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Anionic and cationic drug sorption on interpolyelectrolyte complexes

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ABSTRACT

Interpolyelectrolyte complexes of chitosan and poly(sodium 4-styrenesulfonate) [NaPSS] were synthesized and obtained in the form of solid particles, with two different sulfonate to aminium molar ratios: 0.7, resulting in particles with positive zeta potential ($IPEC^+$), and 1.4, yielding particles with negative zeta potential ($IPEC^-$). Both particles were characterized as potential drug sorbents using differently charged drugs: sodium cromoglycate (negatively charged), and tetracycline hydrochloride (positively charged). The adsorption isotherm for cromoglycate and tetracycline on $IPEC^+$ was adequately described by the Langmuir model, while the $IPEC^-$ sorption of tetracycline followed the Redlich-Peterson isotherm without the occurrence of cromoglycate sorption. The sorption kinetics consisted of two processes, one fast and the other slow, which were correlated to purely surface-related interactions and processes that resulted in diffusion and/or destruction/rearrangement on the particle surface and subsurface, respectively. Charge build up equilibrium and kinetics were also monitored via zeta potential measurements, and the differences between mass drug uptake and particle charging were used to propose adsorption mechanisms for the systems studied in this work.

1. Introduction

Adsorption-related phenomena are the basis of many technologies widely applied in various areas, such as biomedicine, drug loading/delivery, biotechnology and wastewater treatment [1–3]. The development of adsorption processes on a commercial scale requires the availability of suitable low-cost adsorbents with high adsorption capacity and selectivity: in fact, several substrates have been proposed and developed to obtain adsorption processes with high adsorption capacity and selectivity [4–6]. Within this context, interpolyelectrolyte complexes (IPEC) may be promising candidates. The popularity of the IPEC formation technique is due to its simplicity, low cost, low energy requirements, and effectiveness. IPECs are formed when oppositely charged polyelectrolytes electrostatically interact in solution [7,8]. Nonstoichiometric complexes (containing an excess of one component) present high adsorptivity for various species, such as drugs, dyes and proteins, due to the existence of a net charge on them [9].

Chitosan is one of the most promising biopolymers that can be used for forming IPECs [10–12]. Chitosan is a weak positively charged polyelectrolyte and is obtained from chitin by partial alkaline deacetylation [13]. Chitin is an extremely abundant polysaccharide in nature and is present mainly in exoskeletons of shrimp, lobster and crab, products coming from the fishing industry, making this biopolymer cheap and readily available [14,15]. Chitosan is a linear copolymer composed of d − glucosamine and N–acetyl-d–glucosamine units linked by β (1 → 4) glycosidic bonds [16–18]. When the degree of deacetylation (DD) of chitin is approximately 60%, it is called chitosan and becomes soluble in slightly acidic media [19]. The solubilization occurs by protonation of the amine function on the C-2 position of the d–glucosamine repeat units [17]. The pK_A value of chitosan is approximately 6.5 [15,20,21]. It is worth mentioning that IPECs prepared from natural polymers, such as polysaccharides, have the additional advantage of being biodegradable and biocompatible (although synthetic polymer-based IPECs are more adequate to situations in which a given system has to stay for a long time in the organism) [22]. Regarding the preparation and characterization of IPECs, the majority of the studies discusses the formation of IPECs of chitosan with other polysaccharides such as alginate [23], hyaluronic acid [24], pectin [25], chondroitin sulfate [26], and dextran sulfate [27], among others [28], but the combination of chitosan and poly(sodium 4-styrenesulfonate), NaPSS, is under studied [29,30], which makes the IPEC chitosan-NaPSS an interesting field of study.

Specifically, regarding adsorption studies, although one can find in the literature works on the adsorptive capacity of chitosan [31–36], there are fewer publications addressing the equilibrium and kinetic studies of adsorption on IPECs, in order to get important parameters for the optimization of cost and feasibility in the adsorption process [37–39]. The purpose of this work is to present a study on the adsorption of two drugs onto chitosan-based IPECs. For this purpose, we have prepared IPECs based on chitosan and NaPSS with opposite

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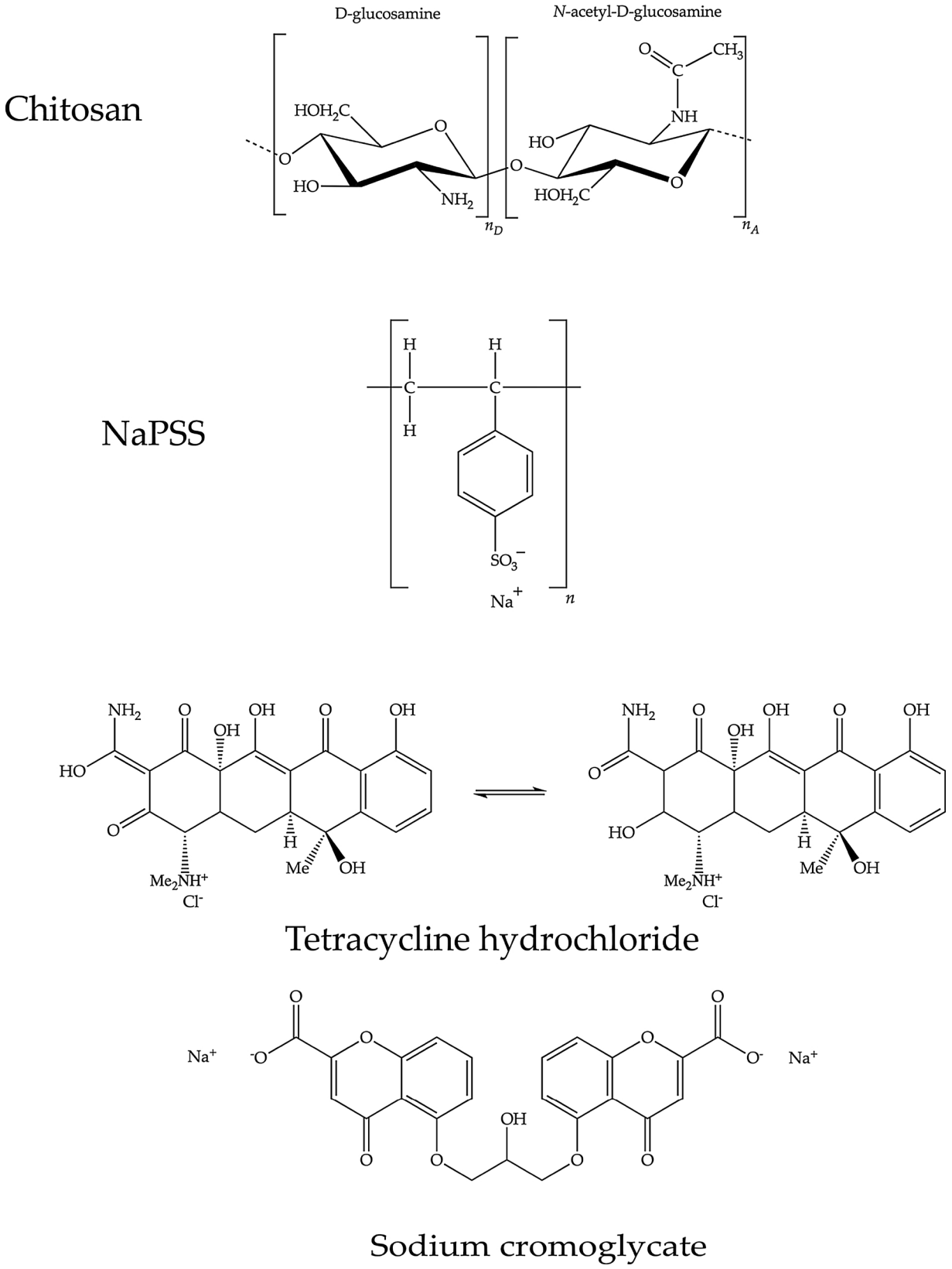

Fig. 1. Chemical structures of chitosan [degree of deacetylation $x_D = 100n_D/(n_A + n_D)$, poly (sodium 4-styrenesulfonate), NaPSS, tetracycline hydrochloride tautomers (molar mass, 480.90 g mol^{-1}), and sodium cromoglycate (molar mass, 512.33 g mol^{-1}).

surface charges using a methodology developed in previous works, where we fully characterized the resultant particles (both in terms of bulk properties and dispersion stability) [40,41]. The drugs used for this study were the positively charged antimicrobial drug tetracycline hydrochloride, and the negatively charged antiallergic drug, sodium cromoglycate.