Report for 2005AK43B: Investigation of the mechanism of arsenic biosorption by modified crab shells

Publications

- Other Publications:
    - Zhang, H. and Schiewer, S. "Influence of chitosan physicochemical properties on its adsorption of arsenate". Presentation given at the 231st American Chemical Society National Meeting, Atlanta, GA, March 26-30 2006.

Report Follows

Investigation of the Mechanism of Arsenic Biosorption by Modified Crab Shells

Problem and research objectives

Problem: potential pollution of surface waters by mining activities

Alaska's economy is largely resource-based with mining being one of the major economic activities in the interior. Water resources may be impacted by mine tailings and leachate. Toxic heavy metals present in these waste streams may bio-accumulate in the food chain if released into the environment. Arsenic is a toxic metalloid that can be associated with gold mining tailings. Therefore it is necessary to properly treat any effluent and waste from mining operations. Especially for industries like mining, where large quantities of waste streams are generated, it is important to develop cost-efficient clean-up technologies. In this respect, biosorption is a promising avenue, since cheap raw materials from other industries can be used as biosorbents. Biosorption combines the advantages of being, on the one hand, highly efficient at metal removal and, on the other hand, much more cost-effective than comparable techniques such as ion exchange (Volesky 1990).

Results from prior research

The first phase of this research project (see last year's report) investigated the production of biosorbents from crab shells. Crab shells are a waste product of Alaska's fisheries industry, which is an important economic factor in the coastal regions. Our goal for the first phase of the research was to produce a material rich in chitosan, which carries amine groups that can bind arsenate.

Our past research showed that by increasing the concentration of NaOH up to 40%, chitin could be efficiently converted to chitosan. The efficiency of this conversion was measured by FTIR as the degree of deacetylation (DDA). Increased DDA lead, to some extent, to increased metal binding. The optimal binding of arsenate was obtained at pH 5, where arsenate is negatively charged and chitosan should be positively charged. This preliminary research indicated that electrostatic interactions between negatively charged arsenate complexes and positively charged amine groups of chitosan are likely an important binding mechanism.

However, the relationships between deacetylation, availability of amine groups, surface charge, and arsenate binding including the binding mechanism were not investigated in our past work. Therefore the goal of the second phase of our research, as reported in this document, addressed this issue.

Hypothesis and objectives

The main ***hypothesis*** of the present research was that amine groups of chitosan play an important role in As binding by modified crab shells.

Objectives of the research were to investigate the effect of pH and electrostatic properties (sorbent charge), characterize the sorbent, and investigate the binding mechanism, particularly with respect to chitosan amine groups.

Materials and Methods

All experiments used double deionized (DDI) water and ACS reagent grade chemicals. Arsenic stock solution with concentration of 10 mM at pH 5 ± 0.2 was prepared by dissolving $Na_2HAsO_4 \cdot 7\ H_2O$ (J.T. Baker) in DDI water.

Preparation of chitin and chitosan. The freeze-dried Alaska king crab shells were crushed manually. The particle size fraction between 1-2 mm was sieved out for further processing. The decalcification of chitin was carried out according to the method suggested by Muzzarelli (17), by soaking the crushed crab shells in 50 g/L hydrochloric acid (HCl) at room temperature for 24 hours. After that, 5% NaOH solutions were used for a three-fold extraction for about 40 minutes to remove the proteins. The chitin produced was washed to neutral pH after those reactions. Chitosan samples with different DDA were obtained by hydrolyzing chitin in concentrated NaOH solutions (10% to 40% (w/w)) at a temperature of 90-12° C for 5-120 minutes. A sample with DDA ~100% was obtained by successive alkali treatments, the samples were hydrolyzed twice with 40% NaOH at 120° C for 120 minutes each, and washed with distilled water till neutral pH before the 2nd treatment.

Determination of degree of deacetylation (DDA). The DDA for chitosan samples obtained by different processing methods was determined with ^{1}H-nuclear magnetic resonance (NMR) spectroscopy. To obtain the ^{1}H-NMR spectra of low DDA chitosan, 10 mg of sample were dissolved in 2 mL 20% (wt./wt.) deuterium chloride (DCl), while for high DDA chitosan the same amount of sample was dissolved into 1.96 mL of D_2O and 0.04 mL of 20% DCl. The spectra were recorded on a 300 MHz ^{1}H-NMR (Varian-Mercury-300BB) spectrometer. The software (VNMR) was employed for data analysis. Dividing the peak area for the acetyl group HAc, which possesses three hydrogen atoms, by three and the signal area H26 of the ring structure, which possesses six hydrogen atoms, by six, allows calculating the fraction of acetylated groups as (HAc/3)/(H26/6).

Determination of crystalline size and crystallinity**.** Powder x-ray diffraction (XRD) was applied to study the crystallographic properties of chitosan after fine grinding. The x-ray diffraction patterns were obtained on a wide-angle x-ray diffractometer (for $Ka_{1,Cu}$, radiation λ is 1.5405Å). The voltage was 40 kV and the intensity was 40 mA. The 2θ angle was scanned between 3° to 35°, and the counting time was 2 s at each step (0.01^o).

Adsorption study. Sorption isotherm and kinetic studies were carried out by using chitosan with 1 g/L concentration and As(V) solution with concentration ranging from 0.75 ppm to 75 ppm. The pH was controlled at 5.0 throughout the adsorption process by adding 0.1N HNO_3 and 0.1N NaOH using an Methohm 719s autotitrator. Continuous mixing was applied by magnetic stirring. Preliminary kinetic studies (data not shown) suggested that 20 minutes were sufficient for equilibration. After 20 minutes, the samples where filtered out through a macrofilter (0.45 µm pore size). The initial and equilibrium concentrations of As(V) were determined by graphite furnace atomic adsorption spectrometry (PerkinElmer AAnalyst 300). The uptake amount q (mg/g) was calculated from the mass balance for arsenic.

Principal findings and significance

Determination of DDA by NMR

Representative ^{1}H-NMR spectra of some chitosan samples with high and low DDA, respectively, are presented in Figure 1. Generally, higher temperature, higher base concentration and longer reaction time will lead to higher DDA. However, to achieve 100% deacetylated chitosan, successive alkali treatment must to be applied.

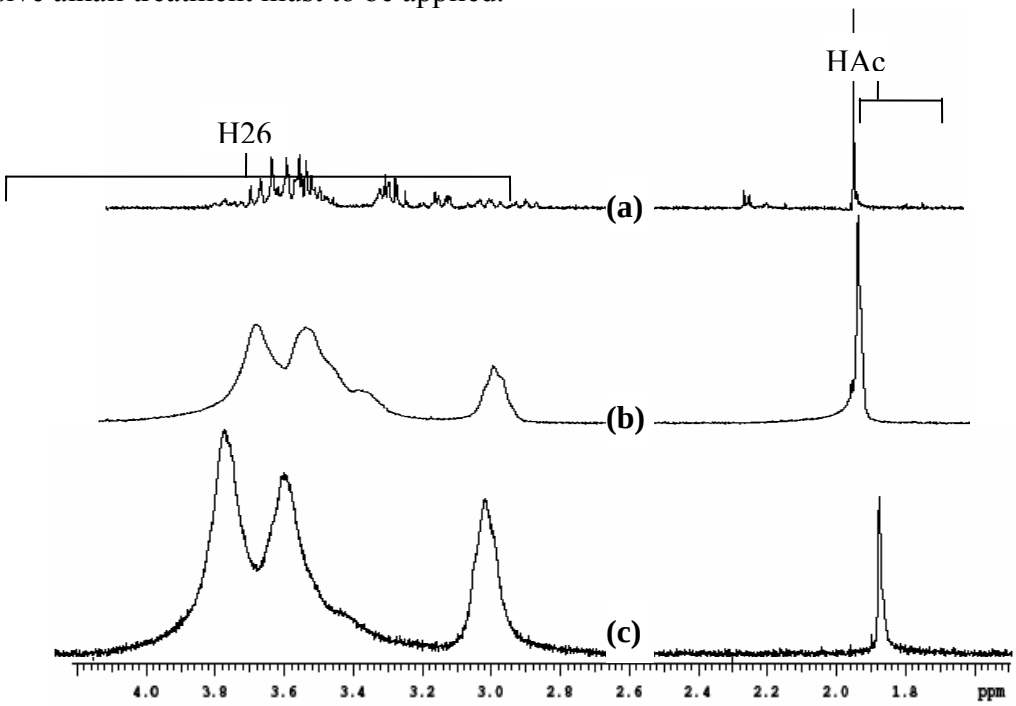

Figure 1. ^{1}H-NMR spectrum for chitosan with (a)DDA~43 (with 20%DCl solution), (b) DDA~71 and (c) DDA~91.

Comparison of FTIR and NMR for determining the DDA

In our past research (see prior report) we used the DDA as determined by FTIR as the measure to quantify the degree to which chitin was converted to chitosan. However, while the FTIR method can reliably be used to compare the efficiency of conversion in qualitative terms, it is not necessarily a quantitatively reliable method. Depending on which peak ratios are calculated based on the obtained FTIR spectra, different DDA values can be calculated from the same samples. Therefore our current research also employed the more complex method of nuclear magnetic resonance (NMR) for determining the DDA. NMR can quantify the numbers of hydrogen atoms in different locations of the chitosan structure and can therefore provide a quantitative measure. The NMR DDA results were used to calibrate the FTIR DDA values. As shown in Figure 2, a very good correlation exists between both methods of measurement. The correlation has a slope of almost one, which is ideal. The offset by a DDA of 0.72 is negligible in the measured DDA range. This indicates that for further research it is possible to utilize either technique. The simpler FTIR method can also be used reliably for DDA determination.

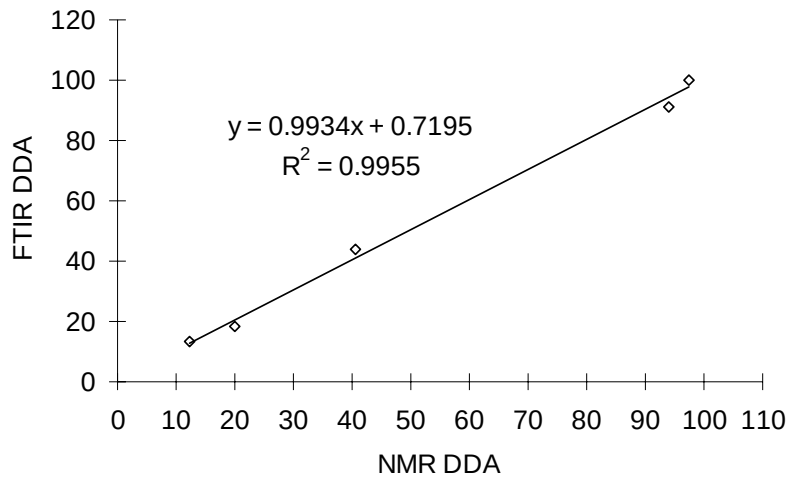

Figure 2. Correlation between DDA values determined by FTIR and NMR, respectively.

Characterization of surface charge by measuring the zeta potential
The zeta potential indicates the surface charge of a particle at a certain distance from the surface (shear plane). For materials that undergo acid base reactions, the surface charge depends on pH. Since chitosan has amine groups, which are positively charged at lower pH values, it is expected that the charge would be positive at low pH and then decrease when the pKa of the surface functional groups is reached.

This is confirmed by our experiment data. As shown in Figure 3, for all chitin/chitosan materials, the surface charge is positive up to ~pH 8. The magnitude of charge increases somewhat with increasing DDA. However, the charges are not directly proportional to the DDA, as one might have expected. At pH 5, for example, where most As binding experiments were performed, only the samples with DDA 13 show a much lower zeta potential than the samples with DDA 42-DDA95, which all have a similar potential.

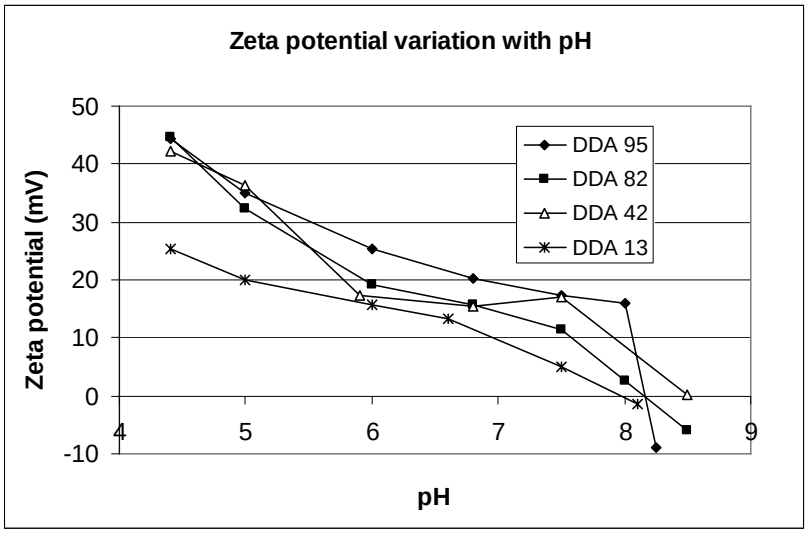

Figure 3. Electrical surface potential of chitin/chitosan with different DDA as a function of pH.

Arsenate uptake

The observation that there are no large differences among samples with DDA > 40 matches the findings with respect to arsenate binding by chitin/chitosan samples with different DDA. Beyond a DDA of 40, no significant improvement of arsenate binding was achieved for increasing DDA, as shown in Figure 4.

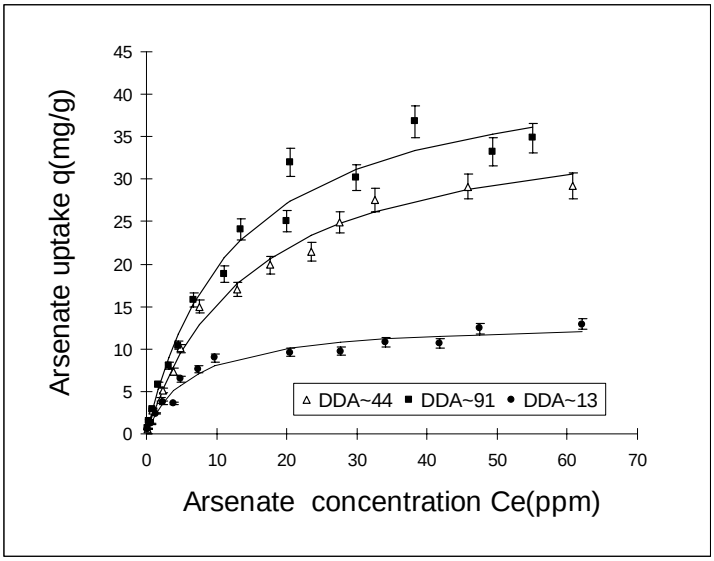

Figure 4. Arsenate sorption isotherms at pH 5 for chitin/chitosan with different DDA.

A potential reason for no increase in arsenate binding beyond DDA 40 may be that not all deacetlylated amine groups are available for arsenate binding. Those in crystalline regions may be less accessible than those in amorphous regions. Therefore the crystallinity and crystallite size were measured using XRD. For DDA lower than 50%, both the CrI and the crystallite size did not vary significantly with increasing DDA, whereas at high DDA (≥ 90 %), the CrI reduced to approximately 60% (data not shown).

References

Muzzarelli, R.A.A. 1973. *Chitin*, Pergamon Press, Oxford, p 17.

Volesky, B. (1990) Removal and recovery of heavy metals by biosorption. In: Volesky, B. (Ed.), *Biosorption of Heavy Metals*, CRC Press, Boca Raton, FL, 7-43.