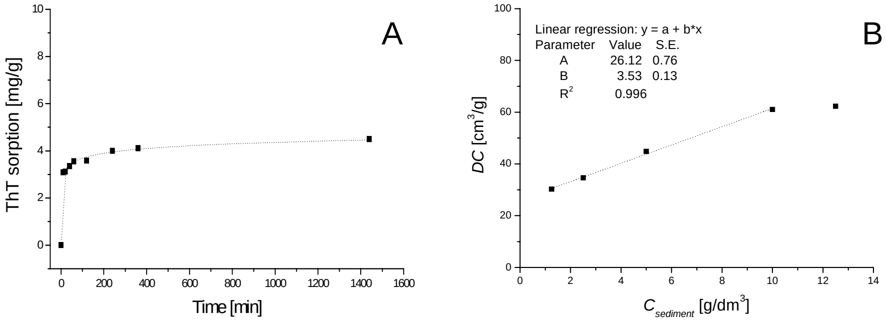

Fig. 3 A. Kinetic of ThT sorption onto river sediment obtained from the Váh River (5 g/dm^3) during 24 h of interaction at initial concentration of ThT C_0 = 40 mg/dm^3 and pH 4.0, on rotary incubator shaker (250 min^{-1}) and at 25 °C. The value of pH after 24 h pH_f = 8.1.

B. Effect of river sediment concentration on distribution coefficient (*DC*) for ThT sorption onto sediment (5 g/dm^3) after 2 h of interaction on rotary incubator shaker (250 min^{-1}) and at 25 °C. Initial ThT concentration C_0 = 100 mg/dm^3 and pH 4.0. Final pH value at the end of experiments: 1.25 g/dm^3 – 7.0; 2.5 g/dm^3 – 7.5; 5.0 g/dm^3 – 7.7; 10.0 g/dm^3 – 8.0; 12.5 g/dm^3 – 8.0. Data represents arithmetical mean from two independent experiments.

Also, the results suggest that many acid and direct dyes will be stable in aquatic systems for long periods of time unless other transformation pathways (e.g. photochemical) are rate determining. VARLIKLI *et al.* (2009) observed the concentration equilibrium reaching for dyes sorption onto sand obtained from Sahara at the time 10 min and found that sorption capacity of sand was higher in the case of cationic dyes (75 % of dye removed from solution) than in the case of anionic dyes (only 21 % of dye removed from solution). On the other hand, LAZARIDIS and KEENAN (2010) determined the concentration equilibrium reaching after 5 h of model soil composed from sand, sediment and clays (ratio 85:10:5) interaction with solution containing azo dye Reactive Black 5.

From the point of view of chemical composition of sediments, it may be stated that the portion of organic and inorganic components of sediments will significantly affect their sorption capacity as well as the rate of these processes. For example LIU *et al.* (2001) found the increasing of cationic dyes sorption onto sediment obtained from Qinghe River (China) after organic carbon (*OC*) removing and in the case of anionic dyes the decreasing of sorption after *OC* removing was observed.

In the real conditions, it can be expected that microorganisms, especially in the form of biofilms, in interaction of toxic organic compounds with components of river or lake sediments will also play a decisive role from the point of view of their accumulation, biodegradation and sorption abilities.

In the next experiments we studied the effect of river sediment concentration on ThT sorption in the range $C_{sediment}$ 1.25 – 12.5 g/dm^3, in time of concentration equilibrium reaching (2 h) and at initial ThT concentration C_0 = 100 mg/dm^3. The dye sorption onto sediment was evaluated by distribution coefficient (*DC*) defined as concentration ratio $[\text{ThT}]_{\text{sediment}} : [\text{ThT}]_{\text{solution}}$. We found that the value of *DC* was increased with increasing sediment concentration and this increase showed linear dependence (R^2 = 0.996) within sediment concentration $C_{sediment}$ 1.25 – 10.0 g/dm^3 (Fig. 3B). Similar result also obtained by VARLIKLI *et al.* (2009) at methylene blue sorption in suspension of Sahara sand. However, it can be expected that sorption ability of river or lake sediments will significantly depend on the size or specific surface of sediment particles as well as aggregates formed between abiological and biological components of sediments, respectively.

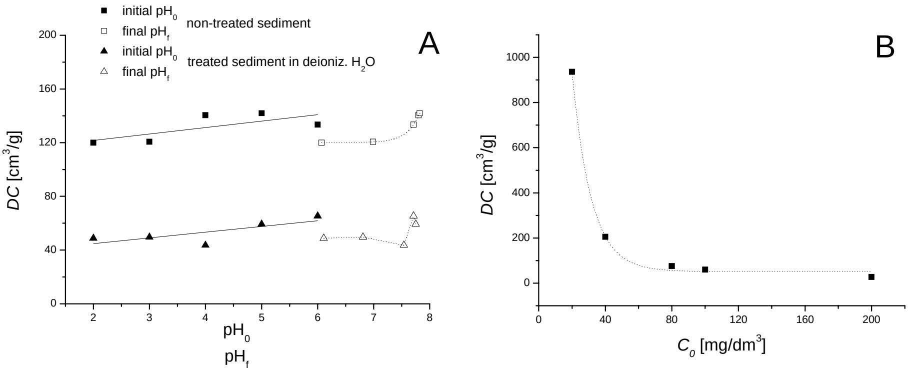

Fig. 4. A. Effect of pH value (initial pH$_0$; final pH$_f$ at the end of experiment) on distribution coefficient (*DC*) for ThT sorption onto non-treated and treated (3-times washed in deionized water) river sediment obtained from the Váh River (5 g/dm^3) after 2 h of interaction on rotary incubator shaker (250 min^{-1}) at initial concentration of ThT C_0 = 40 mg/dm^3 and 25 °C.

B. Effect of initial concentration of ThT on *DC* for ThT sorption onto sediment (5 g/dm^3) after 2 h of interaction on rotary incubator shaker (250 min^{-1}) at initial pH 4.0 and 25 °C. The final pH value at the end of experiment: 20 mg/dm^3 – 8.1; 40 mg/dm^3 – 8.1; 80 mg/dm^3 – 7.6; 100 mg/dm^3 – 7.6; 200 mg/dm^3 – 7.6. Data represents arithmetical mean from two independent experiments.

It is generally known that pH value of the environment strongly affects the behaviour of toxic compounds as well as their binding in the environment. This effect is not only in terms of changes in physico-chemical characteristics of compounds but also from the point of view of functional groups dissociation on the surface of sediment compartments responsible for sorption of these substances. On the Fig. 4A the dependence between *DC* value and initial pH value within the range 2 – 6 or final, equilibrium pH value, respectively are depicted. We found that at all experiments the pH value was increased from the initial value to the final, equilibrium value pH 8, which correspond with value determined according to ISO method No. 10390 (Table 2). This effect was also observed in the case of treated river sediment by 3-times washing in deionized water, however treated sediment showed practically 3-times lower *DC* values.

From the Fig. 4A, it is also clear that *DC* value was increased minimally with increasing initial as well as equilibrium pH value. Similar result was observed by LIU *et al.* (2001) at sorption of cationic dyes Basic Yellow X-5GL and Basic Red 13 onto sediment from Qinghe River within the range of initial pH values 2 – 10.

Another important parameter in the evaluation of toxic organic substances behaviour as well as the risks associated with their input into aquatic systems is their concentration. From this reason, we realized a series of experiments within the concentration range of ThT 20 − 200 mg/dm^3 in deionized water at pH 7.0. From obtained results, it can be concluded that *DC* value exponentially decreased with increasing initial concentration of ThT in solution (Fig. 4B).

Obtained equilibrium data characterizing the sorption of ThT onto river sediment also allow to describe sorption processes by equilibrium adsorption isotherms. Among the most commonly used mathematical models describing sorption processes include adsorption isotherms according to Langmuir and Freundlich.

Langmuir adsorption isotherm describes mono-layer sorption on the surface of sorbent with a limited number of identical sites. In equation includes the parameter Q_{max} defining the maximum specific sorption, which permits to evaluate a various sorbents in terms of their sorption properties as well as the effect of physico-chemical changes in environment on compounds sorption. In contrast, the Freundlich adsorption isotherm calculates with non-homogeneous binding sites thus describes the sorption on heterogeneous surface containing binding sites with different affinity for sorbate.

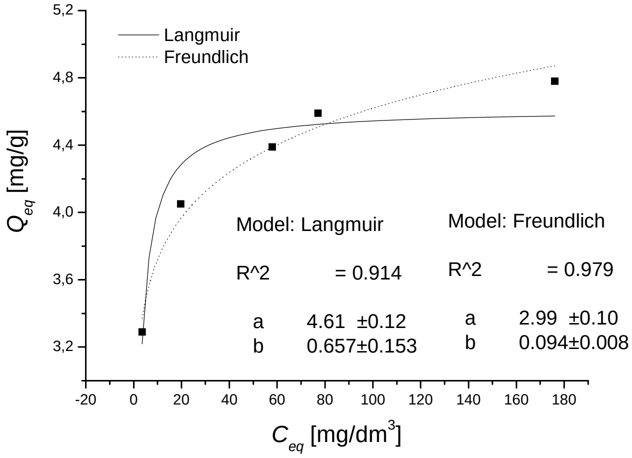

Fig. 5. Description of ThT sorption onto river sediment obtained from the Váh River according to Langmuir and Freundlich adsorption isotherms. Details of experimental conditions see in Fig. 4B.

From description of obtained data as well as from the comparison of coefficients of determination (R^2), it can be concluded that ThT sorption onto river sediment was better described by adsorption isotherm according to Freundlich (R^2 = 0.979) than by Langmuir adsorption isotherm (R^2 = 0.914), which determines the value of Q_{max} parameter 4.61±0.12 mg/g (±SD) (Fig. 5). Obtained parameters from both mathematical equations of adsorption isotherms are presented in Table 4. Also, LIU *et al.* (2001) found that the sorption of five cationic and anionic dyes onto sediment obtained from Qinghe River (China) was better described by Freundlich adsorption isotherm with coefficients of determination in the range R^2 = 0.941 − 0.985. In the case of cationic dyes Basic Yellow X-5GL and Basic Red 13 determined values of Freundlich constants K_F 7.04 and 7.01, respectively, as well as 1/n 0.386 and 0.687, respectively. Similarly, a better description of the sorption of anionic dyes by suspension of sandy and loamy soils with Freundlich adsorption isotherms was observed by MORRIS *et al.* (2008) and QU *et al.* (2008). Also, the Freundlich adsorption isotherm was an appropriate model for description of cationic surfactant cetyltrimethylammonium bromide (CTAB) sorption on marine sediment (CAO *et al.*, 2011).

Table 4. Obtained parameters from adsorption isotherms according to Langmuir and Freundlich describing ThT sorption onto river sediment obtained from the Váh River. Details of experimental conditions see in Fig. 4B.

Langmuir isotherm $Q_{eq} = \frac{Q_{\max} * b * C_{eq}}{1 + b * C_{eq}}$			**Freundlich isotherm** $Q_{eq} = K_F * C_{eq}^{\frac{1}{n}}$			
Q_{max}	b	R^2	K_F	$1/n$	n	R^2
4.61±0.12	0.657±0.153	0.914	2.99±0.10	0.094±0.008	10.6	0.979

Q_{max} – Langmuir constant represents the maximal sorption capacity (mg/g);
b – Langmuir constant represents affinity between sorbate and sorbent (dm^3/mg);
R^2 – coefficient of determination;
K_F – Freundlich constant relating with sorption capacity (dm^3/g of sediment);
n – Freundlich constant relating with sorption intensity (non-dimensional coefficient).

3.3 Sorption and desorption of dye in column system

In this type of experiments a glass column with inside diameter 0.8 cm and height 40 cm was used. In bottom of the column the river sediment obtained from the Váh River was arranged with sediment bed height 5 cm and over sediment the model solution containing thioflavine T (ThT) was maintained with height 30 cm by periodic addition of fresh solution and infiltrated water samples taking. Samples of infiltrated water in aliquot volumes (2 cm^3) were collected and spectrophotometrically analyzed for residual concentration of ThT.

The aim of these experiments was to imitate the conditions occurring near banks of shallow rivers, where vertical transport processes (convection) governed by gravitation and bank infiltration play a decisive role. On the other hand, in the case of bottom and sediments of the river distant from the bank the horizontal transport processes (advection) take place.

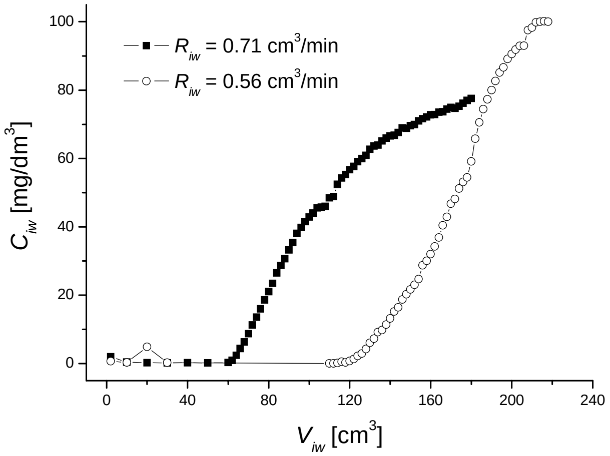

Fig. 6. Concentration of ThT in infiltrated water from experimental column system containing river sediment obtained from the Váh River. Experiment was realized in glass column (diameter 0.8 cm and height 40 cm) with 5 cm of sediment bed and 30±1.5 cm level of model solution with initial concentration of ThT C_0 = 100 mg/dm^3 in deionized water, pH 4.0 and at 22±2 °C. The average flow rate of infiltration water: -■-■- R_{iw} = 0.71±0.08 cm^3/min (±SD); -o-o- R_{iw} = 0.56±0.06 cm^3/min (±SD).

Fig. 6 depicts results from the determination of ThT concentration in infiltrated water that passes through the 5 cm layer of river sediment. We found that in the first tens of millilitres of infiltrated water the concentration of ThT was negligible, and subsequently, the ThT concentration in infiltrated water exponentially increased up to the value of ThT concentration in water column above the sediment layer (C_0 = 100 mg/dm^3). It means that in this phase the river sediment was saturated by ThT dye to such an extent that ThT passed through the sediment without significant interaction. Also, we found that at a slower flow rate of infiltrated water R_{iv} = 0.56 cm^3/min ThT concentration in infiltrated water began to increase in 2-times greater volume of solution (120 cm^3) which passed through the sediment bed in comparison with faster flow rate R_{iv} = 0.71 cm^3/min of solution under identical conditions of column system.

In the next experiment we studied the effect of water composition containing ThT on dye transport through the layer of river sediment. From Fig. 7, it is evident that in the case of synthetic freshwater imitating the composition of water in lake Rostherne Mere (Lancashire) in the UK and containing ThT with initial concentration C_0 = 100 mg/dm^3 we found enhanced transport of ThT through the sediment in comparison with deionized water. This fact can be explained by competitive effect between monovalent or bivalent metal cations occurring in synthetic freshwater and cationic dye ThT as well as saturation of sediment no only with ThT, but also with metal ions contained in the freshwater. It means that the qualitative and quantitative composition of the water of lakes or rivers will be significantly affect the transport of toxic organic compounds, such as cationic or anionic synthetic dyes through sediments.

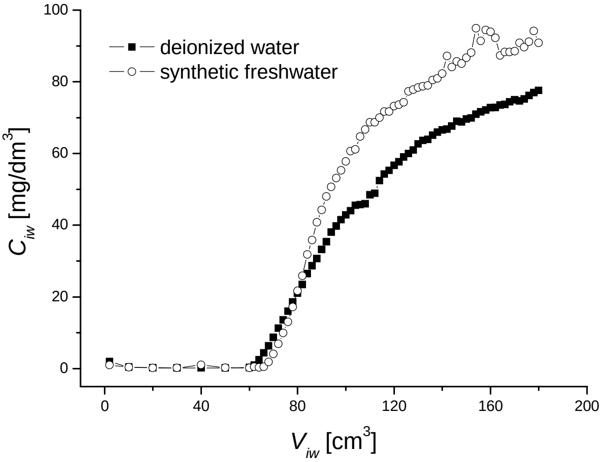

Fig. 7. Concentration of ThT in infiltrated water from experimental column system containing river sediment obtained from the Váh River. Experiment was realized in glass column (diameter 0.8 cm and height 40 cm) with 5 cm of sediment bed and 30±1.5 cm level of model solution with initial concentration of ThT C_0 = 100 mg/dm^3 in deionized water or synthetic freshwater according to SMITH *et al.* (2002), pH 4.0 and at 22±2 °C. The average flow rate of infiltration water: -■-■- R_{iw} = 0.71±0.08 cm^3/min (±SD); -o-o- R_{iw} = 0.62±0.06 cm^3/min (±SD).

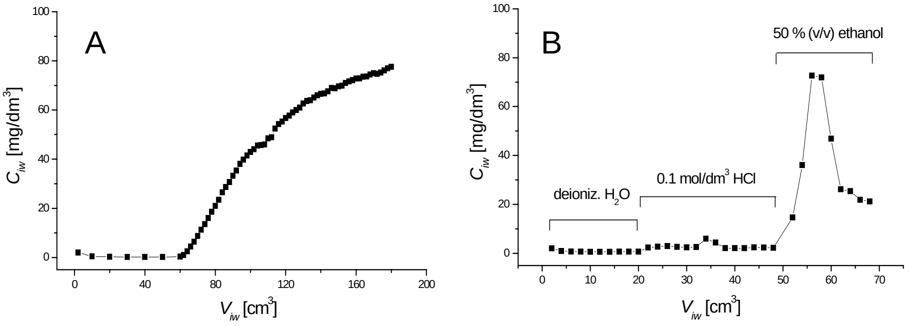

Fig. 8 A. Concentration of ThT in infiltrated water from experimental column system containing river sediment obtained from the Váh River. Experiment was realized in glass column (diameter 0.8 cm and height 40 cm) with 5 cm of sediment bed and 30±1.5 cm level of solution with ThT concentration C_0 = 100 mg/dm^3 in deionized water, pH 4.0 and at 22±2 °C. The average flow rate of infiltration water R_{iw} = 0.71±0.08 cm^3/min (±SD).

B. Concentration of ThT in infiltrated solution from experimental column system containing river sediment after sorption experiment (Fig. 8A). Experiment was carried out identically as sorption experiment with difference that model solution of ThT was replaced with deionized water (10 fraction with 2 cm^3 infiltrated water), 0.1 mol/dm^3 HCl (14 fraction) and 50 % (v/v) ethanol solution (9 fraction).

From the point of view of synthetic dyes transport and behaviour in the environment their chemical stability plays an important role. For this reason it is necessary to study the remobilization of dyes from sediments into the water of rivers or lakes, as well as the gradual release of these substances from lower sediment layers up to groundwater. In terms of this request the desorption of ThT from river sediment by gradually replacement of model dye solution with deionized water, 0.1 mol/dm^3 HCl or 50 % (v/v) ethanol (EtOH) solution we carried out. We found that sorbed amount of ThT in sediment layer was not released by seepage of deionized water and only minimal desorption of ThT in the case of 0.1 mol/dm^3 HCl solution was observed (Fig. 8). The highest desorption of ThT from the sediment layer was found in application of 50 % (v/v) EtOH solution into the column system, and the efficiency of ThT desorption from 5 cm of sediment layer decreased in the order: 50 % EtOH > 0.1 mol/dm^3 HCl > deionized water. From obtained results it can be concluded that the binding of ThT, and possibly other cationic synthetic dyes, onto river sediments under natural conditions will be practically irreversible.

4. Conclusions

Obtained data suggest that sorption of benzothiazole cationic dye thioflavine T (ThT), and possibly other cationic synthetic dyes, onto river sediments under natural conditions will be a rapid and practically irreversible process as well as the further fate of these substances after their input into the aquatic systems and sediments will be probably determined by degradation processes carried out mainly by autochthonous microorganisms as well as photochemical reactions.

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