Mechanism of arsenic removal using chitosan and nanochitosan

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ABSTRACT

Chitosan, a natural polysaccharide copolymer of glucosamine and N-acetyl-glucosamine, possesses one free primary amine and two free hydroxyl groups on each glucosamine unit. It has a polycationic nature and an abundance of amine functional groups. The sorption equilibrium and kinetics of arsenate onto chitosan flakes have been studied. The effect of pH on the adsorption capacity and the uptake kinetics is an important parameter to investigate the adsorption mechanism of anionic species such as arsenate ions on the protonated amine groups of chitosan. The equilibrium sorption and batch kinetic studies of arsenate ions on chitosan were performed at initial As concentration of 250–11,000 $\mu g\,L^{-1}$ and initial pH ranging from pH = 3.50–5.50. The experimental results showed that initially for approximately the first 30 min there is a rapid and high adsorption of arsenate ions onto the chitosan leading to a maximum uptake capacity after this short time. However, this stage is followed by a slow desorption of arsenate from the chitosan with a steady increase in solution pH. A novel reversible pseudo-first order kinetic model was developed and applied to correlate this newly reported adsorption–desorption phenomenon. The physical and chemical properties of chitosan were studied and presented in terms of its surface and structural properties such as the degree of deacetylation, crystallinity, surface charge and its swelling properties.

1. Introduction

The contamination of natural waters by arsenic, as arsenites As(III) and arsenates As(V) is a serious problem in several countries. In addition to arsenic contamination from industry [1,2] the high concentrations of arsenic found in groundwater and surface waters has raised concerns in many parts of the world, including Bangladesh [3], Taiwan [4], India [5], Chile [6], Vietnam [7] and the western United States [8].

Arsenic is known as a poison of acute toxicity and now its long term carcinogenic properties have been demonstrated, particularly with respect to lung and skin cancer [9]. The European Commission [10], the USEPA [11] and the W.H.O. [12] have recently revised the maximum concentration limit for arsenic in drinking water by decreasing it from 50 $\mu g\,L^{-1}$ to 10 $\mu g\,L^{-1}$.

The two species of arsenic complicate the treatment problem. Conventional treatment technologies include coagulation, precipitation, coprecipitation with iron and aluminum compounds [13], adsorption onto a range of materials including alumina, active carbons and aminated species [14,15], ion exchange and membrane technologies such as reverse osmosis [16]. As(V) is better removed than As(III) because of the low surface charge, which makes

As(III) problematic unless it can be oxidized to the As(V) form. Most research is based on oxidation technologies, using iron compounds, for example, the addition of iron salts [17]. Most of these studies were conducted with Fe(III) compounds and minerals. Goethite and hematite have been widely used for the sorption of As(III) and As(V) [18]. Arsenic adsorption on ferrihydrite has been studied [19] and amorphous iron oxide [20]. Other types of adsorbents based on iron such as industrial Fe(III)/Cr(III) hydroxide waste [21] and iron-alumina combinations, such as, fly ash [22] are being increasingly investigated.

The utilization of biomaterials for the treatment of waters and wastewaters containing heavy metal is gaining more attention as a simple, effective and economical means of pollution remediation. In the present study the adsorption of arsenate ions onto chitosan, a biopolymer, has been studied over a range of conditions. Chitosan and its source chitin, derived from waste seafood shells, have been used successfully to adsorb dyes [23,24] and metal ions [25,26]. Chitosan is effective in the adsorption of transition metal ions due to the presence of amino (–NH$_2$) and hydroxyl (–OH) groups on chitosan chains, which serve as coordination and electrostatic interaction sites, respectively [27–29].

The removal mechanisms of metal ions on chitosan adsorbents remain controversial with theories including chemisorptions and complexation. It is reported that the uptake of transition metals on chitosan (R–NH$_2$) is mainly effective via coordination with the

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Nomenclature

CT	contact time in Fig. 1	pH$_i$	initial pH
H	hours in Fig. 1	pH$_e$	equilibrium pH
D	days in Fig. 1	pH$_{pzc}$	point of zero charge
NO	nitrate ions in Fig. 8	pK_a	dissociation constant of arsenic species
CL	chloride ions in Fig. 8	q_e	equilibrium solid-phase concentration, μg g^{-1}
SO	sulfate ions in Fig. 8	q_m	monolayer adsorption capacity, μg g^{-1}
C_0	initial liquid-phase concentration, μg L^{-1}	q_{max}	maximum adsorption capacity, μg g^{-1}
C_e	equilibrium liquid-phase concentration, μg L^{-1}	q_t	solid-phase concentration at time t, μg g^{-1}
k_{+1}	rate constant of adsorption in Eq. (8),	SSE	sum of the squares of the error, dimensionless
k_{-1}	rate constant of desorption in Eq. (9),		

unprotonated amino groups. The uptake of anionic species on chitosan occurs via electrostatic interaction with the protonated amino groups [30].

The investigation of the adsorption equilibrium, adsorption kinetics and mechanism of arsenic on chitosan are of particular interest and importance from both fundamental and practical viewpoints. In the present study the reaction mechanism and adsorption mechanism of arsenic removal with chitosan has been studied and developed based on the physical and chemical properties of chitosan. The surface and structural properties of chitosan and adsorbed chitosan were investigated to determine the changes upon adsorption of arsenic. The speciation changes of arsenic in aqueous phase were determined under various pH conditions and the adsorption/desorption mechanisms of arsenic on chitosan have been discussed.

2. Materials and methods

2.1. Chitosan

Chitosan (poly-β(1-4)-2-amino-2-deoxy-D-glucose) is a partially deacetylated polymer of acetylglucosamine prepared from chitin (poly-β(1-4)-2-acetamido-2-deoxy-D-glucose). The chitosan flakes used in this research were purchased from Sigma Chemical Company and is practical grade material extracted from crab shells with minimum 85% degree of deacetylation.

2.2. Pretreatment of chitosan

The commercial chitosan was sieved to obtain four discrete particle size range of (250–355, 355–500, 500–710 and 710–1000 μm) with stainless steel sieves (BS410/1986, Endecotts Ltd.) and rinsed several times with deionised water to desorb any impurities from the chitosan. Then, the portions were dried under vacuum for 3 days and kept in a dessicator before use. The properties of chitosan, including its density, porosity, specific surface area and its surface charge in terms of the point of zero charge (pH$_{pzc}$) were characterized and shown in Table 1.

2.3. Sodium arsenate and arsenate determination

All chemicals were reagent grade and were used without further purification. All solutions were prepared with deionised water and all laboratory ware was cleaned by soaking in 2% dilute nitric acid (HNO$_3$) and rinsed with deionised water. A stock solution of As(V) was prepared from the dissolution of sodium arsenate heptahydrate salt (Na$_2$HAsO$_4$·7H$_2$O) (Aldrich Chemical Company, Inc.) at a concentration of 500 mg L^{-1}.

Hydride generation inductively coupled argon plasma optical emission spectroscopic analysis (HY-OES-ICP) using a continuous flow system (Perkin Elmer OPTIMA 3000 XL) was used to measure the concentration of arsenic in water. Hydride generation techniques have been combined with ICP optical emission spectrometry (ICP-OES) for the routine determination of the concentration of arsenic since 1978. Three calibration standards (100, 500 and 1000 μg L^{-1}) were prepared and the samples were automatically measured five times in one aspiration. Three quality control standards (100, 500 and 1000 μg L^{-1}) were measured before and after the analysis of samples.

2.4. Equilibrium studies

The equilibrium contact time required for chitosan adsorbent was determined by agitating several sets of 0.0250 g of commercial chitosan, with particle size range of 250–355 μm, with 50 ml of six initial concentrations of arsenate solution (C_0 = 1.0, 2.0, 3.0, 5.0, 7.5 and 10.0 mg L^{-1}) in a capped 125-ml HDPE bottles at initial pH ranging from pH$_i$ = 3.50 ± 0.05 to pH$_i$ = 5.50 ± 0.05 and a constant temperature of 24 ± 2 °C for 10 days with an orbital shaker (Heidolph UNIMAX 1010 and Heidolph INKUBATOR 1000) at 200 rpm. The concentrations of arsenate in the aqueous phase at the time intervals of 1, 2, 4, 6, 8, and 10 days were determined by collecting a sample from one set of adsorbent and adsorbate solution. After 8 days it appeared that the slow arsenate ions desorption process had completed and true equilibrium was achieved. To ensure true equilibrium is achieved all equilibrium studies in this work would use a safe contact time of 14 days. The arsenate solutions with initial concentrations ranging between 250 and 11,000 μg L^{-1} were prepared by diluting a 500 mg L^{-1} stock solution with deionised water. The pH values of the As(V) solutions were initially adjusted by addition of diluted hydrochloric acid (0.01 M, 0.1 M and 1 M) and were measured with a digital pH meter (Orion, model 420A pH meter). The equilibrium adsorption capacities of arsenate on chitosan with the presence of chloride ions, nitrate ions and sulfate ions were also investigated. Three commonly used diluted inorganic acids (0.1 M), namely hydrochloric acid, nitric acid and sulfuric acid were employed for the initial pH adjustment of the arsenate solution to pH$_i$ = 3.5, 4.0 and 5.0 in the study of effect of co-existing anion.

2.5. Batch kinetic experiments

The adsorption kinetic studies of As(V) on chitosan were evaluated by agitating several sets of 0.850 g of commercial chitosan with particle size range of 250–355 μm in 1.7 L of As(V) solution for 24 h in the batch kinetic system, which has been described previously [31]. The pH of the As(V) solutions with the concentration of 3000 μg L^{-1} was initially adjusted to the initial pH, pH$_i$ = 3.50, 4.00 and 5.00 by the addition of dilute hydrochloric acid and dilute sodium hydroxide similar to the equilibrium studies. The volume-