

Report for 2004AK26B: Development of Crab Shell Based Biosorbents for Removing Anionic Metal Complexes From Contaminated Water

- Conference Proceedings:
 - Zhang, H.; Schiewer, S. 2005. Arsenic (V) sorption on crab shell based chitosan. In: Proceedings of ASCE EWRI World Water & Environmental Resources Congress, Anchorage, AK, May 15-19 (7 pp.).
- Other Publications:
 - Zhang, H.; Schiewer, S. 2005. Poster presentation: Arsenic (V) sorption on crab shell based chitosan. In: Proceedings of ASCE EWRI World Water & Environmental Resources Congress, Anchorage, AK, May 15-19.

Report Follows

Problem and research objectives

Mining is one of the major economic activities in Alaska's interior. Mining operations generate leachates from mine tailings containing toxic heavy metals. Due to the large amounts of waste streams to be treated, it is important to develop cost-efficient methods to remove heavy metals from contaminated waters such as tailing leachates.

A particularly cost-effective method for heavy metal removal from waste streams is the emerging process of biosorption. Biosorption is defined the passive uptake of heavy metals by biomass. This process 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). One reason for this cost-effectiveness is that waste products from other industries can be used as biosorbents.

Alaska's Fisheries industry, which is an important economic factor in the coastal regions, produces large quantities of crab shells as waste products. These crab shells contain chitin as one of their main constituents. Chitin/chitosan, which is produced industrially from materials such as crab shells, can be effective at binding heavy metals (Guibal 1999, McAfee 2001, Navarro 2000), however they are rather costly. Since chitosan contains positively charged amine groups, it can be hypothesized that crab shells will be particularly suitable for removing anionic metal complexes. The current project focuses on utilizing crab shells as low cost biosorbents for the removal of heavy metals from aqueous solutions, for example mine leachates.

The goal of the proposed project was to develop an efficient biosorbent from waste crab shells. The objectives were to

- Optimize the processing methods and conditions (temperature, concentration of reagents) to convert waste crab shells into an efficient biosorbent
- Characterize the resulting biosorbent material
- Test the obtained modified crab shell materials in arsenic biosorption studies
- Compare different crab shell derived materials regarding their sorption capacity.
- Investigate the effect of pH on sorption performance and determine optimal conditions.

Methodology

All experiments used double deionized water (DDI) and ACS reagent grade chemicals. Arsenic stock solution was prepared by dissolving $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ in double deionized water.

a) Preparation of chitin and chitosan

The freeze-dried crab shells were crushed manually. The particle size fraction between 1-2 mm was selected for further processing. According to the method suggested by Muzzarelli (1977), the decalcification was carried out by soaking the crushed crab shells in 50 g/L hydrochloric acid (HCl) at room temperature for 24 hr (8 hr, 3 fold). After that, 5% NaOH solutions were used for a three-fold digestion of about 40 min to remove the proteins. The chitin produced was washed to neutral pH after those reactions. The deacetylation of chitin was achieved by soaking the chitin samples in NaOH solutions of various concentrations ranging from 10% to 40% (w/w) at 121°C in an autoclave for 120 minutes.

b) IR Spectroscopic studies

Fourier transform infrared (FTIR) measurements were carried out as described by Yoshihiro et al (1996). Accordingly, KBr discs were prepared from dried mixture of about 1 mg of the sample and 100mg of KBr powder. The IR spectrum was recorded on a Thermo IR100 spectrometer. DDA is measured by calculating the ratio of the absorbance of a probe band (PB),

whose intensity changes with DDA with the absorbance of a reference band (RB), whose intensity does not change with DDA. The intensities of the adsorption bands were determined based on the baseline method.

c) Arsenic (V) sorption

The arsenic biosorption was carried out by contacting known quantities of sorbent (1g/L) with arsenic anion solutions within a range from 0.01mM to 2.5 mM at an initial pH value 5. The pH was adjusted manually with HNO₃ or NaOH as required. Biosorption was performed under magnetic agitation at 200 rpm at 20° C for 2 hours. Membrane filters (0.45 µm) were used to separate the sorbents from the equilibrium solution. Arsenic concentrations in the solutions before and after the sorption process were determined by an inductively coupled plasma mass spectrometer (ICP-MS).

d) Titration

Titration of the sorbents was carried out on a Metrohm 719 titrator. The samples were suspended or dissolved in 0.3N HCl solutions, and titrated by 0.1 N NaOH. A curve with 2 inflection points was obtained, from which both the pK_a of the amino group and the amount of surface charge on the sorbent were calculated.

Principal findings and significance

FTIR determination of chemical modification effectiveness (conversion to chitosan).

The main goal of the chemical treatment was to obtain a sorbent with a high content of chitosan, which contains amine groups. Chitosan is obtained by deacetylation of chitin. Therefore the degree of deacetylation (DDA) indicates how efficient the treatment was.

To evaluate the degree of deacetylation, FTIR spectra, which indicate the presence and abundance of functional groups in the tested material, were used. To interpret the FTIR spectrum, the peak of carbonyl stretching in the amide group at 1650 cm⁻¹ and 1630 cm⁻¹ was chosen as to indicate the amount of amide groups, and the peak of CO stretching at 1070 was chosen as the reference band to indicate the total amount of monomers as suggested by Duarte et al. (2002).

For a certain source of chitin, the DDA is determined by three factors i.e. base concentration, reaction temperature and reaction time. The results presented in Fig. 1 show a linear relationship between the DDA and base concentration for fixed reaction temperature and reaction time. Sorbents with DDA ranging from 14% to 89% were obtained for adsorption studies.

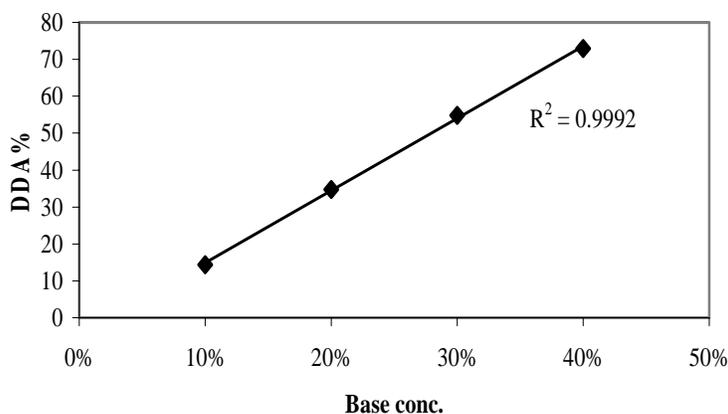


Fig. 1 Influence of base concentration on DDA

Arsenic Adsorption isotherms

The sorption capacities of sorbents with different DDA were evaluated by conducting isotherm studies. The results (Fig. 2) show that the uptake of As (V) increased with an increase of DDA from 10% to 50%, whereas at very high DDA (approximately 90%), the adsorption capacity of the sorbent decreased. This is because DDA determines both the amount and availability of the functional group which can bind As (V). It has been shown (M.L.Duarte et al., 2002) that in the DDA range from 0-80%, the amount of amino groups increases and the crystallinity of the polymer decreases with the increase in DDA, which means that more binding sites are exposed. However, in the very high DDA range (approximately 90%), the As(V) uptake decreases even though the amount of functional groups is increased. This probably occurs because of re-crystallization due to high deacetylation (M.Jaworska et al., 2003). Increased crystallinity may reduce binding site accessibility due to tight packing of chitosan fibers, creating steric hindrance for arsenic. In the present research, the influence of crystallinity on sorbent's adsorption capacity still needs to be confirmed via X-ray diffraction.

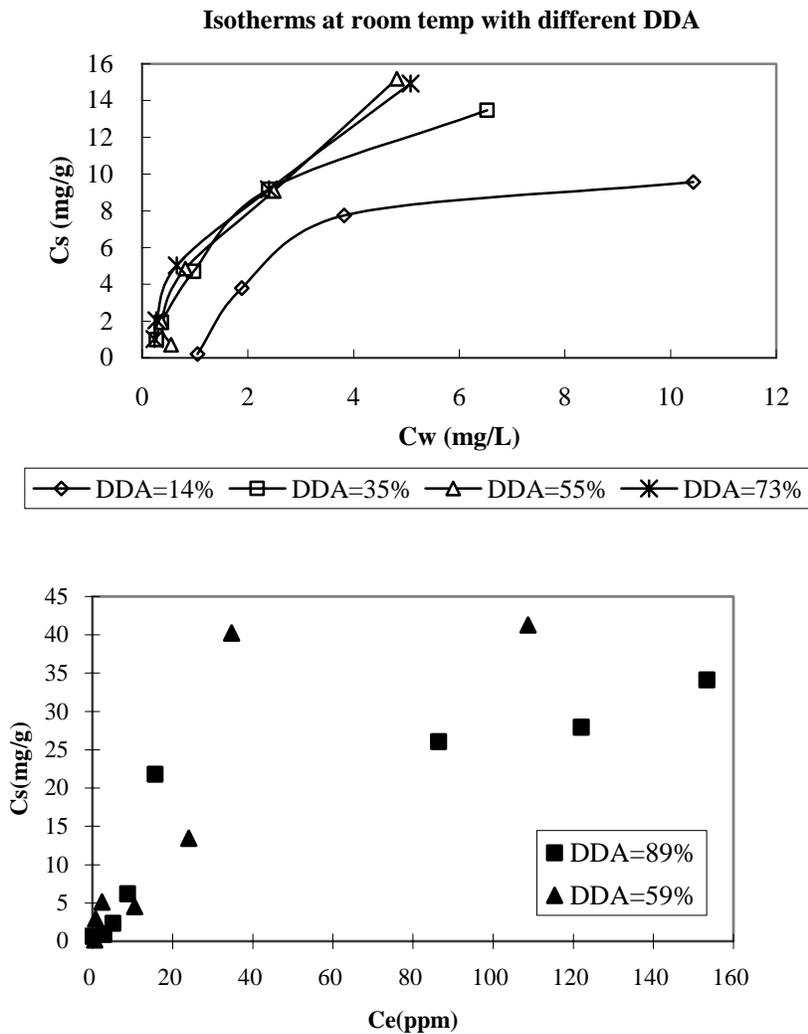


Fig. 2. Adsorption isotherms (a) with DDA ranging from 14 – 73% (b) at DDA 59% and 89%

3.2 Optimization of pH

Sorbent with DDA 59% was used to study the change in As(V) sorption capacity with pH. As shown in Fig. 3, the maximum uptake was observed at pH 5, while at both pH 2 and pH 8, the uptake is very low. This difference in uptake can be explained by analyzing the surface charge of sorbent as well as sorbate. The pK_a 's for As(V) are 2.2/6.7/11.6 ($H_3AsO_4/H_2AsO_4^-/HAsO_4^{2-}$). Therefore, at pH above 3 at least approximately 80% of As(V) is in the form of negatively charged species. For chitosan, both the buffer capacity of the amino group and the total surface charge (Fig 4) were calculated from the potentiometric titrations. Since the buffer intensity reaches a maximum at the pK_a , it can be seen from Fig. 4 that the amino group in the sorbent has a pK_a at approximately 6.8. This implies that at pH below 6, most of the amino groups were positively charged. Thus, the maximum uptake is expected in the pH range 3-6, which was confirmed by uptake measurements shown in Figure 3.

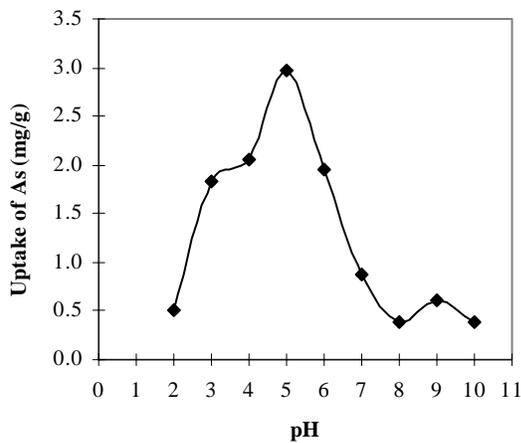


Fig.3 pH influence on As(V) adsorption

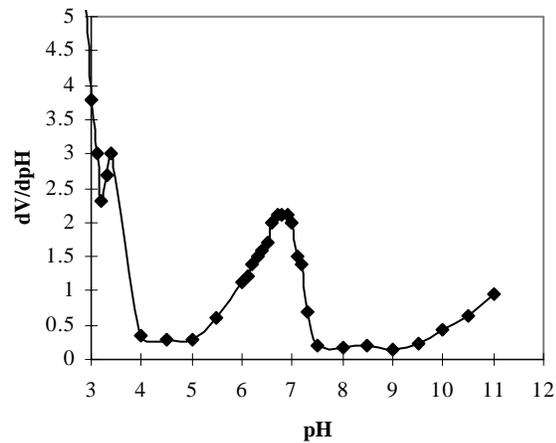


Fig.4 Buffer intensity of sorbent containing solution

The amount of charge on the sorbent can be calculated using charge balance calculations:

$$ENC: [X] = [OH^-] + [Cl^-] - [Na^+] - [H^+]$$

Where X is the charge in equivalent /mol;

Cl^- and H^+ added as HCl;

OH^- and Na^+ are added during titration.

Here $[H^+]$ and $[OH^-]$ are calculated from pH, and $[Na^+]$ as well as $[Cl^-]$ are assumed be same amount as added initially.

Fig.5 shows that at low pH the sorbent is positively charged. However, in addition to amino groups, hydroxyl groups and probably the bridge oxygen, which might also be protonated may also contribute towards the total positive charge. The steep slope of the curve suggests that the weakly bound protons will be released with a slight increase in pH. In the pH range 3.5 to 5.5, only amino groups are protonated, and the total amount of positive charge is almost constant. At even higher pH, the amino group is also gradually deprotonated, and the total charge of sorbent becomes neutral. Therefore, the

surface charge curve helps in understanding the higher uptake of As (V) at pH 5, and decreased uptake at higher pH.

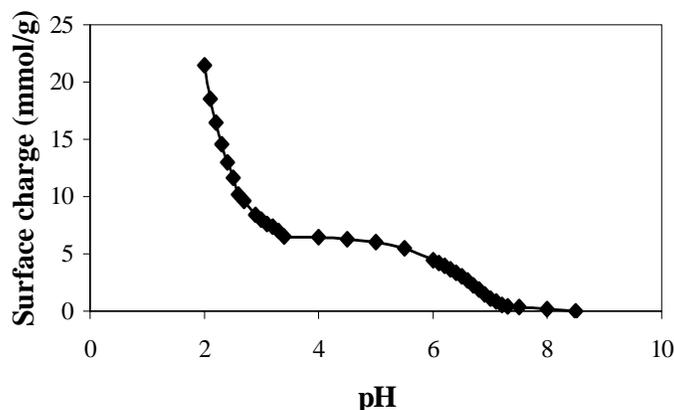


Fig. 5 Surface charge variation pH

Conclusions:

The degree of deacetylation (DDA), a very important factor in determining the amount of functional groups and crystalline character of the sorbent, increases with treatment temperature and NaOH concentration.

The adsorption capacity of the sorbent increases in the DDA range from 10%-80% because of increasing amino group content and reduced crystallinity. However, when the DDA reached 90% or higher, the sorption capacity of the sorbent decreased due to re-crystallization of chitosan.

Arsenate uptake is optimal around pH 5. This can be explained by the magnitude of charge on both sorbent and sorbate, which varies with pH. Below pH 6-7, crab shell chitosan has positively charged amino groups, which can bind arsenic oxyanions. Since arsenate is negatively charged above pH 2-3, it is in the pH range between 3 and 6 that almost all amino groups in chitosan are positively charged the As (V) is negatively charged. This matches well with the observed As uptake between pH 3 and 6, with a maximum around pH 5, suggesting that electrostatic attraction plays an important role in the adsorption process.

The results of this ongoing research show that biosorption of As(V) by crab shell based chitosan is a promising technique to treat the arsenic contamination. Ongoing research focuses on investigating the mechanism of As uptake by modified crab shells.

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