Innovative water treatment by chitosan modified diatomaceous earth (DE) for small public water systems in rural areas

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Abstract
Small public water systems play a vital role in providing safe drinking water to many rural areas in many states in the U.S. In view of the growing amounts and types of pollutants, providing safe drinking water is becoming increasingly difficult for small public water systems because of their unique geographical, financial, technical and operational constraints. The objective of this study was to develop a drinking water treatment technology for resource-constrained small public water systems using chitosan modified diatomaceous earth (DE) to remove a group of dissolved contaminants (natural organic matters, arsenic, and nitrate). Chitosan is an effective biosorbent for various dissolved contaminants mainly due to its high density amino groups and hydroxyl groups. DE of different sizes and permeability was modified by a chitosan to achieve the uniform thin coating on DE surfaces. The new adsorbent had the unique properties of both DE (good mechanical strength, large surface area, and good permeability) and chitosan (ubiquitous biopolymer with outstanding versatile adsorption capacity). The adsorption performance in removing the target contaminants was examined by batch adsorption tests.

Three Summary Points of Interest
• Chitosan modified DE showed effective removal of natural organic matters, precursors of disinfection byproduct.
• Chitosan modified DE is more effective in removing arsenate than arsenite.
• The performances of all chitosan modified DE in removing nitrate were not significant.

Keywords: Chitosan, diatomaceous earth, small water systems, arsenic, natural organic matter
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Introduction

Diatomaceous earth (DE), or diatomite, is commonly used in water filtration as filter media for small water systems identified by the EPA (EPA, 1997). There are nearly 200 DE water treatment plants in operation in the US (Bhardwaj and Mirllis, 2001). Actually, ~60% of DE produced in the U.S. is used for water filtration (USGS, 2007). DE filtration is effective in removing suspended solids as well as Giardia cysts, algae and asbestos (EPA, 1990). However, DE is not effective in removing dissolved contaminants (color, odor, taste, dissolved organics and inorganics) (WADOH, 2003; EPA, 1997). Chitosan is a cationic biopolymer derived from chitin, the second most abundant natural fiber (next to cellulose), which is found in the shells of shrimp and crab. Chitosan is an effective biosorbent for various dissolved contaminants mainly due to its high density amino groups (-NH2) and hydroxyl groups (-OH) (Bhatnagar and Sillanpää, 2009; Crini and Badot, 2008; Gerente et al., 2007; Varma et al., 2004; Guibal, 2004). Chitosan has the highest adsorption capacity among the biopolymers (Wan et al., 2010; Crini and Badot, 2008). Chitosan can be a low-cost adsorbent and has been used to remove dissolved organic contaminants (humic acid, fulvic acid, phenols, and dyes) and dissolved inorganics, such as metals (Cu, Cd, Hg, Ni, Zn, Pb, Cr, Al, As, and Mo etc.) and anions (sulfate, nitrate, fluoride), as summarized by Bhatnagar and Sillanpää (2009). The objectives of this proposed work are to develop a novel sustainable drinking water treatment technology suitable for small rural water systems by using chitosan modified DE.

Methods

Chitosan with a low molecular weight was selected to modify the surface of DE so that a thin layer of chitosan with a high degree of uniformity was formed. Commercial DE from World Minerals® was used for the experiments. In consultation with the Oneida County Health Department (OCHD), the most common contaminants which can potentially cause maximum contaminant level (MCL) violations in the Mohawk Valley of New York state are arsenic and nitrate. OCHD also has great concern about disinfection byproducts (due to the presence of natural organic matters) because disinfection is the only treatment for many of its small rural water systems.

The typical coating process will include: 1) pretreatment of DE (HCl, NaOH, or HF, if necessary); 2) dissolution of chitosan in acetic acid (2%) to prepare a dilute chitosan solution (1-4%); 3) surface modification of DE with chitosan by intensive mixing, sonication, or by elution of DE in a column with chitosan solution; 4) curing of chitosan on DE with NaOH; and 5) post-modification treatment, such as rinsing and drying. Batch studies will be conducted to examine the adsorption of target contaminants (natural organic matters, arsenic, nitrate and fluoride), alone and in combination, by agitating contaminated water (100 ml) dosed with predetermined amounts of the chitosan modified DE. After adsorption, modified DE will be separated from water by filtration and the contaminant levels in the filtrate will be analyzed to assess the adsorption performance.

Results & Discussion

Characterization of chitosan modified DE

The scanning electronic microscopy (SEM) image of chitosan modified DE is presented in Figure 1. The surface of DE was covered with a layer of chitosan. The surface coverage appeared to be uniform, although lumps of chitosan was found in certain locations.

NOM Removal by chitosan modified DE

Humic acid (Sigma-Aldrich) was used as a surrogate for natural organic matters (NOM). UV-Vis
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A spectrophotometer (Shimadzu UV-2600) was used to measure the concentrations of NOM using UV 254 as an indicate. DE modified with chitosan using various methods were able to remove NOM. The representative performance of chitosan modified DE in removing NOM is presented in Figure 2. It is evident that chitosan modified DE was effective in removing NOM. At a dose of 0.5 g/L, NOM concentration was reduced from 30 mg/L to less than 1 mg/L, representing >97% removal.

![Figure 2](image2.png)

Figure 2. Removal of NOM using 2.5% chitosan coated DE at different doses. NOM initial concentration: 30 mg/L as humic acid.

**Nitrate removal by chitosan modified DE**

Great effort was made to evaluate the performance of nitrate removal using chitosan. Different coating methods and procedures were attempted. However, none of the products obtained could significantly remove nitrate. A typical nitrate removal performance is presented in Fig. 3. The nitrate concentration only decreased slightly at the highest dose (0.5 g/L). Therefore, it is concluded that chitosan modified DE was not effective in removing nitrate.

![Figure 3](image3.png)

Figure 3. Removal of nitrate using 2.5% chitosan coated DE at different doses. Nitrate initial concentration: 20 mg/L.

**Arsenic removal by chitosan modified DE**

Arsenic typically exists in water as arsenate (As(V)) and arsenite (As(III)). Both As species were studied in this projects. Presented in Figure 4 is the arsenate and arsenite removal using chitosan modified DE at different doses. The concentrations of both As species were reduced significantly. Because chitosan modified DE can remove both As species, the adsorption represents a unique advantage in removing As from water.

![Figure 4](image4.png)

Figure 4. Arsenic Removal using chitosan modified DE at different doses. Chitosan content: 8%; Initial As concentration: 500 ppb.

The effect of pH on arsenite was presented in Figure 5. Clearly, pH had significant impacted on arsenite adsorption onto chitosan modified DE. Lower pH favored arsenite adsorption. Similar trend existed for arsenate. In addition, other competition anions in the water including chloride, nitrate, sulfate and carbonate had some interference with arsenic adsorption.

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Figure 5. Effect of pH on arsenite adsorption onto chitosan modified DE.

Student Training
Three students were trained and partially funded by this project: Robyn Christoferson, Stephen Nguyen and Alex Eanniello. All students were trained in basic laboratory safety, surface modification, adsorption tests, water quality analysis, and data analysis.

Publications/Presentations
- Xinchao Wei, Carolyn Rodak, Robyn Christoferson, Stephen Nguyen “Contaminants removal by chitosan modified diatomaceous earth for small public water systems”, The 2017 AEESP Research and Education Conference, June 20-22, 2017, Ana Arbor, MI
- Xinchao Wei, Nathaniel Cady, Aaron Mosier “Synergistic effect of metal combinations in ferrite nanoparticles for As (III&V) removal,” The 252th ACS

References