

EFFECT OF CHITOSAN AS ACTIVE SUBSTANCE IN HYDROGEL ON THE DIFFUSION OF DYES

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Abstract

Cation active chitosan was studied as the active substance incorporated into an inert hydrogel to affect its transport and barrier properties. The inert hydrogel was based on thermo-reversible agarose which can be prepared in defined shape and size required for the mathematical description of studied transport. Amido Black 10B was chosen as a model anionic dye able to interact with chitosan. Agarose hydrogels with the contents of chitosan equal to 2, 5, and 10 µg per gram of hydrogel were prepared. Diffusion experiments were realized at three different temperatures (30, 40, and 50 °C).

Transport experiments in hydrogels provided the values of effective diffusion coefficients involving the effect of interactions between chitosan and dye under given conditions. The incorporation of chitosan into inert hydrogel resulted in the decrease in the dye diffusivity. An apparent equilibrium constant as the ratio between immobilized and free movable dye particles was determined on the basis of the comparison of dye diffusivities in hydrogels enriched by chitosan with values obtained for pure agarose hydrogel. The increase in temperature enhanced diffusion rate as expected. The increase in diffusion coefficients with increasing temperature showed on the predominant influence of higher mobility in comparison with temperature dependence of reaction rate.

Keywords: Chitosan, dye, hydrogel, applications, testing methods

1. INTRODUCTION

Dyes are widely used in various industries such as textiles, paper, leather, and plastics. The wastewaters from these industries often contain dyes, which were discharged into natural systems. The presence of dyes in wastewater thus poses a risk for environment and human health [1,2]. The removal of dyes from waters becomes a major challenge due to the difficulty in treating such wastewaters by conventional treatment methods such as chemical and biological oxidation methods [3,4]. However, the commonly used technique for removal of dyes from wastewater is adsorption [3-7].

Chitosan can be considered as one of the most efficient adsorbents for the removal of pollutants from water [8-11]. It is a deacetylated derivative of chitin [5,8,9,12]. As one of the most representative biopolymers, it is a multifunctional polysaccharide comprising of copious chelating groups including primary and secondary hydroxyl groups, as well as highly reactive amino groups [7,13]. Chitosan it is low-cost, biodegradable, biocompatible, renewable, and non-toxic, so it can be considered as a "green" adsorbent [1,7,10,14,15]. However, the disadvantage of pure chitosan is that it can be dissolved only in acidic solutions. Other disadvantage is its low chemical stability [1,7-9]. Due its advantageous properties it can be employed in many fields, such as food, environment, and medicine, based on different research objectives [8-10,16-21]. Chitosan as a cationic polymer that shows high affinity for most dyes, especially for anion ones [8-10].

Amido Black 10B was chosen for this study as a model azo dye. It exhibits considerably high toxicity and can damage human respiratory system and cause skin and eye irritations [10,22]. Its anion active character provides high affinity to cationic chitosan and creates conditions for its effective removal from environment. Interactions of chitosan with Amido Black 10B are studied mainly as batch adsorption [1,2,6,7,10-12]. Well-

known adsorption isotherms (Langmuir, Freundlich) are used for the mathematical description of experimental results [1,23,24]. The experiments can provide such information as adsorption capacity and distribution constant. Some studies are focused also on the adsorption kinetics [1,7,10,23-25], where pseudo-first-order and pseudo-second-order kinetic equations were usually applied to experimental data. Some author attributed the intraparticle diffusion as the rate limiting step if the adsorbed amount is proportional to square root of time [1,26,27].

In this study, we decided to investigate the diffusion and interactions of chitosan with dye directly in the migration. Study of diffusion in chitosan materials are relatively scarce. Several authors studied the diffusion of different substances through chitosan-based membranes [28-30], beads [30,31], thin films [32], and hydrogels [33]. We used agarose hydrogel enriched by chitosan as an active substance able to (partially) immobilize dye in the diffusion. The experimental arrangement as well as the mathematical description were adopted from our previous works [8,9,34,35]. Experimental data were fitted by Equation (1) derived on the basis of on Fick's laws and initial and boundary conditions listed in Table 1.

$$c = c_s \operatorname{erfc} \frac{x}{2\sqrt{Dt}} \quad (1)$$

where t is time, x is distance from interface, c is concentration of dye, c_s is concentration at interface, and D is the diffusion coefficient of dye in pure agarose hydrogel. If Equation 1 is applied for the data obtained for the diffusion of dyes in hydrogels enriched by chitosan, the diffusion coefficient D in Equation 1 and (following) Equation 2 should be replaced by effective diffusion coefficient (including interactions between dyes and chitosan). Both diffusion coefficients can be determined from the slope of the dependence of the total diffusion flux m_t on the square root of time [8,9,34,35]:

$$m_t = 2c_s \sqrt{\frac{Dt}{\pi}} \quad (2)$$

Table 1 Initial and boundary conditions of diffusion experiments

Time t	Distance x	Concentration c
$t = 0$	$x > 0$	$c = 0$
$t > 0$	$x = 0$	$c = c_s$
$t > 0$	$x \rightarrow \infty$	$c = 0$

2. MATERIALS AND METHODS

Chitosan (medium molecular weight), agarose (routine use class) and Amido Black 10B were purchased from Sigma Aldrich (St. Luis, MO, USA). Acetic acid for the preparation of chitosan solution was purchased from Lachner (Neratovice, Czech Republic). The exact molecular weights of chitosan and agarose were determined by means of size exclusion chromatography coupled with multiangle static light scattering, differential refractive index, and UV/VIS detection (SEC chromatographic system from Agilent Technologies, detectors from Wyatt Technology). The exact molecular weights were 251 ± 4 kDa for chitosan and 146 ± 3 kDa for agarose [8,9]. Deacetylation degree of chitosan was determined by potentiometric titration described by Garcia et al. [36]. The degree was determined as 83.8 ± 0.2 % mol.

The preparation of hydrogels was based on the thermo-reversible gelation of agarose solution described in previous works [8,9,34,35]. Agarose hydrogel gelatinized from the solution of agarose in water. Agarose content in hydrogel was 10 mg g^{-1} . The mixture was slowly heated with continuous stirring up to $80 \text{ }^\circ\text{C}$, stirred at this temperature order to obtain a transparent solution, and finally sonicated (1 min) to remove gasses. Afterwards, slowly poured into the PMMA spectrophotometric cuvette (inner dimensions: $10 \times 10 \times 42 \text{ mm}$). The cuvette orifice was immediately covered with pre-heated plate of glass to pre-vent drying and shrinking of

gel. Flat surface of the boundary of resulting hydrogels was provided by wiping an excess solution away. Gentle cooling of cuvettes at the laboratory temperature led to the gradual gelation of the mixture.

Agarose-chitosan hydrogels were prepared from agarose solution mixed with the solution of chitosan. An accurately weighed amount of chitosan was dissolved in 50 cm³ of acetic acid (5 % wt.). The solution was titrated by 1M NaOH up to pH equal to 7 and diluted by distilled water (the final volume was 100 cm³). Agarose content in hydrogels was 10 mg g⁻¹, the contents of chitosan were 0.2, 0.5, and 1 mg g⁻¹.

Four cuvettes (with all types of hydrogels) were placed into 250 cm³ of dye solution. The solution was stirred continuously by the magnetic stirrer and the dye were left to diffuse from the solution into the hydrogels through the square orifices of the cuvettes. Diffusion experiments were triplicated, it means that three different vessels were used. The durations of the diffusion experiments were 24, 48 and 72 h. In these time intervals, the cuvettes were taken out of the solution and the UV-VIS spectra were measured in dependence on distances from the interface between hydrogel and donor solution. Varian Cary 50 UV–VIS spectrophotometer (Agilent Technologies, Palo Alto, CA, USA) equipped with the special accessory providing controlled fine vertical movement of the cuvette in the spectrophotometer was used for this purpose [8,9,34,35]. Concentration of dyes was determined at different positions in the hydrogels by means of calibration line. The spectra were calibrated for the hydrogels with the known concentration, homogeneously distributed in the whole volume of the hydrogel. Experiments were performed at three different temperatures (30, 40, and 50 °C). Data are presented as average values with standard deviation bars.

3. RESULTS AND DISCUSSION

In **Figure 1**, examples of experimental data are shown. Data are fitted by Equation 1 (**Figure 1a**) and Equation 2 (**Figure 1b**). We can see that the amount of dye decreases with increasing content of chitosan. Simultaneously, the concentration profiles increase with time (it is not shown but it can be deduced on the basis of time dependencies of diffused amount in **Figure 1b**).

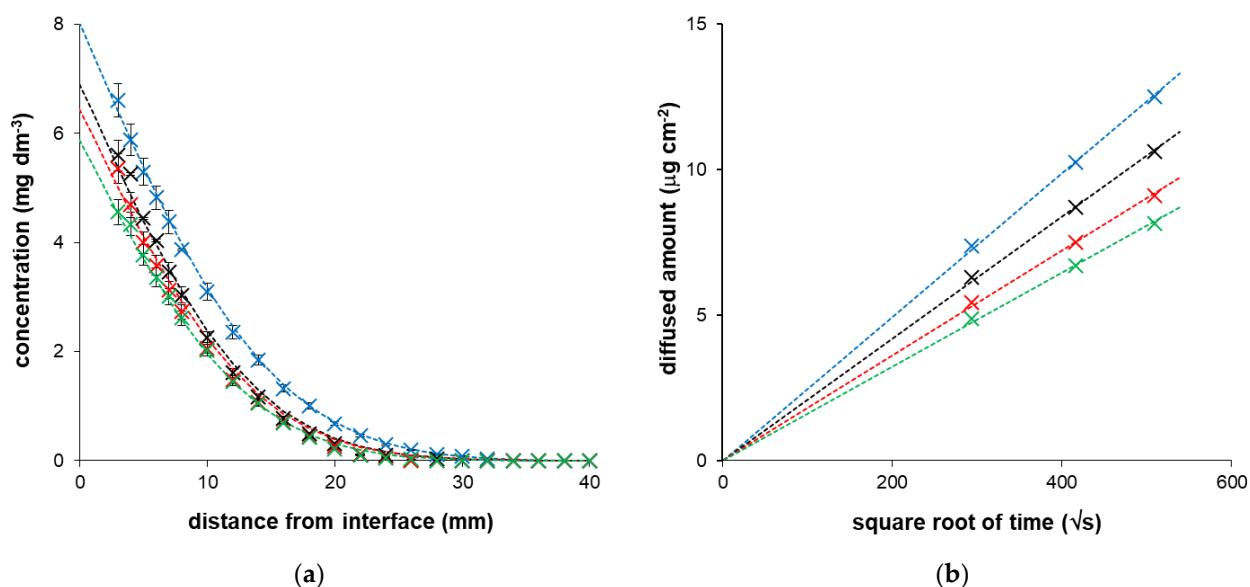


Figure 1 Concentration profiles of Amido Black 10B after 48 h at 50 °C (b) and the dependence of amount diffused through the interface at 30 °C (a) for pure agarose hydrogel (blue) and hydrogel enriched by chitosan: 0.2 mg g⁻¹ (black), 0.5 mg g⁻¹ (red), and 1 mg g⁻¹ (green).

The reason is that the mathematical model describing the diffusion takes account only free movable dye particles and it is “blind” to particles which are immobilized by chitosan. Therefore, the total amount of dye as

well as the concentrations can be higher in comparison with free movable dye particles. As mentioned above the effective diffusion coefficients include interactions between chitosan and dye. If the chemical reaction between dye and chitosan is much faster than the diffusion, the local equilibrium can be assumed to exist between the free and immobilized dye particles. It means that the front of diffusing particles penetrates into the hydrogel containing non-occupied chitosan binding sites. Dye thus can interact immediately with chitosan and the quick local equilibrium can be achieved.

Table 2 Diffusion coefficients and surface concentrations of Amido Black 10B in hydrogels

chitosan (mg g ⁻¹)	30 °C		40 °C		50 °C	
	$D \cdot 10^{10}$ (m ² s ⁻¹)	c_s (mg dm ⁻³)	$D \cdot 10^{10}$ (m ² s ⁻¹)	c_s (mg dm ⁻³)	$D \cdot 10^{10}$ (m ² s ⁻¹)	c_s (mg dm ⁻³)
0	4.25 ± 0.34	8.04 ± 0.38	5.65 ± 0.15	8.47 ± 0.32	6.04 ± 0.53	8.91 ± 0.65
0.2	3.49 ± 0.28	6.91 ± 0.41	4.49 ± 0.39	8.36 ± 0.57	5.14 ± 0.27	8.63 ± 0.67
0.5	3.32 ± 0.25	6.44 ± 0.13	3.88 ± 0.36	7.53 ± 0.32	3.98 ± 0.33	8.03 ± 0.26
1	3.15 ± 0.14	5.88 ± 0.29	3.70 ± 0.32	7.40 ± 0.21	3.88 ± 0.32	7.87 ± 0.54

The determined diffusion coefficients as well as surface concentrations for all realized diffusion experiments are listed in **Table 2**. As expected, surface concentrations decreased with the increasing content of chitosan and increased with increasing temperature. According to initial and boundary conditions (**Table 1**), the remained constant during whole diffusion experiments. Diffusion coefficients also decreased with increasing content of chitosan and increased with temperature. It corresponds with the character of diffusion coefficient which should be directly proportional to temperature if other conditions and properties of hydrogel remain the same. As can be seen, the change in diffusion coefficients is much higher if the temperature increased from 30 to 40 °C. The reason is that more parameters changed with temperature. Temperature affected both hydrogel properties and chemical interactions between dye and chitosan which resulted in curved character of the temperature dependence of diffusion coefficients. Hydrogel properties are also affected by the chitosan content as described in previous works [8,9].

4. CONCLUSION

In this contribution, the diffusion of Amido Black 10B in hydrogels were studied. Agarose hydrogel was enriched by chitosan as active substance able to interact with dye particles and (partially) immobilize them in hydrogel structure. The effect of the content of chitosan as well as the effect of temperature were investigated. It was found that experimental data can be effectively fitted by the proposed mathematical model derived on the basis of Fick laws. Measured concentration profiles and profiles calculated using Equation 1 and determined diffusion coefficients were in agreement. Surface concentrations as well as diffusion coefficients increased with increasing temperature and decreased with the increasing content of chitosan as assumed. The temperature dependence of diffusion coefficient had curved character because temperature can also affect properties of hydrogels and the rate and equilibrium of interactions between chitosan and dye particles.

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