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Spectral study of fluorone dyes adsorption on chitosan-based polyelectrolyte complexes

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ABSTRACT

Polyelectrolyte complexes of the chitosan–chondroitin sulfate and chitosan–hyaluronate polycation–polyanion pairs were synthesized and characterized as potential dye adsorbents at different pH levels. Equilibrium isotherm analysis was applied to investigate the efficiency and the mechanism of the adsorption of fluorone dyes (fluorescein, eosin Y, erythrosin B) on the synthesized complexes. The inefficiency of the fluorescein adsorption was proved by two different quantitative spectroscopic methods. The adsorption isotherm for both eosin Y and erythrosin B was adequately described in terms of the Langmuir–Freundlich model. The observed room-temperature phosphorescence of the adsorbed erythrosin B was attributed to the surface inhomogeneity of the synthesized complexes. The revealed variation in the adsorption properties of fluorone dyes was related to the differences in their ionic forms as well as in their polarity and hydrophobicity.

1. Introduction

Chitosan (aminopolysaccharide, 2-amino-2-deoxy-β-D-glucan) exhibits high adsorption capacity due to its cationic nature in acid media. Recently chitosan is widely used for wastewater treatment in textile, paper, plastics and dyestuffs industries [1]. Chemical modification of chitosan by both covalent and ionic cross-linking improves mechanical resistance as well as reinforces the chemical stability of chitosan in acidic solutions. Sodium tripolyphosphate is widely used as a cross-linking agent to produce chitosan beads with the size ranging from nanometers down to micrometers [2–5]. Anionic polysaccharides like heparin, hyaluronate, and chondroitin sulfates can be also used to obtain chitosan particles in a form of a polyelectrolyte complex (PEC) [6,7]. Such PECs combine the biodegradability and biocompatibility with high adsorptivity for anionic species. Structured chitosan can be successfully applied for tissue reconstruction and production of controlled release systems [2,8,9]. Recent publications on dye biosorption on chitosan-based materials have been comprehensively reviewed by Grini and Badot [1]. Equilibrium isotherm analysis has been successfully applied to the investigation of dyes' adsorption mechanisms and efficiency [1,3,10,11].

A series of fluorone dyes (fluorescein, eosin Y, erythrosin B) represent an attractive model set of substances with a gradual variation in their spectral, photophysical and acid–base properties [12–17] caused by a consequent halogen substitution in the chromophore structure. A number of publications have been devoted to the sorption of fluorescein or eosin Y on biomolecules [18–20] as well as chitosan [1,21,22] and chitosan-based beads and nanoparticles [1,3,23]. Unfortunately, the comparison of the results obtained in these studies is rather a challenge due to quite different conditions including temperature, pH, homogeneity and particular properties of adsorbent.

In the present work a comparative study of the adsorption of three fluorone dyes (fluorescein, eosin Y, erythrosin B) onto chitosan-based PECs at three different pH values (3.8, 4.6, 5.6) was carried out. In contrast to the previous studies the results were obtained under the same or quite similar conditions. For this purpose two different PECs from natural polysaccharides (polycationic chitosan and chondroitin sulfate or hyaluronate as polyanionic cross-linkers) were synthesized and characterized. The adsorption efficiency of fluorone dyes on chitosan-based PECs was evaluated by methods of molecular spectroscopy and further discussed in terms of acid–base, polar and hydrophobic properties of dyes. Some conclusions on mechanisms of the adsorption of fluorone dyes on chitosan PECs were drawn.

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2. Experimental

2.1. Materials

Sodium salts of fluorescein (Fluka), eosin Y (Sigma–Aldrich) and erythrosin B (Aldrich) were used in the present work (Fig. 1). Low-viscosity chitosan (Fig. 2) from shrimp shells was obtained from Sigma. Sodium salts of chondroitin sulfate A (Fig. 2) from bovine trachea and hyaluronic acid (Fig. 2) from *Streptococcus equi* were supplied by Sigma–Aldrich. Acetate buffers at pH values of 3.8, 4.6, and 5.6 and ionic strength 0.01, 0.05, and 0.09 respectively were used for the preparation of dye solutions. The initial dye concentration in solution was constant and equal to 10^{-3}% (here and further in the text 1% is the ratio of a dry weight of the dye or PEC (in grams) to the 1 ml of volume solution. The range of the pH variation was constrained by the stability of dyes – e.g., erythrosin B is unstable at pH 3.8.

2.2. PEC synthesis

The method used for the synthesis of PEC1 from chitosan and chondroitin sulfate was similar to the previously described [6]. A chitosan solution with the concentration of 0.1% was pre-cleaned from insoluble impurities by filtering onto a 0.8 μm pore size membrane. The chondroitin sulfate solutions at pH 3.8, 4.6, and 5.6 at concentrations of 0.125%, 0.125% and 0.1% respectively were added dropwise to the chitosan solution under vigorous stirring using magnetic stirrer for at least two hours. The addition was stopped after the occurring of opalescence. The experimentally determined volume ratios for polycation (chitosan) and polyanion (chondroitin sulfate) solutions amounted 2:1, 2.5:1 and 10:1 at pH values of 3.8, 4.6 and 5.6 correspondingly. The molecular polymer fraction was separated from the colloid solution by centrifugation using centrifuge 2–16 PK (Sigma Zentrifugen GmbH, Germany) at 12,000 *g* for 20 min. After the elimination of the molecular fraction the precipitate was ultrasonically resuspended for 20 min in a buffer solution. The synthesis of PEC2 from chitosan and hyaluronate was carried out in a similar way. The concentration of the used hyaluronate solutions was 0.02%, 0.03% and 0.04% at pH values of 3.8, 4.6 and 5.6 respectively, the experimentally found volume ratios for chitosan–hyaluronate solutions amounted in this case 3:4, 1:1 and 3:1 for the corresponding pH values.

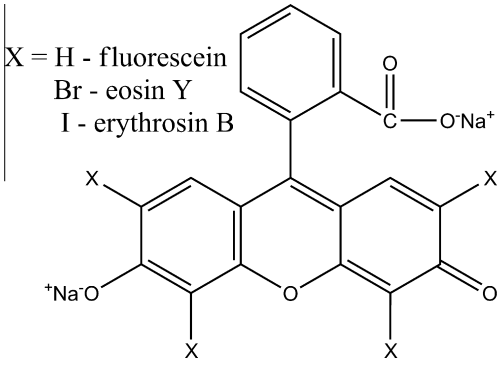

Fig. 1. Molecular structure of fluorone dyes.

2.3. Dynamic light scattering (DLS) and ξ-potential

The particle size distribution in the solutions under investigation was measured by dynamic light scattering method using Zetasizer Nano ZS (Malvern Instruments Ltd., Malvern, UK). The scattering angle was 173 grad; the laser emission wavelength was 532 nm. The analysis of the autocorrelation function was carried out in an approximation of solid spherical particles. Each sample was measured in 4 series with 20 repetitions in each series. ξ-Potential measurements were performed on the same device; the data were acquired in 4 runs with 50 repetitions in each run for each sample.

2.4. Yield of particles

The following approach was used for the determination of mass concentration and particle yield of PEC. Colloid solution of 3 ml volume in a flat aluminum flask was dried in an oven at the temperature of 80 °C during several hours. The flask was weighted using Sartorius microbalances before and after drying procedure. The mass of PEC particles was determined as the difference between the initial and dry weight of the flask after the consideration of the dry mass of the buffer solution. The yield was calculated relative to the concentration in the initial mixture. The measurement was repeated 3–5 times for each solution.

2.5. Scanning electron microscopy (SEM)

The shape and size of PEC were investigated by SEM using inlens field emission scanning electron microscope (S-5500, Hitachi, Japan). To prepare the SEM samples, a droplet of PEC was deposed on aluminum stubs and dried.

2.6. Spectral measurements

Absorption spectra of dyes in solution were measured by Lambda 620 spectrophotometer (Perkin Elmer, USA) under consideration of light scattering effects. PEC solutions were added to initial dye solutions of 2 ml volume. The mixtures were shaken and kept for 7–10 min before the measurement.

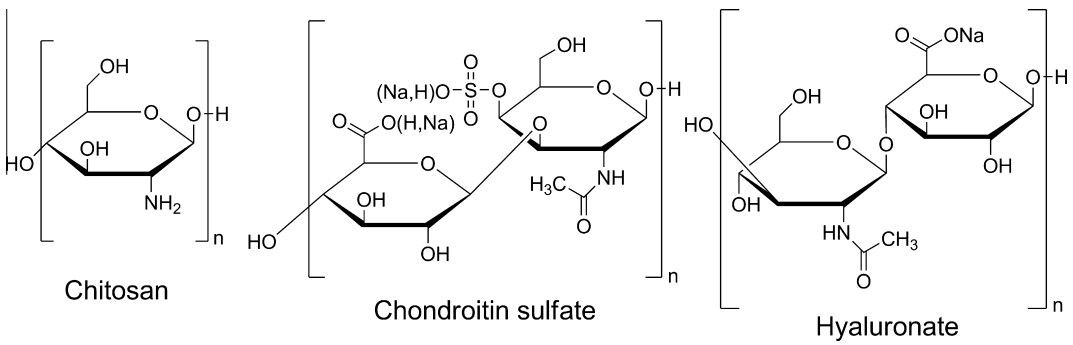

Fig. 2. Molecular structure of the polysaccharides used for PEC preparation.