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Biosorbent for tungsten species removal from water: Effects of co-occurring inorganic species

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Abstract

The effect of co-occurring inorganic species on the removal of tungsten from water was investigated using biosorbent (i.e., chitosan coated montmorillonite clay). Simulated natural water and well water from Fallon, NV were used for this study. The concentrations of tungsten (21–541 mg/L) and inorganic species ($[H_2CO_3] = 0$–4.2 mg/L, $[H_4SiO_4] = 0$–90 mg/L, and $[SO_4^{2-}] = 0$–400 mg/L) in simulated feed water were varied. The concentration of tungsten in the well water was 26 µg/L. The pH level of simulated feed water and well water was adjusted to 4 since this pH was found to be the most effective pH for the tungsten removal using chitosan coated clay. Tungsten removal without the existence of co-occurring inorganic species decreases from 99.8 to 87.1% with an increase in initial tungsten concentration from 21 to 541 mg/L. It reduces further as the co-occurring inorganic species concentration increases. The percentage of the tungsten removal ranges between 68.2–93.8%, 66.7–94.2%, and 53.6–93.7% for simulated natural water containing varied amount of H_2CO_3, H_4SiO_4, and SO_4^{2-}, respectively. The adsorption kinetic data could be best described by the pseudo second order expression. The adsorption equilibrium data was modeled with the Langmuir, Temkin, and Freundlich equations and was found to be represented well by the Langmuir equation. The essential characteristics of the Langmuir isotherm indicate that the adsorption of tungsten on chitosan coated clay is favorable regardless of the presence of interfering species. Compared to natural clay, chitosan coated clay has about 116 times larger adsorption capacity per gram of chitosan, which makes it a superior adsorbent. However, the maximum tungsten adsorption capacity decreases in the presence of co-occurring species since the co-occurring species suppress the adsorption. For the well water treated with biosorbent, the tungsten concentration in the product water was found to be lower than the detection limit (1 µg/L) of the inductively coupled plasma mass spectrometer (ICP-MS). The repeatable results obtained from the treatment of both simulated and well water suggest that using chitosan coated clay can be an efficient adsorbent for tungsten removal from contaminated sites.

Keywords: Tungsten; Biosorbent; Chitosan; Clay; Water treatment; Adsorption kinetics; Adsorption dynamics

1. Introduction

High level of tungsten detected in water resources has become a concern for several of the counties in the western United States of America (USA). The level of tungsten was found to be 25 µg/L (ppb) in the drinking water of Fallon, NV [1]. In 2003, the Center for Disease Control and Prevention (CDC) conducted a urine analysis for the residents of Fallon and the tungsten level in the urine of 80% of the sampled residents was found to be about eleven times higher than the level observed for the USA population [1]. Furthermore, sixteen child leukemia cases have been diagnosed in Fallon, NV and three children have died since 1997 [2]. Although there is no scientific evidence linking tungsten ingestion to the high rate of leukemia clusters found in children, local residents and some authorities believe that the high tungsten level might be the main reason for it. Therefore, the CDC nominated tungsten to be investigated further by the National Toxicology Program (NTP) [3].

Tungsten occurs naturally in ground water if the aquifers are in contact with the tungsten containing rocks. At ground

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water pH levels (between 6 and 9), the alkaline metals found near tungsten containing rocks may interact with tungsten species to form soluble sodium or potassium tungstate salts and contribute to an increase of tungsten concentration in the aquifer [4]. Tungsten in water may also exist due to mining and industrial activities such as the release of poorly treated effluents from tungsten mines or tungsten treating plants and the smelting of tungsten ores in open air.

The amount of tungsten in water has not been regulated by the United States Environmental Protection Agency (U.S. EPA). Therefore, there was a lack of motivation to establish a water treatment technology for tungsten. The physical and chemical characteristics of tungsten in water will influence the effectiveness of the treatment methods. Depending on the pH level, tungsten in aqueous solutions exists in multiple and unstable ionic species [5]. At pH of 6.2 and higher, the dimeric tungstate ions (WO_4^{2-}) are in equilibrium with $W(OH)_8^{2-}$. Between pH 6.2 and 6.0, thermodynamically unstable species coexist in water (i.e., $HWO_4^-/(H_2O)W(OH)_7$, $H_2WO_4/(H_2O)_2W(OH)_6$, $HWO_3^+/(H_2O)_3W(OH)_5^+$, and $WO_2^{2+}/(H_2O)_4W(OH)_4^{2+}$). At a pH of about 6, the formation of dimeric $[W_2O(OH)_8]^{2+}$, trimeric $[W_2O_7(OH)]^{3-}$ and $[HW_4O_{12}(OH)_4]^{3-}$, tetrameric $[W_4O_{12}(OH)_4]^{4-}$, hexameric $[W_6O_{20}(OH)_2]^{6-}$ species, and the reversible formation of paratungstate A ($[HW_6O_{20}(OH)_2]^{5-}$) and paratungstate B ($[H_2W_{12}O_{42}(OH)_2]^{10-}$) occur. When the pH level is 4, the formation of pseudo metatungstate $[HW_6O_{20}]^{3-}$ and metatungstate $[H_2W_{12}O_{40}]^{6-}$ take place. If the pH level is lower than 4, tetrameric $[W_{10}O_{32}]^{4-}$ ions exist. At pH 1, tungstate species precipitate to form tungstic acid ($WO_3 \cdot 2H_2O$) [5]. Furthermore, the co-occurring inorganic species may also compete with tungsten species for the adsorption sites, thus, having an overall impact on tungsten removal. For carbon species, under oxidizing conditions and below pH 6.4, H_2CO_3 is the dominant form. From pH 6.4 to 10.3, HCO_3^{1-} ions and above pH 10.3, CO_3^{2-} ions are the dominant species. Silica is only soluble at very high pH (above about pH 12.6). Below this pH, the dissolved form of silica is H_4SiO_4. Sulfur exists in aqueous media as SO_4^{2-} for a wide range of pH (between pH 2 and 14) [6]. Therefore, at pH 4 (the pH of interest) the co-occurring inorganic species will exist in the forms of H_2CO_3, H_4SiO_4 and SO_4^{2-}.

Water treatment techniques such as ion exchange, coagulation, and membrane filtration are well known for heavy metal removal. However, the costs associated with their practical application to remove trace amounts of impurities render these methods infeasible. In our previous study, we synthesized and characterized a biosorbent for tungsten removal (chitosan coated clay) [7]. Chitosan, a product derived from chitin by alkaline *N*-deacetylation, is a natural, nontoxic, biodegradable, and hydrophilic polymer [8,9]. Its molecular structure is similar to cellulose. Chitin is the second most abundant natural polymer after cellulose and widely found in the exoskeleton of shellfish and crustaceans [10]. The price of chitosan is about \$15.43/kg [8]. The price of montmorillonite clay $[(Ca,Na,H)(Al,Mg,Fe,Zn)_2(Si,Al)_4O_{10}(OH)_2 \cdot xH_2O]$ is about \$0.04–0.12/kg, which is 20 times cheaper than activated carbon [10,11]. The tungsten removal efficiency of biosorbent and natural clay was studied using simulated water at various pH levels. Biosorbent was found to be more effective than natural clay and pH 4 was the most effective pH for the removal of tungsten using both biosorbent and natural clay [7]. However, the removal of tungsten in the presence of co-occurring inorganic species has not been investigated using this biosorbent.

The objective of this research is to study the effect of co-occurring inorganic species (carbonate, silicate, and sulfate) on the tungsten removal efficiency, adsorption dynamics, and adsorption equilibrium using biosorbent. The feed water conditions in terms of tungsten and co-occurring inorganic species concentrations were varied. Finally, the efficiency of the biosorbent was tested using the water samples received from an operational well (Fallon, NV).

2. Experimental

2.1. Materials

Low molecular weight chitosan was purchased from Sigma-Aldrich (Milwaukee, WI) and used as received. Sodium tungstate (99% purity), epichlorohydrin (99% purity), and bentonite K10 (montmorillonite) were purchased from Acros Organics (Gell, Belgium).

Sodium salts of co-occurring inorganic species: sodium carbonate (Na_2CO_3), sodium silicate ($Na_2SiO_3 \cdot 9H_2O$), and sodium sulfate (Na_2SO_4) were certified ACS grade and purchased from Fisher Scientific. Certified standard sodium hydroxide (1 N NaOH) and hydrochloric acid (1 N HCl) solutions and glacial acetic acid were obtained from Fisher Scientific (Pittsburgh, PA) and used as received. Double distilled deionized water (DDI or ultraclean water) was used for the preparation of stock solutions and simulated natural water. Well water samples were provided by the city of Fallon, NV. The chemical analyses of selected co-occurring inorganic species in well water before and after treatment listed in Table 3 below were performed by Sierra Environmental Monitoring, Inc. using SM 2320 B method for bicarbonate and carbonate, EPA 300.0 method for sulfate, and EPA 200.8 method for tungsten. The pH of the received well water was 9.2.

2.2. Coating clay particles with chitosan

A single batch of clay particles was coated with crosslinked chitosan using the procedure described in Ref. [7]. The weight of coated chitosan on clay particles was determined by a pyrolysis method. About 500 mg of biosorbent, acid treated clay, and 250 mg chitosan beads were separately weighed and placed in dry ceramic dishes. Dishes containing the materials were heated in a Thermolyne 1400 furnace (Barnstead International, Dubuque, IA) at a temperature of