Journal of Molecular Liquids 206 (2015) 262–267

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Removal of As(V) from wastewater by chemically modified biomass

Wencheng Song *, Min Zhang, Jun Liang, Guoming Han

School of Life Science, Anhui Agricultural University, Hefei 230036, PR China

ARTICLE INFO

Article history:
Received 29 December 2014
Received in revised form 4 February 2015
Accepted 2 March 2015
Available online 4 March 2015

Keywords:
As(V)
Trametes versicolor
Polyethylenimine
Surface modification
Biosorption

ABSTRACT

Herein, biomass of *Trametes versicolor* was modified by polyethylenimine (modified biomass) for its potential application of As(V) removal from aqueous solutions. The interactions of modified biomass with As(V) were studied, along with their biosorption kinetics. The results revealed that As(V) biosorption on modified biomass was affected by solution pH and ionic strength, and was a spontaneous and endothermic process. Modified biomass presented higher biosorption capacity for As(V) than that of most other biosorbents under similar experimental conditions. These results indicate the modified biomass is a promising material for the enrichment and separation of As(V) pollution from large volume aqueous solutions.

1. Introduction

Arsenic pollution has aroused considerable concerns because arsenic is a ubiquitous, toxic and carcinogenic chemical contaminant present in environment. In many parts of the world, high level arsenic has been detected in drinking water [1,2]. It can be released into aqueous system through geochemical reactions, industrial waste discharges or even the agricultural use of arsenical pesticides [3]. Long-term exposure to arsenic can lead to serious health problems, such as skin lesions, and cancers of bladder, liver, kidney, nasal passages, and stomach [4]. Consequently, it is an urgent and important mission to develop effective technology and materials for the effective removal of arsenic from aqueous solution, especially from drinking water. Generally, inorganic arsenic species, As(V) and As(III), are believed to be more toxic than the organic forms [5,6]. Besides, As(V) and As(III) are usually dominant arsenic species in surface waters and in groundwater systems, respectively [7,8]. In surface solution pH range 4–10, the dominant As(V) species ($H_2AsO_4^-$ and $HAsO_4^{2-}$) are negatively charged [9]. To keep arsenic free in drinking water, several arsenic removal techniques have been developed, including coagulation and flocculation, precipitation, adsorption, ion exchange and membrane filtration [10,11]. Adsorption is widely regarded as one of the most promising technologies because it is cost-effective, little by-product, and simple operation. Biosorption has gained important credibility in recent years because of its eco-friendly nature, excellent performance, and low cost domestic technique for remediation heavily metal contaminated wastewater [12–14].

Cell wall of microorganisms, consisting abound polysaccharides, proteins and lipids, offers many functional groups (such as carboxylate, hydroxyl, thiol, sulfonate, phosphate, amino and imidazole groups) for the binding of metal ions [15]. Hence, many microorganisms, including bacteria, yeasts, fungi and algae [16–21], can be used as biomaterials for the enrichment and uptake of heavy metal ions from wastewater. Fungi have been recognized as promising low-cost adsorbents for the removal of heavy metal ions from aqueous solutions [20]. The surface charge of fungal organisms is normally negative in pH range of 3–10 [5], which is in favor of the adsorption of cationic heavy metal ions from aqueous solutions [22–25]. However, limited information is available on the removal of anionic metals by biomass. Removal of anionic metals and metalloids, such as arsenate, chromate, molybdate and selenate, requires either chemical pretreatment of the aqueous solution and/or modification of biosorbent to specifically bind anions or neutral molecules [26]. Herein, several chemically modified biosorbents were examined for their enhanced ability to bind anions [27–30].

In this study, polyethylenimine (PEI) modified *Trametes versicolor* (modified biomass) was used to examine the feasibility of As(V) management. The effect of experimental conditions such as solution pH, contact time, and temperature was investigated. Moreover, equilibrium, kinetic and thermodynamic parameters were studied in details.

2. Experimental

2.1. Culture conditions

The fungi were cultured and prepared following the procedures outlined in previous studies [31,32]. The biomass was cultivated in potato dextrose agar (PDA) medium (4 g/L potato starch, 20 g/L dextrose, and 15 g/L agar). The Erlenmeyer flasks (250 mL) containing 100 mL of culture medium were inoculated and incubated on a rotary shaker (150 rpm) at 28 °C. Biomass was harvested by centrifugation at

* Corresponding author.
E-mail address: wencsong@hotmail.com (W. Song).

http://dx.doi.org/10.1016/j.molliq.2015.03.007
0167-7322/

8000 rpm for 15 min after 6-day incubation and washed thoroughly with distilled water. The biomass was freeze-dried, ground into particles less than 0.45 mm in diameter and stored in desiccators until used for biosorption studies.

2.2. Surface modification

Firstly, 15 g of the dried raw biomass was suspended with 5 g of PEI in 200 mL of distilled water for 3 h, and then 1 mL of glutaraldehyde solution (25%) was added as a cross-linker with stirring for 3 h. Afterward, modified biomass was centrifuged to separate the solid and liquid components and then washed enough with distilled water to remove the residue free PEI on the surface of biomass. Finally, the modified biomass was freeze-dried and stored in a desiccator until the biosorption experiments [28,33].

2.3. Characterization of biomass

Scanning electron microscopy (SEM) images were obtained on a field emission scanning electron microscope (FEI-JSM 6320F). Fourier transferred infrared spectroscopy (FT-IR) analysis was carried out on Perkin Elmer 100 spectrometer in KBr pellet. Potentiometric acid–base titration was conducted by using a computer-controlled titration system (DL50 Automatic Titrator, Mettler Toledo).

2.4. Biosorption of As(V) on biomass

The biosorption of As(V) on biomass was investigated by batch technique. Certain amounts of biosorbent suspension and $NaNO_3$ solution were mixed in Erlenmeyer flasks. After that, As(V) solution was added to achieve the desired concentrations of different components and pH was adjusted to the desired values with dilute HNO_3 and/or NaOH with a pH meter using a combination glass electrode (Mettler FE20K). The suspensions were shaken for 24 h to achieve biosorption equilibrium and then centrifuged at 9000 rpm for 15 min. The concentrations of As(V) were determined by an inductively coupled plasma atomic emission spectroscopy (ICP-AES) (ICP 6300, Thermo Fisher Scientific, USA). The amount of As(V) adsorbed on biosorbent was calculated from the difference between the initial concentration and the finial one (Biosorption % $= (C_0 - C_e) \times 100\% / C_0$ and $K_d = (C_0 - C_e) / (C_e \times m)$, where K_d is the distribution coefficient, m (g) is the mass of biosorbent, and V (L) is the volume of suspension). All the experimental data were the average of duplicate determinations, and the average uncertainties were <5%.

2.5. Procedure of potentiometric acid–base titration

0.05 g biomass was spiked into 0.01 mol/L $NaNO_3$ background electrolyte at $T = 293$ K, and purged with argon gas for 2 h under vigorous stirring to exclude atmospheric CO_2. The initial pH of suspension was adjusted to pH 3.0 by adding 0.5 mol/L of HNO_3, and then the suspension was titrated to pH 11.0 with 0.05 mol/L of NaOH at a variable increment (0.008–0.15 mL). The equilibrium value was taken when showing a drift less than 0.03 mV per minute. The data sets of pH versus the net consumption of H^+ or OH^- were used to obtain intrinsic acidity constants.

3. Results and discussion

3.1. Characterization

SEM micrographs of biomass are shown in Fig. 1. The biosorbent displays surface texture and porosity before modification (Fig. 1A) and exhibits roughness and complexity of the wall surface after modification (Fig. 1B). This is because chemical treatments may lead to rearrangement and displacement of the remaining wall constituents, thus these changes after modification indicated PEI graft on biomass are obtained by electron microscopic image [34].

FTIR spectra of the pristine and modified biomass are displayed in Fig. 2A. The FTIR spectrum of pristine biomass shows predominant bands at 3500–3200 cm^{-1} (Bonded hydroxyl OH of water and R-NH_2), 2930–2857 cm^{-1} (–CH stretching vibration in –CH and –CH_2), 1735 cm^{-1} (>C═O stretching of the protonated carboxylic or ester groups or fatty acids), 1710 cm^{-1} (C═O of the carboxylic groups in amino acids), 1655 and 1556 cm^{-1} (C═O stretching and N–H stretching vibration in amide bond respectively), 1320 cm^{-1} (S═O of the sulfonates groups and COO^- groups of the fatty acids), and 1043 cm^{-1} (–CO stretching vibration in –COH). The phosphate group also presents certain characteristic absorption peaks (P═O stretching at 1150 cm^{-1}, P–OH stretching at 1040–910 cm^{-1}, and P–O–C stretching at 1050–970 cm^{-1}) [35–37]. After the modification with PEI, the amide I (C═O stretching of amides) and II bands (N–H and C═N stretching of amides) [38,39] appeared at 1655 and 1556 cm^{-1} are shift to 1652 and 1550 cm^{-1}, respectively. Additionally, the disappearance of the carboxyl peak at 1247 cm^{-1} and the shift of the alcohol group at 1081 cm^{-1} suggest that –OH groups are also involved in the modification process and amide groups are introduced onto biomass surface [40,41]. Therefore, lots of functional groups on surface of biomass account for their large biosorption ability.

The titration curves were collected in 0.01 mol/L $NaNO_3$ solution (Fig. 2B). At pH < 7.57, the surfaces of pristine biomass are positively charged, while at pH > 7.57, the surfaces of pristine biomass are negatively charged. However, the surfaces of modified biomass are positively charged at pH < 10.23, and the surfaces of modified biomass are negatively charged at pH > 10.23. The grafting PEI on the surfaces of biomass increases the point of zero change (pH_{pzc}) from 7.57 to 10.23. This change should be attributed to the protonation of amine groups in PEI molecules on the biomass surface [42]. From the electrostatic

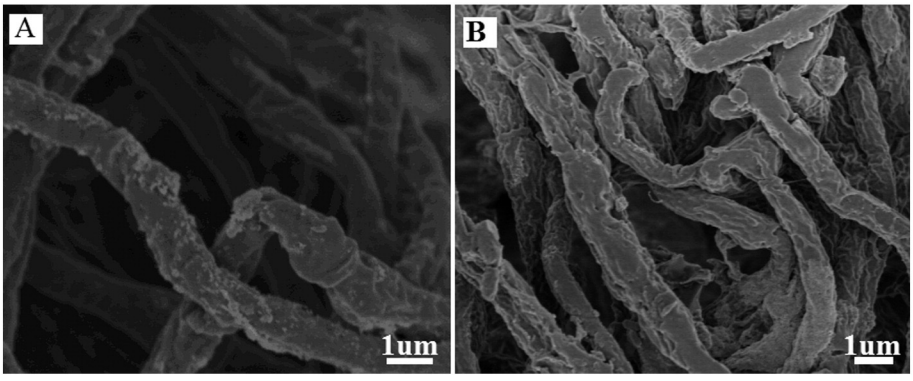

Fig. 1. SEM micrographs of biomass (A) pristine biomass, (B) modified biomass.