



Adsorption study of an organo-arsenical with chitosan-based sorbents



Louis Poon, Shaguftah Younus, Lee D. Wilson*

Department of Chemistry, University of Saskatchewan, 110 Science Place, Saskatoon, Saskatchewan S7N 5C9, Canada

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ABSTRACT

In this study, chitosan-based copolymers were prepared at various weight ratios of chitosan (C) to glutaraldehyde (G): 1:1 (CG11), 2:1 (CG21), and 3:1 (CG31). The sorption properties of these copolymers were investigated with roxarsone in simulated aquatic conditions at pH 7 in phosphate buffer, similar to that found in poultry litter leachate. The relative sorption capacity (Q_m ; mmol/g) of the sorbents are listed in parentheses in descending order: CG11 (1.80) > CG31 (0.945) > CG21 (0.802) > chitosan (0.416). The sorptive properties of the copolymers are comparable to granular activated carbon (GAC), a standard carbonaceous sorbent material, where $Q_m = 2.36$ mmol/g. The adsorption properties of phenolic adsorbates such as *o*-nitrophenol, *p*-nitrophenol, and roxarsone with the CG copolymers and GAC were investigated at various pH and compared with phosphate and carbonate buffer systems.

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1. Introduction

4-Hydroxy-3-nitrobenzene arsonic acid (roxarsone; ROX) is an organic arsenical feed additive for the poultry industry to control intestinal parasites and to increase growth weight [1–4]. Upon excretion, a large proportion of ROX remains unchanged in the feces with about 20% of the compound being converted to various toxic forms. ROX has relatively low toxicity toward animals with an LD₅₀ for mice determined to be 800 ppm [5]. The LD₅₀ value is far greater than the 1.1 ppm value of arsenic compounds found in pools of leachate water contaminated by poultry waste [6]. Therefore, the 20% degradation by-products of ROX compounds such as monomethyl arsenite, dimethyl arsenite, arsenite and arsenate are of considerable concern to human health [1,5,6]. These arsenic compounds, especially arsenite and arsenate have a reported phytotoxicity of 1–50 mg As/kg in soil and are known carcinogens [6]. These toxic by-products are formed through photochemical and microbial degradation of ROX in poultry feces and keratinous material of feathers [2,6]. In the case of leachate in soil and aquatic environments, adsorptive methods represent a suitable approach for the physical removal of arsenicals such as ROX, arsenite, and arsenate whilst minimizing further chemical degradation.

Physical adsorption involves the formation of a noncovalent complex between an adsorbate and an adsorbent through various intermolecular interactions such as van der Waal's, dipolar, and H-bonding. Adsorption studies have been reported between ROX with carbon nanotubes or metal oxides [7,8]. The monolayer

adsorption capacity (Q_m) of multi-walled carbon nanotubes (MWCNTs) with ROX was reported to be relatively low ($Q_m = 13.5$ mg/g) at 293 K in aqueous solution. The synthesis of carbonaceous materials such as CNTs and MWCNTs typically require elaborate synthetic routes such as chemical vapor deposition [9], therefore; such carbonaceous materials are not practical adsorbent materials for the remediation of ROX. By contrast, adsorption of ROX with goethite and aluminum oxide (type C) are readily available and promising inorganic adsorbents [8] according to their greater Q_m values (goethite; $Q_m > 526$ mg/g and aluminum oxide; $Q_m > 131$ mg/g) relative to MWCNT. The above Q_m values were obtained by graphical estimates of isotherm results reported in Ref. [8]. The relatively high sorption capacity for goethite and aluminum oxides are partly attributed to the pH conditions (pH 5) since a large decrease in Q_m (~62.5%) occurs near pH 7 [8]. Therefore, the sorption capacity at ambient conditions is favored for goethite ($Q_m > 2.0$ mmol/g) over aluminum oxide ($Q_m > 0.3$ mmol/g) at these conditions, in agreement with the favorable equilibrium constants for these adsorbents with ROX [Goethite (0.56 mM⁻¹) and aluminum oxide (0.103 mM⁻¹)]. Thus, there is a need to develop versatile sorbent materials with favorable uptake properties for the removal of arsenicals. Chitosan is a polysaccharide derivative of the biopolymer chitin [10,11] that has been used as an adsorbent for many types of waterborne pollutants such as phenolic dyes [12,13], heavy metals [14–16], and organics [17]. Adsorption of arsenate with chitosan and chitosan-based copolymers was previously reported [14,15] where chitosan was found to have a low sorption capacity ($Q_m = 10$ mg/g) with arsenate at pH 3.5. Glutaraldehyde cross-linking of chitosan affords copolymer sorbents with enhanced adsorption properties due to formation of micropores and greater

* Corresponding author. Fax: +1 306 966 4730.

E-mail address: lee.wilson@usask.ca (L.D. Wilson).

accessibility of the active adsorption sites [15]. The adsorption capacity of chitosan-glutaraldehyde copolymers with arsenate oxoanions was estimated to range considerably ($Q_m = 40\text{--}228$ mg/g) and to correlate with the cross-linker content [15]. The Q_m values of such copolymers are greater than those for chitosan at pH 8.5 and such materials may be suitable sorbents for roxarsone uptake in its various protolytic forms (cf. Fig. 1A).

Herein, we report a sorption study of chitosan and its copolymers (CG) cross-linked with glutaraldehyde in aqueous solution with roxarsone and two types of phenolic dyes [*o*-nitrophenol (ONP) and *p*-nitrophenol (PNP); cf. Fig. 1B and C]. The results are compared with GAC at variable pH, salt concentration, salt type, copolymer cross-linking density, and different adsorbates (ROX, ONP and PNP). This paper will examine these variables and their effect on the equilibrium sorption properties of the various adsorbate/adsorbent systems. The pH conditions were chosen according to the pK_a values of ROX (cf. Fig. 1A) to focus on a single protolytic form of ROX for each pH condition. The salt type (phosphate and bicarbonate) and level (10–100 mM) are known to attenuate adsorption by competitive binding [8,18–20]. An understanding of the effects of phosphate anion species on the sorption properties of CG copolymers is relevant for the sorptive removal of ROX in aqueous solution. The relevance of phosphate in poultry litter relates to the release of organophosphates into ground and surface water through leaching, in addition to ROX and its by-products.

2. Experimental

2.1. Materials

Granular Activated Carbon (GAC; Norit Rox 0.8) was provided by Norit America and used as received. Low molecular weight chitosan (75–85% deacetylation, and molecular weight range: 50,000–190,000 kDa), 50 wt.% glutaraldehyde in water, glacial acetic acid, sodium hydroxide, methanol (HPLC grade) were obtained from Sigma–Aldrich Canada Ltd. (Oakville, ON). Ultrapure water (Millipore) was used for all experiments with a resistivity of 18.5 Ωcm .

4-Hydroxy-3-nitrobenzene arsonic acid (Roxarsone; ROX) was obtained from Haohua Industry Co. Ltd. (Jinan City, China) was purified by recrystallization from water. ROX is stored in the dark to prevent photodegradation. Sodium hydroxide, potassium

phosphate monobasic, sodium bicarbonate, *p*-nitrophenol, and *o*-nitrophenol were ACS grade and obtained from Sigma–Aldrich Canada Ltd. (Oakville, ON).

2.2. Synthesis

Chitosan-glutaraldehyde (CG) cross-linked polymers were synthesized with variable amounts of glutaraldehyde using a fixed mass of chitosan. Table 1 lists the conditions and the various copolymers with their abbreviations. Briefly, an aqueous chitosan solution (2% w/w) was prepared by dissolving 2 g of chitosan in 100 mL of 2% (v/v) acetic acid solution. A viscous mixture was formed after complete dissolution for ~ 12 h at room temperature with a final pH at 3.94. An aqueous solution of 0.01 M NaOH was added drop-wise to the chitosan solution until the pH was 5.6. A desired amount of 50% glutaraldehyde was added as listed in Table 1. Copolymers with variable chitosan: glutaraldehyde weight ratios were prepared: CG11 (1:1), CG21 (2:1), and CG31 (3:1). Gelation of the reaction mixture occurred rapidly and the transparent gel became a dark yellow over a 1 h period. The gel was left overnight to allow aging to occur. Thereafter, a 2 M aqueous solution of NaOH was added drop-wise into the gel phase for $\sim 3\text{--}4$ h until a dark brown suspension was produced and the final pH reached pH ~ 7 . The insoluble copolymer products were vacuum filtered and subsequently washed with several portions of Millipore water (500 mL) and cold acetone (50 mL). The material was then crushed after partial air-drying and then allowed to air dry further for 24 h. The product was ground with a mortar and pestle and the dark brown powdered product was washed in a Soxhlet extractor using methanol for 48 h at 60 °C. The product was dried under vacuum at 60 °C and then ground with a mortar and pestle, followed by sieving through a 40-mesh sieve to ensure uniform particle size, followed by storage in a desiccator until further use.

2.3. Copolymer characterization

2.3.1. FT-IR spectroscopy

IR Spectra were obtained using a Bio-RAD FTS-40 Spectrometer in diffuse reflectance mode Fourier Transformation (DRIFT) with and corrected against KBr matrix as background. 16 scans were acquired per sample over a range of 500–3500 cm^{-1} in Kubelka–Munk intensity units. Samples were prepared in a 1:1

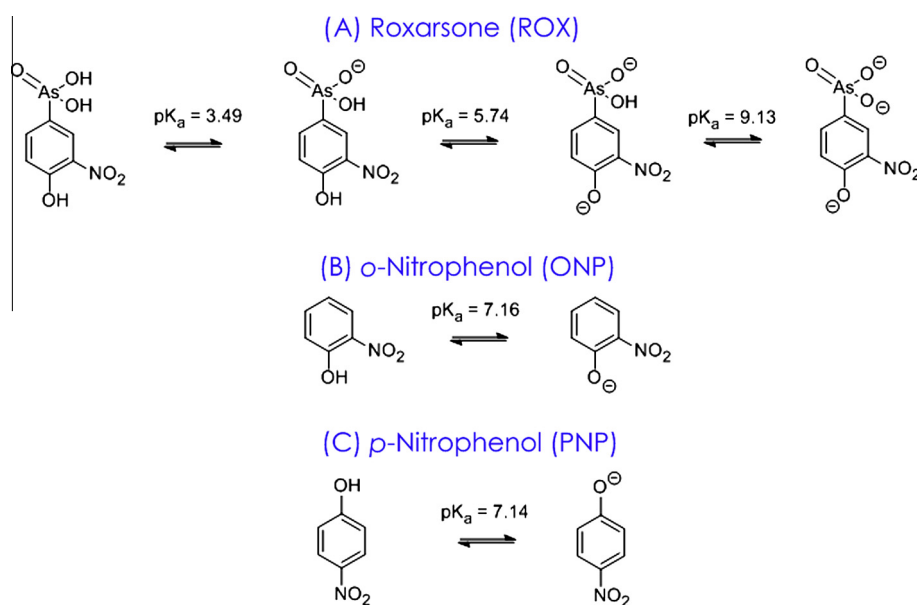


Fig. 1. Molecular structure and pK_a of roxarsone (ROX), *p*-nitrophenol (PNP), and *o*-nitrophenol (ONP) [7].

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