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Synthesis and characterization of a novel fish scale-immobilized chitosan adsorbent—Preliminary features of dichlorophenol sorption by solution calorimetry

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HIGHLIGHTS

- A novel fish scale-immobilized chitosan adsorbent was synthesized and characterized.
- It was evaluated the sorption of dichlorophenol on the new adsorbent.
- Simultaneous sorption data of quantity and energy were found by solution calorimetry.
- The interactions of fish scales/dichlorophenol are due to surface reactions.
- Excellent sorption features at adsorbent/dichlorophenol interface were found.

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ABSTRACT

Brazilian Corvina fish scales were cross linked with polyglutaraldehyde and chemically modified with chitosan gel. Characterization has pointed that chitosan has good and stable adhesion on the fish scales. The sorption of dichlorophenol-2,6-indophenol (DPI) on the novel material was studied by isothermal solution calorimetry. The non-symmetric shapes of the calorimetric plots indicate that the DPI sorption sites of the adsorbent are not energetically uniform. The enthalpies of the DPI sorption processes were highly exothermic (from −536.7 to −50.9 kJ mol^{-1}). The analysis of both the characterization of the materials and the calorimetric results has suggested that the interactions at the fish scales/DPI interface are due to surface reactions. The present work underlines the excellent features of the new fish scale-based adsorbent for use in phenol sorption applications at solid/solution interfaces.

1. Introduction

Most phenols including phenol, chlorophenols, nitrophenols and aminophenols are pollutants of high priority because of their toxicity and possible accumulation in the environment. Phenols are introduced into surface water from industrial effluents such as those from the coal tar, gasoline, rubber proofing, pharmaceutical and steel industries and chemical spills [1]. Current methods for removing phenolics from wastewater are expensive, and may lead to contamination of ground water [1].

Adsorption has been a promising option for the removal of non-biodegradable organics from aqueous streams [2]. Many researches have focused on the use of alternative adsorbents from recyclable materials, due to their cost effectiveness and good removal performance [3,4]. Fish scales can be an alternative adsorbent, due to the presence of specific chemical groups of fish scale collagen, such as hydroxyl, carboxyl, amine and amide [5,6]. The structural stability of collagens is enhanced by chemical cross linking the molecule by polyglutaraldehyde (PGA) reaction [7]. However, the fibrillar nature of fish scale collagen and the presence of PGA decrease the amount of available sorption sites of fish scale collagen [8].

The rationale for this work is that fish scale-immobilized chitosan would be a new potential adsorbent for use in sorption studies at solid/solution interfaces. Chitosan bears amine and alcohol functions, and may interact with inorganic/organic pollutants by covalent, electrostatic and/or hydrophobic interactions [9]. The specific properties of fish scale collagen and chitosan may be used to produce materials with unique properties for sorption of important pollutants in water streams.

A novelty of this work is the use of solution calorimetry to determine both the quantity and the energy of sorption without

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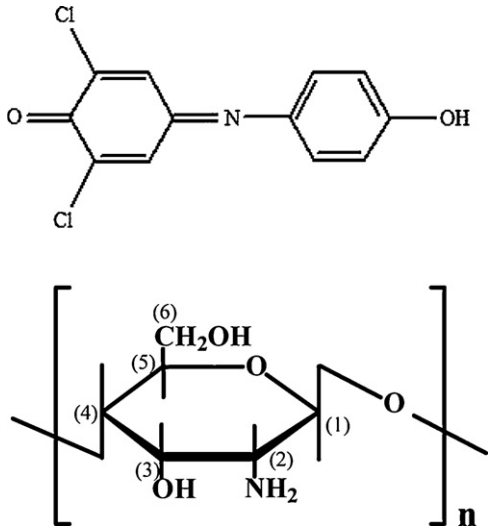

Fig. 1. Chemical structures of dichlorophenol-2,6-indophenol (above) and chitosan (below).

the need for additional analytical investigation [10,11]. The calorimetric results give information on thermodynamics of the process, energetics and analysis, which are all essential for characterizing the sorption mechanisms [10,11]. However, less attention has been paid to the direct calorimetric investigations of phenols interactions on naturally occurring materials. The calorimetric data are invaluable to assess many sorption features at the fish scale/dichlorophenol interface.

2. Materials and methods

2.1. Reagents and solvents

All chemicals/reagents used were of analytical reagent grade. The scales of Corvina fish (*Micropogonias furnieri*) were collected from a Fishermen's Market located in Aracaju, state of Sergipe, Brazil. Mature fish scales were washed repeatedly with water to remove adhering dust and soluble impurities from their surface and allowed to dry at 35 °C for 12 h. The chitosan powder (CHIT) was a free gift from C.E. Roeper, Hamburg, Germany. The degree of deacetylation (82%) was determined by FTIR [12]. Dichlorophenol-2,6-indophenol (DPI) was from Sigma–Aldrich and used without purification. The chemical structures of chitosan and DPI are shown in Fig. 1.

2.2. Preparation of the adsorbent

The fish scale collagen was crosslinked under mild conditions using a 0.10% (w/v) pH 7.0 PGA aqueous solution as described earlier [13]. A pale brown material was obtained (hereafter described as PGA-scale for simplicity). Chitosan was dissolved in 1.0 wt% acetic acid solution. The PGA-scale (50 g) was then added to 100 mL of the chitosan gel and the suspension was mechanically agitated for 3 h at room temperature. The suspension was filtered and the solid residue washed repeatedly with water and dried at 45 °C for 6 h. A dark brown material was obtained (hereafter described as ESC-QUIT for simplicity) and cut into small 5 mm × 5 mm square membranes of 0.5 mm of thickness. A schematic sequence of chitosan immobilization on the PGA-scale is shown in Fig. 2.

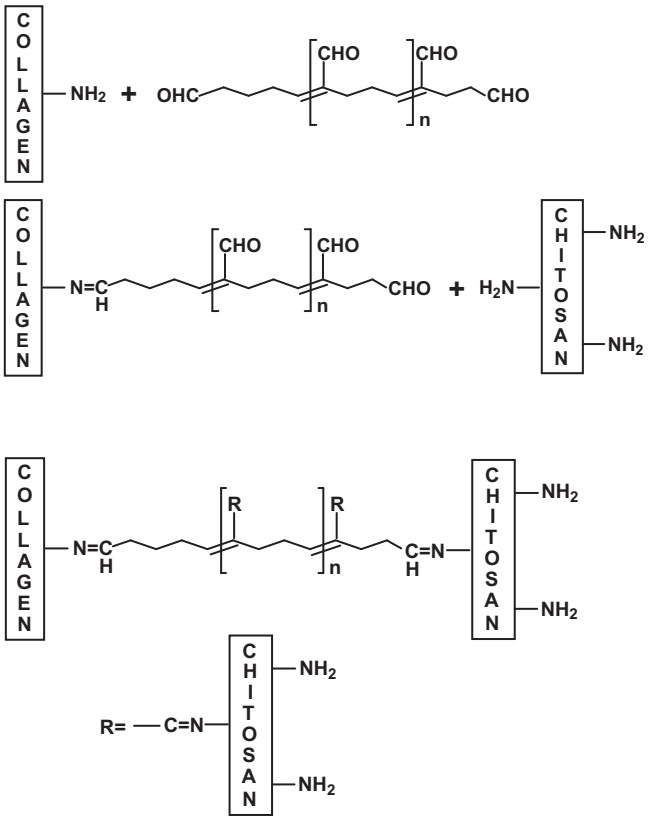

Fig. 2. Idealized schematic sequence of the fish scales cross linking with PGA and their chemical modification with chitosan.

2.3. Characterization of the materials

The determination of the pH of point of zero charge (pH_{pzc}) of the adsorbent (ESC-QUIT) was carried out using a procedure similar as described earlier [14]. The morphological characterization of the materials was carried out with a scanning electron microscope (SEM, JEOL-JSM 6360-LV). The samples were previously coated with gold (thickness of about 12 nm). The Raman spectra were acquired with a Bruker Senterra Raman System equipped with an Olympus microscope with a 50× objective to focus a Melles Griot laser beam on the sample. The spectra were excited by the 785 nm line from an air-cooled He–Ne laser. The thermogravimetric analyses (TG and DTG) were made using about 10 mg of material, under nitrogen atmosphere from 25 to 800 °C, in a SDT 2960 thermoanalyzer, from TA Instruments. XRD analysis were performed in a Shimadzu diffractometer, in the 2θ range from 5° to 60° (accumulation rate of 0.02° min^{-1}), using Cu Kα radiation. The solid-state reflectance spectra of the samples were recorded on an Ocean Optics UV–vis spectrophotometer from 400 to 900 cm^{-1} at a resolution of 4.0 cm^{-1}.

2.4. Solution calorimetry experiments

Microcalorimetric determinations were performed in a C80 microcalorimeter from Setaram, using the membrane breaking (thin Teflon®) technique [15]. Briefly, 100 mg of ESC-QUIT and 0.5 mL acetic acid/sodium acetate buffer solutions at pH 3.0 were put into the lower of the calorimetric vessel. In this work, HAc/NaAc buffered solutions at pH 4.0 were used in all calorimetric experiments. It was found that the chemical structure of fish scale collagen can be denatured in both very acidic and very alkaline media [7]. Additionally, 2.5 mL of a DPI aqueous solution were put in the lower part of the calorimetric vessel. Calorimetric output was of thermal