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Kinetic simulating of Cr(VI) removal by the waste *Chlorella vulgaris* biomass

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ABSTRACT

Waste microalgae biomass, one of the most abundant residues from biodiesel production, can be used as a low-cost biosorbent for heavy metal removal. The ability and mechanism of Cr(VI) removal by lipid-extraction residue of *Chlorella vulgaris* were investigated in this study. The removal of Cr(VI) increased as the pH decreased from 4.0 to 0.5, or temperature increased from 15 °C to 45 °C. The Sips isotherm well-fitted the experiment data, and the maximal biosorption capacity of waste *C. vulgaris* biomass for total chromium was 43.3 mg/g at pH 1.5 and a temperature of 25 °C. X-ray photoelectron spectroscopy revealed that the majority of Cr(VI) bound on the biomass was reduced to Cr(III) with its subsequent partial biosorption. The results of Fourier Transform Infrared Spectrometer study indicated that both carboxyl and amino groups on the biomass were the main binding sites for Cr(VI) biosorption, while carbohydrate was mainly responsible for reduction of Cr(VI). Finally, the proposed kinetic model based on the indirect reduction mechanism well described the Cr(VI) removal behavior at various pHs (0.5–2) and temperatures (15–45 °C).

1. Introduction

Hexavalent chromium (Cr(VI)) is a heavy metal that is known to be carcinogenic and mutagenic, and is widely found in wastewater produced from the leather tanning, mining, textile dyeing, steel fabrication, wood preservation and electroplating industries [1]. Due to the toxicity of Cr(VI) pollution, it has resulted in many problems affecting both human health and aquatic ecosystems. Several methods are used for chromium removal from industrial effluents, like adsorption, membrane ultrafiltration, reverse osmosis, membrane bioreactor, electrolytic recovery techniques and ion exchange [2,3]. However, these methods tend to be expensive due to operational cost, not eco-friendly, or ineffective at Cr(VI) concentrations ranging from 1 to 100 mg/L [4]. In recent years, biosorption has emerged as a cost-effective and efficient alternative for the removal of heavy metals from wastewater. Many types of biomass have been studied for Cr(VI) removal, including bacteria, fungi, algae, industrial byproducts and agricultural biowastes [5–9]. Among these biosorbents, algae are attractive because of their ubiquitous occurrence and cheap availability both in fresh and saltwater. Moreover, some algae, such as *Chlorella* sp. [4,10], *Ceramium virgatum* [11], *Sargassum muticum* [12] and *Oedogonium hatei* [13], exhibit high Cr(VI) removal abilities.

In addition, *Chlorella* sp. has been also considered as a promising candidate for the commercial lipid production, due to its fast growth, high lipid content, and high flexibility to adapt to diverse culture conditions [14,8]. However, the biodiesel production from microalgae can result in producing the waste biomass and causing negative environmental impact due to disposal problem [15]. Thus, a sustainable approach is to utilize the waste biomass without lipid content as a low-cost biosorbent for heavy metal removal [16]. Many types of algae biomass have been selected for Cr(VI) removal from aqueous solution as they contain some functional groups with reductive and adsorptive characteristic. *Chlorella vulgaris* is a most common *Chlorella* sp. strain. Although *C. vulgaris* waste is one of the most abundant residues from biodiesel production, there have no reported studies in literature on the removal of Cr(VI) using waste *C. vulgaris* biomass. Moreover, as various reports have shown that the mechanism for Cr(VI) biosorption by biomass materials is usually based on adsorption-couple reduction, Cr(VI) can be removed through direct or indirect

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reduction mechanisms [1,17]. Murphy et al. [18] reported that carboxyl and amino groups have been shown to be especially important in the indirect reduction mechanism for Cr(VI) removal by seaweed biomass. Some models developed based on indirect reduction mechanism could successfully described the Cr(VI) removal behavior in aqueous phase under various Cr(VI) concentrations [4]. However, few models have simultaneously considered the effects of solution chemistry variables (*i.e.* solution pH, temperature, contact time, and initial concentration), which are most important parameters to affect the removal rate of Cr(VI) by biomass materials.

In this study, the possible use of waste *C. vulgaris* biomass as an alternative biosorbent for Cr(VI) removal was investigated. The mechanism of Cr(VI) removal by waste *C. vulgaris* biomass was characterized by Scanning Electron Microscopy/Energy dispersive X-ray analysis (SEM/EDS), X-ray photoelectron spectroscopy (XPS) and Fourier Transform Infrared (FT-IR). In addition, a modified kinetic model based on biosorption and bioreduction reactions was developed to fit the experimental data obtained at various pHs and temperatures, and the parameters related to both reactions were investigated.

2. Materials and methods

2.1. Preparation of biomass

C. vulgaris (FACHB-31) was purchased from the Institute of Hydrobiology, the Chinese Academy of Sciences, Wuhan, China. *C. vulgaris* was cultivated in a transparent acrylic column (internal diameter of 6.5 cm and length of 60 cm) containing approximately 1 L Modified Bristol medium, which consisted of $NaNO_3$ 0.75 g, K_2HPO_4 0.075 g, KH_2PO_4 0.175 g, $MgSO_4{\cdot}7H_2O$ 0.075 g, NaCl 0.025 g, $CaCl_2{\cdot}2H_2O$ 0.025 g, $FeCl_3{\cdot}6H_2O$ 0.0005 g and trace metal solution 0.1 mL/L. The trace metal solution contained H_3BO_3 0.61 g, $MnSO_4{\cdot}7H_2O$ 1.69 g, $ZnSO_4{\cdot}7H_2O$ 2.87 g, $(NH_4)_6Mo_7O_{24}{\cdot}7H_2O$ 0.0124 g, and $CuSO_4{\cdot}5H_2O$ 0.025 g/L. The culture was incubated at 25 ± 1 °C under continuous illumination of 4.0 klux light intensity and air-aerated with a flow rate of 0.3 vvm. After cultivation, *C. vulgaris* biomass was harvested by centrifugation, washed twice with deionized water, and freeze-dried. The lipid content of the lyophilized biomass was extracted by a Soxhlet extractor with n-hexane solvent. The residual biomass after lipid extraction was freeze-dried, homogenized by grinding with mortar and sieved (the perforations on the sieve being 100 mesh).

2.2. Batch experiments for Cr(VI) biosorption and bioreduction

The removal of Cr(VI) was examined by measuring the time-dependent concentrations of Cr(VI) and total chromium in a batch system. The test solutions were prepared by dissolving the exact quantities of $K_2Cr_2O_7$ (Sigma) in deionized-distilled water. In all experiments, the working volume was 30 mL in a 150 mL conical flask agitated on a shaker at 200 rpm, and the pH was adjusted to the desired values according to the following experimental design with 5 M HCl.

The batch experiments for Cr(VI) removal were determined under various initial pHs (from 0.5 to 4) and temperatures (from 15 to 45 °C) at an initial Cr(VI) concentration of 50 mg/L. The effect of initial Cr(VI) concentrations on the total Cr biosorption was investigated by another experiment using 3 g/L biomass, initial pH 1.5, and varied initial Cr(VI) concentrations (from 25 to 500 mg/L) at room temperature (25 ± 1 °C). Liquid solution samples (100 μL from each flask) were collected at regular time intervals and centrifuged at 10,000 rpm for 5 min, after which the Cr(VI) and total chromium concentrations of the supernatant were analyzed immediately. The total volume of withdrawn samples never exceeded 4% of the working volume. The Cr(VI) removal capacity was obtained by using the following expression:

$$Q(\mathrm{VI})_t = \frac{C(\mathrm{VI})_0 - C(\mathrm{VI})_t}{[B]} \quad (1)$$

where $Q(\mathrm{VI})_t$ is Cr(VI) removal capacity at any instant of time t (mg/g), $C(\mathrm{VI})_0$ is the initial concentration of Cr(VI) (mg/L), $C(\mathrm{VI})_t$ is the concentration of Cr(VI) at any instant of time t (mg/L), and $[B]$ is the biomass dosage (g/L).

The total chromium biosorption capacity was calculated as follows:

$$Q_t = \frac{C_0 - C_t}{[B]} \quad (2)$$

where Q_t is the total chromium biosorption capacity at any instant of time t (mg/g), C_0 is the initial concentration of total chromium (mg/L), C_t is the concentration of total chromium at any instant of time t (mg/L).

The Cr(VI) bioreduction capacity can be expressed as follows:

$$Q(\mathrm{III})_t = \frac{C(\mathrm{III})_t}{[B]} \quad (3)$$

where $Q(\mathrm{III})_t$ is the Cr(VI) bioreduction capacity at any instant of time t (mg/g), and $C(\mathrm{III})_t$ is the concentration of Cr(III) at any instant of time t (mg/L).

2.3. Analysis

The concentrations of Cr(VI) and total chromium in supernatant were determined using a colorimetric method, as described in the Standard Methods [19]. The absorbance of the pink-colored complex formed from reacting Cr(VI) with 1,5-diphenylcarbohydrazide was measured at 540 nm by a UV spectrophotometer (UV-1800, Shimadzu, Japan). To estimate the total chromium concentration, the Cr(III) was first converted to Cr(VI) by oxidation with potassium permanganates at high temperature under acidic conditions. The Cr(III) concentration was obtained by subtracting the content of Cr(VI) from that of total chromium.

The elemental composition of the biomass before and after lipid extraction was determined by the elemental analyzer (Vario EL III, Elementar, Germany). The surface area of the biomass was determined by a bet surface area (BET) analyzer (Tristar 3000, Micromeritic, USA) with a multipoint BET isotherm using N_2 as the adsorbate.

The surface morphology of the biomass (before and after lipid extraction) and Cr-loaded biomass was visualized by a scanning electron microscope coupled with energy dispersive X-ray analysis (LEO 1530, LEO, Germany). The samples were mounted on a stainless steel slab with double-sided sticky tape prior to coating with a thin layer of gold under high vacuum conditions.

Infrared spectra of the control (biomass before and after lipid extraction) and the biomass submerged in 500 mg/L Cr(VI) at initial pH 0.5 and 1.5 with a reaction time of 12 h and 180 h were obtained using a Fourier Transform Infrared Spectrometer (Nicolet Avatar 330, Thermo Electron, USA).

The detailed oxidation state of the chromium ions on the biomass was characterized using X-ray photoelectron spectroscopy (Quantum 2000, Physical Electronics, USA). The Cr-laden biomass was obtained through contact with 500 mg/L Cr(VI) at initial pH 0.5 and 1.5 for with reaction times of 12 h and 180 h. Prior to mounting for XPS, the biomass was washed with deionized-distilled water several times, and then freeze-dried. $CrCl_3{\cdot}6H_2O$ (Sigma) and $K_2Cr_2O_7$ (Sigma) were used as Cr(III) and