



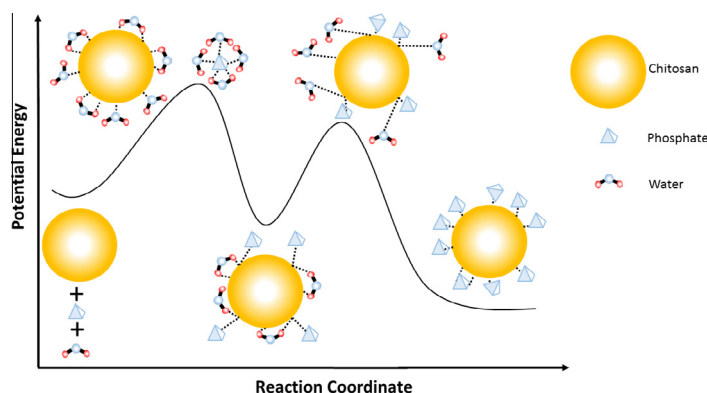
Phosphate uptake studies of cross-linked chitosan bead materials



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GRAPHICAL ABSTRACT



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ABSTRACT

A systematic experimental study is reported that provides a molecular based understanding of cross-linked chitosan beads and their adsorption properties in aqueous solution containing phosphate dianion (HPO_4^{2-}) species. Synthetically modified chitosan using epichlorohydrin and glutaraldehyde cross-linkers result in surface modified beads with variable hydrophile-lipophile character and tunable HPO_4^{2-} uptake properties. The kinetic and thermodynamic adsorption properties of cross-linked chitosan beads with HPO_4^{2-} species were studied in aqueous solution. Complementary structure and physicochemical characterization of chitosan beads via potentiometry, Raman spectroscopy, DSC, and dye adsorption measurements was carried out to establish structure-property relationships. The maximum uptake (Q_m) of bead systems with HPO_4^{2-} at equilibrium was 52.1 mg g^{-1} ; whereas, kinetic uptake results for chitosan bead/phosphate systems are relatively rapid ($0.111\text{--}0.113 \text{ min}^{-1}$) with an intraparticle diffusion rate-limiting step. The adsorption process follows a multi-step pathway involving inner- and outer-sphere complexes with significant changes in hydration. Phosphate uptake strongly depends on the composition and type of cross-linker used for preparation of chitosan beads. The adsorption isotherms and structural characterization of bead systems illustrate the role of surface charge, hydrophile-lipophile balance, adsorption site accessibility, and hydration properties of the chitosan bead surface.

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1. Introduction

The fate and transport of inorganic phosphate species (P_i) in the environment is an issue of global concern, as evidenced by the build-up of P_i in aquatic environments and its relevance to ecosystem and human health [1]. Adsorption is an established method for

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contaminant removal due to its low operating cost and facile infrastructure requirements. However, there is a need to develop improved sorbent materials with greater adsorption capacity and selectivity toward waterborne contaminants [2,3], especially in the case of hydrophilic adsorbates. Typical industrial adsorbents include clays, zeolites, and activated carbon [4–23] but these adsorbents have limited application for the removal of phosphate anion species due to their relatively low selectivity and adsorption capacity [24–27]. Chitosan and its modified forms display versatile adsorption properties toward cation and anion species due to the presence of amine and hydroxyl groups [28–32]. These polar functional groups of chitosan allow for synthetic modification via cross-linking to yield materials with variable morphology such as powders or beads [28–31] that differ from unmodified chitosan. Chitosan beads have been used for the efficient removal of dyes [33], heavy metals [34], and inorganic ions [35]. Chitosan beads/films and its modified forms [18,21,26,27,36] differ from conventional powder materials due to their variable acid stability, mechanical strength, pore-size and surface area (textural) properties, and surface chemical groups [33]. Chitosan beads cross-linked with different types of agents possess variable surface functionality and textural properties that contribute to unique interfacial interactions and variable adsorption properties. Tunable adsorption properties occur due to pH dependent electrostatic interactions and surface functional groups with variable hydrophile-lipophile properties at the surface binding sites. The affinity between adsorbent-adsorbate systems can be further understood by the “law of matching water affinities”, as described in detail elsewhere [37,38].

In a previous report [39], chitosan beads were prepared using two types of cross-linkers [epichlorohydrin (EP) and glutaraldehyde (GA)] where differences in the relative uptake relate to their relative hydrophile-lipophile properties. While there is a unique dependence of the kinetic and equilibrium sorption properties of chitosan bead/phosphate dianion (HPO_4^{2-}) systems, a molecular-level understanding of such adsorption and interfacial phenomena is lacking. Hence, there is a need to develop an understanding of the relationship between the structure and sorption properties for these chitosan bead systems, especially at alkaline conditions that favour phosphate dianion (HPO_4^{2-}) species. To address this knowledge gap, systematic sorption properties of chitosan bead/ HPO_4^{2-} systems were studied using complementary methods such as Raman spectroscopy, DSC, dye adsorption, and potentiometry to establish structure-property relationships. Herein, we report on the structure and physicochemical properties of the bead/ HPO_4^{2-} systems, along with a study of the dynamic and equilibrium uptake properties of such chitosan bead systems with HPO_4^{2-} species at pH 8.5 in aqueous solution.

The adsorption process for trihydrogen phosphate (H_3PO_4) with chitosan cross-linked beads was reported at pH 3–4 by Sowmya and Meenakshi [40], while phosphate uptake was reported by Leduc et al. [41] for chitosan-based hydrogels using kinetic adsorption models. Phosphate adsorption by hydrogels was found to be limited due to external transport where diffusion into the outer boundary layer governs the rate of adsorption. While the uptake of phosphate by chitosan beads may bear resemblance to hydrogel systems, phosphate exists as anion species (e.g., HPO_4^{2-} and H_2PO_4^-) in typical aquatic environments at pH 6–8. To gain a greater understanding of anion adsorption, studies that relate the structure and adsorption properties of cross-linked chitosan beads with phosphate anions at typical aquatic conditions is required. This study contributes a molecular level understanding of aspects of sorbent structure and physicochemical characterization of the adsorption properties of chitosan beads. Raman spectroscopy, DSC, potentiometry, along with kinetic and equilibrium uptake studies at variable temperature and pH are used to examine the role of

phosphate speciation, sorbent surface potential, cross-linker type and composition, and the role of hydration effects on the adsorption and interfacial properties chitosan bead/ HPO_4^{2-} systems. Studies related to phosphate uptake with chitosan bead materials have been reported [39]; however, a detailed molecular level understanding of this system is currently lacking. This study contributes to an improved understanding of phosphate uptake beyond a recent report [39] in several ways: (i) the role of surface modification of chitosan beads (cross-linker type and composition), (ii) the role of hydrophile-lipophile balance and hydration processes on the uptake properties of phosphate dianion species. The results of this study are anticipated to catalyze further research and development of new sorbent materials for the controlled uptake of phosphate and other types of hydrophilic oxoanions such as arsenic.

2. Materials and methods

2.1. Materials

Glutaraldehyde (GA), epichlorohydrin (EP), and low molecular weight chitosan (75–85% deacetylation, and a molecular weight range: 50,000–190,000 kDa) were obtained from Sigma-Aldrich Canada Ltd. (Oakville, ON). All materials were used without further purification unless specified otherwise.

2.2. Synthesis of cross-linked chitosan beads

Fig. 1 shows the materials design of cross-linked chitosan beads with two types of cross-linkers, where the details of the synthesis and characterization are described elsewhere [39]. According to previous SEM results [39], the chitosan bead surface undergoes variable cross-linking relative to the inner bead core. This effect is in accordance with the variable mass transfer of reagents from the outer bead interface to its inner core, according to the phase inversion synthesis. Table 1 lists the sample ID of the bead systems and the two types of cross-linkers and their composition (2.5 and 5 wt.%) used in this study.

2.3. Characterization

The materials characterization of the chitosan beads using TGA, FT-IR spectroscopy, CHN elemental analysis, and SEM have been reported [39]. Complementary aspects of structure and physicochemical characterization of the bead materials is reported herein. Raman spectra were obtained using a Renishaw system 2000 whose resolution ($= \lambda/2$) is 0.257 μm (laser spot size). Raman shifts were obtained at ambient temperature with an excitation wavelength at 785 nm with the following operating conditions: spectral range (2000–500 cm^{-1}), power (20 mW with 50% load), objective lens (20 \times), cosmic ray removal (On), detection time (10 s), and the number of accumulation scans (2 times).

Surface characterization of the chitosan beads was carried out using a dye adsorption method where the variation in the absorbance of phenolphthalein (PHP) was measured using a Varian Cary-100 Scan UV-Vis spectrophotometer at $\lambda_{\text{max}} = 552$ nm. The residual phosphate species after adsorption was estimated using the vanado-molybdo-phosphoric-acid complex, where the absorbance of the dye complex ($\lambda_{\text{max}} = 400$ nm) was obtained by colorimetric analysis [42].

Differential scanning calorimetry (DSC) measurements of the bead samples was performed using a TA Q20 thermal analyzer from 25 to 400 $^{\circ}\text{C}$. The scan rate was set to 10 $^{\circ}\text{C}/\text{min}$, and dry nitrogen gas provided purging and temperature regulation of the sample compartment. Samples were in sealed aluminum pans

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