Journal of Colloid and Interface Science 414 (2014) 33–40

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Evaporation induced self assembled microstructures of silica nanoparticles and *Streptococcus lactis* cells as sorbent for uranium (VI)

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ARTICLE INFO

Article history:
Received 17 July 2013
Accepted 25 September 2013
Available online 5 October 2013

Keywords:
Microstructures
Silica nanoparticles
S. lactis
Uranium (VI)
Uptake

ABSTRACT

An assembled microstructure of silica nanoparticles and *Streptococcus lactis (S. lactis)* cells has been synthesized by evaporation induced self assembly, with the objective of its application in bioremediation. Different morphologies have been realized by tuning the physico-chemical conditions of the assembly process. The potential of these microstructures in removal of uranium (VI) has been evaluated. Morphology dependent uptake has been demonstrated and maximum uptake was seen for the spray dried doughnut shaped microstructure (SDSM). For a fixed morphology, the variation in uptake varies with solution pH, contact time, temperature and initial uranium (VI) concentration. The U (VI) removal was significantly rapid, with more than 85 ± 2% of total uptake in 10 min. The maximum sorption capacity (q_{max}) of U (VI) at pH 5.0 and temperature 298 K was 169.5 mg/g using SDSM as sorbent. The kinetic data of adsorption of U (VI) are best described by a pseudo-second-order kinetic model. Calculated thermodynamic parameters reveal an endothermic and a spontaneous adsorption process. The present work opens up the possibility of a means for the functionalization of silica microstructures through the incorporation of micro-organism and the potential for the use of these functionalized materials for bioremediation.

1. Introduction

The removal of uranium from waste water is of great significance for human health and environmental protection. The use of conventional remediation methods such as chemical precipitation, reverse osmosis, ion-exchange, filtration and evaporative recovery, are expensive and ineffective at low metal concentrations [1–3]. In comparison with conventional techniques, adsorption technique has a number of advantages [4–6]. Among the available adsorbents, nanoparticles like titanium oxide, iron oxides, zero-valent iron, etc. are classified as promising ones for heavy metal removal [4,7,8]. Also nanosize silica i.e. silica gel and silica particles [9–13] has been widely used for sorption of uranium ions. Because of high reactivity and high environmental mobility, nanoparticles offer a number of advantages [14] over conventional environmental remediation technologies [15,16]. However, there are a number of serious issues concerning the environmental fate of nanoparticles, their harmful impact on human health and some technical bottlenecks like difficulty in separation from aqueous systems, poor mechanical strength etc. [4,5,7,8,17]. This may significantly limit their widespread application as remediation material, particularly where methods involve free-release of these nanoparticles to the environment [18].

Another form of silica based materials is functionalized mesoporous silica. These have received extensive attention as promising sorbent for the removal of hazardous chemicals and heavy metal ions [19–24]. But complicated synthesis process, high cost and chemical instability in aqueous solution [19] have limited its practical application. As an alternative, we have synthesized self assembled microstructures of silica nanoparticles, through one step evaporation induced self assembly process [25–27], wherein spray drying has emerged as an efficient and fast process to obtain micrometric structures [28].

In previous studies, a variety of microbial systems have also been identified for bioremediation of uranium [2,29–36]. It has been reported that bacterial cell wall contains polysaccharides, proteins and lipids, which provide various functional groups like carboxyl, carbonyl, hydroxyl, sulfate, phosphate, etc. which helps in binding with metal ions [6,32,36]. But the limitation of applying microbial biomass directly for remediation is its small size with low density, poor mechanical strength and less rigidity [34]. Physical entrapment of biomass in a matrix is the most suitable way for enhancing its mechanical strength, imparting operational flexibility and for effective biomass utilization. Our goal is to develop a robust and stable bio-hybrid material containing nanoparticles and micro-organisms to achieve the functionalization of material as

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http://dx.doi.org/10.1016/j.jcis.2013.09.046

well as remediation of U (VI) by the combined effect of nanoparticles and micro-organisms in order to overcome the limitation of using silica nanoparticles and micro-organism alone.

In this work, self assembled microstructures containing *Streptococcus lactis* cells and silica nanoparticles were synthesized through facile one step evaporation induced self assembly process, using a spray dryer. Further, it has been demonstrated that these microstructures can be used as a model system for bioremediation of uranium wherein bacterial cells helped in the functionalization of the microstructures. To the best of our knowledge for the first time, bioremediation of uranium has been carried out with spray dried self assembled microstructures containing *S. lactis* cells and silica nanoparticles. This approach opens a new window of interest to the exploration of silica nanoparticles and microbial cells in the field of bioremediation.

2. Materials and methods

2.1. Materials

Silica colloidal dispersion (~15 nm) was obtained from VISA Chemicals, Mumbai, India. Overnight grown *S. lactis* cells in MRS Broth were used for study. Polyethyleneimine (PEI, average Mw $\sim 7.5 \times 10^5$) was purchased from Sigma Chemical Co., MO, USA. Microstructures were synthesized using spray dryer LU222, LABULTIMA, India. A stock solution (2000 ppm) of uranium (VI) was prepared by dissolving appropriate amount of UO_2 $(NO_3)_2{\cdot}6H_2O$ (Merck, Germany) in double-distilled water. 0.1 M HNO_3 or 0.1 M NaOH was used to adjust pH of the solution in the range of 2.0–7.0. All chemicals were of analytical grade.

2.2. Synthesis of incinerated and non-incinerated materials

S. lactis was chosen as a model organism due to its GRAS status. Overnight grown *S. lactis* cells were centrifuged (HeroLab centrifuge, HiCen 21 C) at 9000 rpm for 10 min. The pellet was weighed and 6% cell suspension was prepared. The suspension was mixed with 2% colloidal silica solution. This mixed suspension of silica and cells were passed through the spray dryer. After spray drying, dried powder was obtained. In another preparation, overnight grown *S. lactis* cells were treated with 2% polyethyleneimine (PEI) for 30 min with stirring, following which the cells were harvested by centrifugation and washed in order to remove the unbound PEI. After washing, spray drying (under identical condition as those for the previous experiment) was performed with silica and PEI coated *S. lactis* mixed colloidal suspension. Some amount of the spray dried powder was further incinerated at 673 K for 10 h. These spray dried incinerated and non-incinerated materials were used for uranium uptake studies.

2.3. Characterization

An environmental scanning electron microscope (Quanta 200 ESEM, FEI, USA) was used to characterize the microstructures. Thermogravimetric analysis (TGA) of the sorbents under study was performed using Netzsch Thermal analyser (STA 409 pc Luxx) at a heating rate of 10 K/min under a flow of nitrogen. Fourier transform infrared spectroscopy (FTIR) of the sorbents under study was recorded using Jasco FT-IR 660 plus spectrometer. All spectra were recorded over wavenumber 3700–400 cm^{-1} region with a resolution of 4 cm^{-1}.

2.4. Batch adsorption experiments

Batch adsorption experiments were conducted to obtain rate and equilibrium data. The reaction mixture containing U (VI) solution of 50 mg/L concentration (initial pH-5.0) and 1 g/L of sorbent (unless otherwise mentioned) was agitated on a rotary shaker (MaxQ 4000, Thermo, USA) operating at room temperature (298 K) and 150 rpm. From each flask, at regular intervals, aliquots were taken out and centrifuged at 9000 rpm for 5 min (Eppendorf centrifuge, Model-5810R, Germany) to separate the solid sorbent from the solution. The supernatant were analyzed for residual U (VI) concentration. Estimation of uranium (VI) was done by arsenazo (III) method [37]. In each set, uranium solution without sorbent was used as a control. Percentage removal and uptake (q) were obtained by using the following expressions:

$$\text{Percentage removal}(\%) = [(C_0 - C)/C_0] \times 100 \quad (1)$$

$$q = [(C_0 - C)V]/M \quad (2)$$

where q (mg U/g sorbent) is the amount of U (VI) adsorbed onto unit amount of the adsorbent, C_0 and C (mg/L) are the concentration of the U (VI) in the solution before and after sorption, respectively. V (L) is the volume of the aqueous solution and M (g) is the dry weight of the sorbent.

2.5. Kinetics, sorption isotherm and thermodynamic studies

For kinetic study, uranium solution (initial pH-5.0) of concentration 50 mg/L was contacted with SDSM (1 g/L) and samples were withdrawn at regular intervals for estimating uranium. Lagergren's pseudo-first and pseudo-second-order equation were used to model the kinetics of uranium sorption. Isotherm study was carried by varying uranium concentration (50–600 mg/L) at fixed sorbent concentration of 1 g/L. Samples were collected after incubation period (120 min), which was sufficient for the reaction to reach equilibrium. In order to examine the relationship between sorbent and aqueous concentration of uranium at equilibrium, Langmuir and Freundlich isotherm models were used to fit the data. U (VI) solution (50 mg/L) was contacted with SDSM (1 g/L) and incubated at different temperatures of 288 K, 298 K, 308 K and 318 K to determine the thermodynamic parameters. U (VI) solution as well as the biomass was incubated at the desired temperature before contact. 0.1 M NaOH was used to adjust initial pH of the uranium (VI) solution to 5.0.

2.6. Statistical analysis

All experiments were carried out in triplicate and the mean values with ± standard deviation were plotted.

3. Results and discussion

3.1. SEM of the spray dried materials

SEM micrographs of obtained microstructures indicate that depending on physico-chemical condition these microstructures have different morphologies. In Fig. 1a, a microstructure comprising *S. lactis* cells and silica nanoparticles is in the form of doughnut, further named spray dried doughnut shaped microstructure (SDSM) and the presence of cells can be seen on the surface of SDSM. However, Fig. 1b shows that after incineration there are prominent imprints of *S. lactis* cells on the SDSM. In Fig. 1c, one observes a microstructure comprising of PEI treated *S. lactis* cells and silica nanoparticles having a spherical shape called spray dried spherical shaped microstructure (SSSM) wherein the cells are less prominent and Fig. 1d shows that after incineration, SSSM with prominent imprints of *S. lactis* cells are seen. From Fig. 1, it is clear that there is a change in the shape of microstructures from doughnuts to spheres with the PEI treatment imparted to the *S. lactis*