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The biosorption of Sr(II) on *Bacillus subtilis*: A combined batch and modeling study

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ABSTRACT

The batch macroscopic experiments showed that the biosorption kinetics of Sr(II) on *Bacillus subtilis* can be fitted by pseudo-second-order kinetic model very well, and adsorption isotherms can be satisfactorily fitted by Langmuir model with high correlation coefficient ($R^2 > 0.995$). The independent of ionic strength of Sr(II) biosorption on *B. subtilis* at pH 2.0–11.0 indicated the inner-sphere surface complexation. The maximum adsorption capacity of Sr(II) on *B. subtilis* calculated from Langmuir model at pH 5.0 and 293 K was 49.75 mg/g. The fitted results of the surface complexation modeling revealed that the biosorption of Sr(II) on *B. subtilis* can be simulated by diffuse layer modeling with two inner-sphere surface complexes such as $SOSr^+$ and $SOSr(OH)_2^-$ species. Theses observation indicated that *B. subtilis* can be regarded as a promising bio-adsorbent candidate for the preconcentration and immobilization of radionuclides from aqueous solutions in the environmental remediation.

1. Introduction

The understanding of fate and transport of radionuclide at bacteria-water interface is of vital importance to decontaminate radionuclide from aqueous systems by using biosorption techniques [1]. The prevailing pathway for human exposure to radionuclides is via groundwater transported away from such sites, which may be potentially harmful to both human health and the biodiversity of ecosystem [2]. Therefore, it is require us to remove these radionuclides within the scope of permissible concentration before discharge into sub-surface environments.

Bacillus subtilis (*B. subtilis*) as a ubiquitous gram-positive bacterium presents massive functional groups (phosphoryl, carboxyl and hydroxyl groups), which has been extensively investigated to remove a variety of environmental contaminants such as organics [3–6], heavy metals [7–11], and radionuclides [12–15]. Omoike and Chorover [16] found that the phosphoryl and carboxyl functional groups of *B. subtilis* played important roles in the formation of uranyl complexes at low and circumneutral conditions, respectively. In addition, Gorman-Lewis et al. [13] further demonstrated that the stable surface complexes of uranyl species and *B. subtilis* could was observed via electrostatic interactions and covalent bonding. However, the few studies towards the biosorption of Sr(II) on *B. subtilis* are available by using surface complexation modeling [17–20].

The aims of this paper are to (1) characterize the morphology and nanostructures of *B. subtilis* using transmission electron microscopy (TEM), zeta potential (ζ) techniques, X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR); (2) to investigate the effect of reaction time, pH, ionic strength and temperature on the biosorption of Sr(II) onto *B. subtilis* by batch techniques; (3) to demonstrate biosorption mechanism between *B. subtilis* and Sr(II) by using surface complexation modeling. This manuscript focused on the application of non-metallic reducing bacteria on the removal of a variety of radionuclides from aqueous solutions in the environmental remediation strategy.

2. Materials and methods

2.1. Materials

Non-metallic reducing bacteria of *B. subtilis* were extracted from fermented sausage, which were provided from the College of Life Science at Huanyin Institute of Technology. Briefly, the as-prepared *B. subtilis* cells were cultured in a beef extract-peptone medium at 293 K. Next, the cells were harvested by centrifugation (2800 × *g*, 15 min) during the logarithmic phase and were washed three times using Milli-Q water. The stock solutions of Sr(II) (0.1 mmol/L) were prepared by dissolving $Sr(NO_3)_2$ (99.99% purity, Sigma-Aldrich) after dissolution and dilution with 0.01 mol/L HNO_3 solution. The other chemicals were commercially purchased as analytical reagents from Sinopharm Chemical Reagent Co., Ltd., and used as received without further purification.

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2.2. Characterization

The morphology and functional groups of *B. subtilis* was characterized by TEM, zeta potential, XPS and FTIR techniques. The sample for TEM observation was prepared by dissolving the *B. subtilis* in ethanol under vigorous stirring conditions. The zeta potentials were measured using Zetasizer NanoZS (Malvern Instruments). Each sample was measured at least three times. The XPS spectrum was conducted on a thermo ESCALAB 250 electron spectrometer with multidetection analyzer using Mg Kα radiation source (1253.6 eV) at 10 kV and 5 mA under 10^{-8} Pa residual pressure. Surface charging effects were corrected with C 1s peak at 284.6 eV as a reference. The recorded lines of C 1s were fitted by using XPSPEAK41 program. The FTIR spectrum was recorded in pressed KBr pellets (Aldrich, 99%, FT-IR grade) by using a Nicolet 8700 FT-IR spectrometer at room temperature.

2.3. Adsorption experiments

The biosorption of Sr(II) on *B. subtilis* were conducted in 10 mL polycarbonate tubes at 0.01 mol/L NaCl and 293 K. Briefly, 3 mL of 2.4 g/L *B. subtilis* suspension and 0.6 mL of 0.1 mol/L NaCl were added into10 mL polycarbonate tubes, and then 2.4 mL of 60 mg/L Sr(II) solutions were stepwise added into the aforementioned solutions. The pH of suspension was adjusted to 2.0–11.0 by adding the negligible volume of 0.01–1.0 mol/L NaOH or HNO_3 solutions, and then suspension was agitated on a shaker for a reaction time of 24 h. The biosorption isotherms of Sr(II) on *B. subtilis* were performed at pH 5.0 and $T = 293$ K by batch technique. The experiments were conducted under the same conditions as the above pH-dependent biosorption experiments except that the different concentrations of Sr(II) used. Subsequently the suspensions were shaken for 24 h to ensure that the adsorption reaction could achieve adsorption equilibrium (preliminary experiments found that this was adequate for the suspension to achieve equilibrium). The solid phases were separated from liquid phases by centrifugation at 7000 rpm for 15 min. To eliminate the effect of Sr(II) adsorption on tube walls, the biosorption of Sr(II) without *B. subtilis* was carried out under the same experimental conditions. The concentration of Sr(II) in aqueous solutions was determined by atomic absorption spectroscopy (AAS-6300C, Shimadzu). The amount of adsorbed Sr(II) was determined from the difference between the concentration initially added and that remained after batch adsorption.

2.4. Surface complexation modeling

Fein et al. demonstrated that *B. subtilis* presented three functional groups such as phosphoryl, carboxyl and hydroxyl groups [3–5,11]. These equilibrium constants (log *K*) were obtained by potentiometric titration and/or optimizing all parameters, which was comparable with the previous studies [7–9,12,21]. The pH-dependent adsorption of Sr(II) on *B. subtilis* was fitted by using diffuse layer model (DLM) with an aid of Visual MINTEQ v. 2.6 mode [22].

3. Results and discussion

3.1. Characterization

The morphology and microstructure of *B. subtilis* were characterized by TEM image. As shown in Fig. 1A, *B. subtilis* displayed the rod-like aggregates with approximately 0.25 μm wide × 1.0 μm long [23]. Fig. 1B showed the difference in the zeta potentials of *B. subtilis* at the different pH conditions. One can see that the negatively charged *B. subtilis* was observed at pH > 3.5. The oxygenated functional groups of *B. subtilis* were demonstrated by FTIR spectra. As shown in Fig. 1C, the strong and wide peaks at ~3415 and 1650 cm^{-1} were assigned to the stretching vibration of —OH groups and —C═C groups, respectively [20]. The other characteristic peaks of *B. subtilis* at 2929, 1729, 1425 and 1085 cm^{-1} were corresponded to the stretching vibration of C—H, C═O, C—OH and C—O—C groups, respectively [23,24]. The bands at ~1240 cm^{-1} can be attributed to the stretching vibration of P═O peaks of C—PO_3^{2-} group [25]. The results of FTIR spectrum

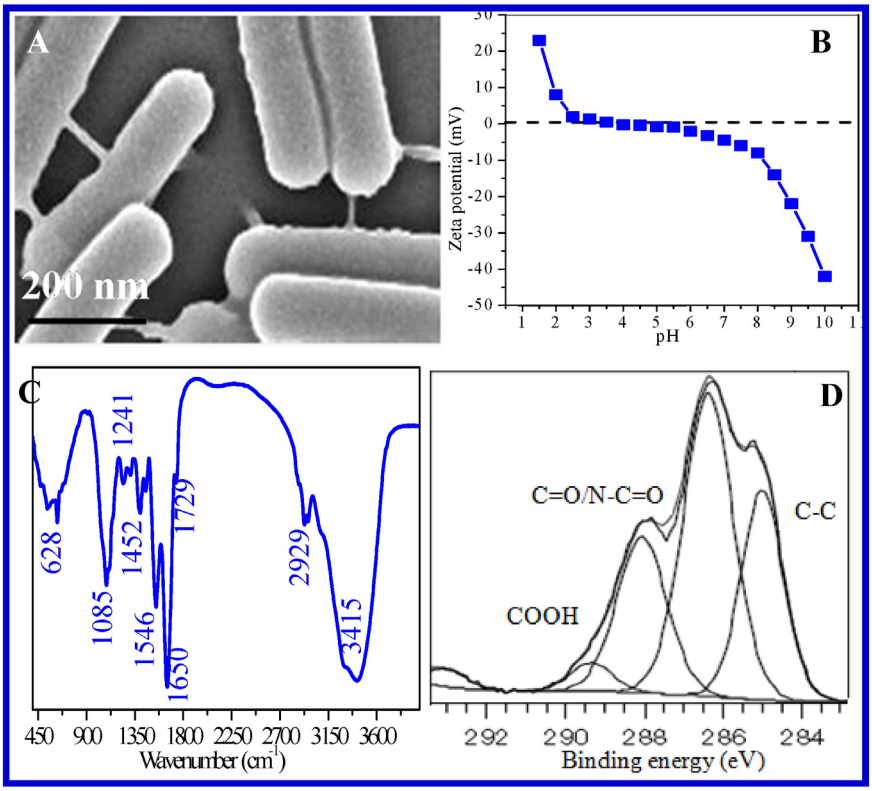

Fig. 1. Characterization of *B. subtilis*. A: TEM image; B: zeta potentials; C: FTIR spectrum; D: XPS spectrum.