Biocomposite of Thermoacidophilic Cyanidiales and Iron Hydroxide in Removal of Hexavalent Chromium

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Abstract

Hexavalent chromium [Cr(VI)] is a poisonous contaminant with more toxic and mobility than trivalent chromium [Cr(III)] in wastewater and soil systems. However, Cr(VI) is considered as insoluble compounds in aqueous resulting could not remove by precipitation. A high-chromate-selective biosorbent, Cyanidiales, are thermoacidophilic red microalgae survived in extensive temperature (25-56℃) and acidic environment (0.5-5.0). Therefore, we aimed to conduct the capacity and related mechanisms of Cr sorption on two species of Cyanidiales [Gp (*Galdieria partita*) and Cc (*Cyanidium caldarium*)] at pH 2 and pH 5 using synchrotron-based high resolution Fourier-transform infrared (FTIR), and Cr K-edge X-ray absorption (XAS) analyses. Additionally, we synthesized innovative biocomposite material consisting of Cyanidiales and Fe hydroxides, leading to promoted removal efficiency for heavy metals. Maximum sorption capacity was observed in Cc (151.7 mg g^{-1}) and Gp (103.9 mg g^{-1}) at pH 2. Furthermore, the significantly promoted Cr adsorption capacity was obtained after Fe hydroxides modification in Cc (188.3 mg g^{-1}) and Gp (167.1 mg g^{-1}). However, despite Cyanidiales generally performed all mechanisms against Cr toxicity, individual defense responses were highlighted by different Cyanidiales species. The different alternation of secondary structure proteins in vitro of Gp and Cc were evidenced in this study. Consequently, collective results suggested that Cr tolerance on Cyanidiales was regulated according to three mechanisms including adsorption using organic functional groups on algae, inorganic precipitate on the algae surfaces as $Cr(OH)_3$, and complexed with proteins in vitro of algae.

Keywords - Cyanidiales, thermoacidophilic, Cr sorption, XAS, proteins.

Introduction

Chromium (Cr) occurs in the environments primarily in hexavalent chromium [Cr(VI)] and trivalent chromium [Cr(III)]. However, Cr(VI) with carcinogenic and mutagenic is particular environmental pollutant in soil and aquatic system. The toxicity and mobility of Cr(VI) are higher than Cr(III). While Cr(VI) usually be considered as insoluble compounds in aqueous so that could not separate it by precipitation. The Cyanidiales are considering as superior material to remove the metals due to their tolerance for a wide range of temperature (room temp - 56 ℃) and acidity (pH 0.2 - 5) [1]. Therefore, in this study, we conducted the green innovative biocomposites Cyanidiales to reduce Cr(VI) to Cr(III) and retention the Cr on the red microalgae. To develop the reduction and accumulation capacity of Cr in Cyanidiales [Gp (*Galdieria partita*) and Cc (*Cyanidium caldarium*)], the Cr isotherm was conducted at pH 2 and pH 5 for 6 h in room temperature, respectively. In addition, to determine the Cr retention mechanisms, the X-ray absorption spectroscopy (XAS) and Fourier transform infrared spectroscopy (FTIR) base on synchrotron technic were used.

Materials and Methods

Synthesis of biocomposites and sorption isotherm

The algae cells was mixed with 0.1 M $FeCl_3$ solutions and placed under dark condition at pH 2 in an orbital shaker set at 120 rpm for 48 h. The solid to liquid ratio was fixed at 80 g L^{-1}. The sorption isotherms were conducted with the cell density of 0.5 mg L^{-1} at pH 2.0 to 5.0.and reacted with Cr at 25℃ for 6 h. The sorption data were fitted using the Freundlich isotherm models.

Spectroscopic Analysis.

The red algae with sorbed Cr were analyzed using FTIR and linear combination fitting (LCF) of Cr K-edge XAS. The FTIR spectra were collected at the beamline 14A of the National Synchrotron Radiation Research Center (NSRRC). The collected spot size is 10 μm (H) x10 μm (V) with the resolution of 4 cm^{-1} from 4000-650 cm^{-1}. The spectra were analysed using the OMNIC 8.0 software. Speciation of sorbed Cr on red algae was determined using the Cr K-edge XAS collected at beamline 17C of NSRRC. The linear combination fitting (LCF) of Cr X-ray absorption near edge structure (XANES) with reference standards including Cr(III) and Cr(VI) species was both performed. All of the XAS data were background removed, normalized, and merged using the IFEFFIT program.

Results and Discussions

Among all algae, the Cr sorption capacity were in the order of Cc (151.7 mg g^{-1}) > Gp (103.9 mg g^{-1}) at pH 2, and Gp (72.3 mg g^{-1}) > Cc (71.3 mg g^{-1}) at pH 5 (Fig. 1a). After the algae composite with Fe hydroxide, the Cr sorption capacity were in the order of Cc/Fe (188.3 mg g^{-1}) > Gp/Fe (167.1 mg g^{-1}) at pH 2, and Gp/Fe (61.2 mg g^{-1}) > Cc/Fe (11.1 mg g^{-1}) at pH 5 (Fig. 1b). The Cr speciation retention on algae were primarily Cr-hydroxide [$Cr(OH)_3$] and Cr complexed with acetate (Tab. 1). In addition, the variation of secondary structure proteins in algae was been detected (Fig. 3). We suggested that organic Cr complexation concomitant with the transport to cell vacuoles, and the specific thiol-Cr chelation involved in disruption of secondary structure proteins. Conclusively, the retention mechanisms of Cr on Cyanidiales suggested not only Cr bound with proteins and functional groups from vivo and vitro, but precipitate on the surfaces of the algae as $Cr(OH)_3$ (Fig. 4).

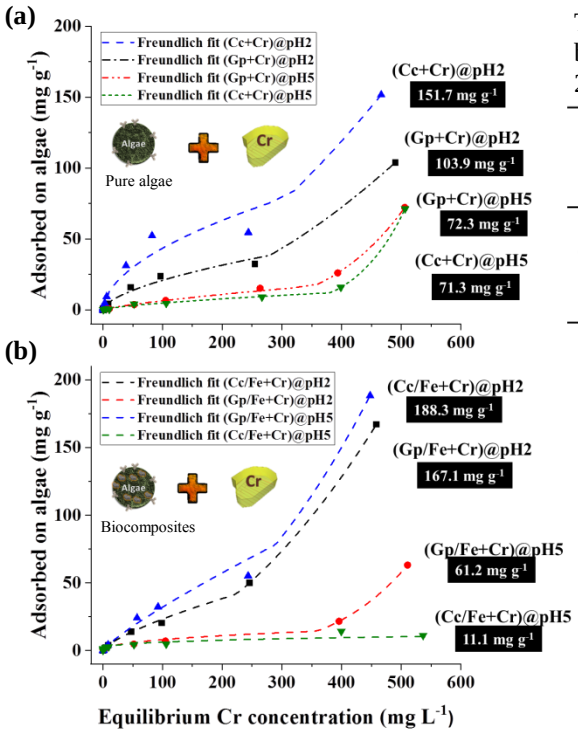

Fig 1. Cr sorption isotherms on (a) algae [(Gp (*Galdieria partita*) and Cc (*Cyanidium caldarium*)] at pH 2.0 and 5.0, and (b) biocomposites with algae (Gp and Cc) and iron hydroxide at pH 2.0 and 5.0 for 6 h along with Freundlich fitting results.

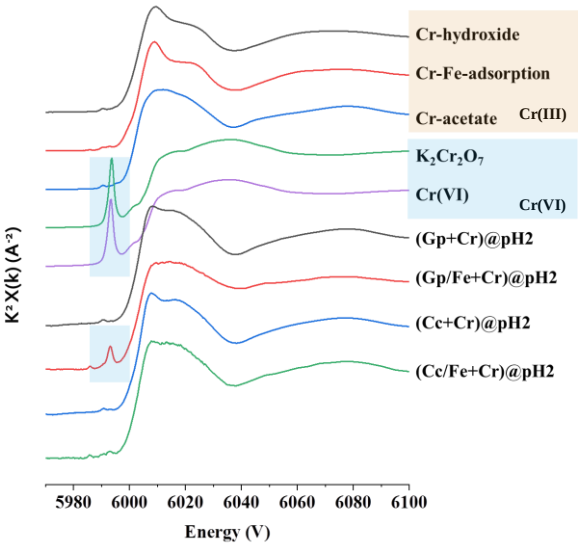

Fig 2. The X-ray absorption near edge structure (XANES) spectra with reference standards including Cr-hydroxide, Cr-Fe-adsorption, Cr-acetate, $K_2Cr_2O_7$, and Cr(VI) species and Cyanidiales after Cr sorption at pH 2.0. (Gp+Cr)@pH2, (Gp/Fe+Cr)@pH2, (Cc+Cr)@pH2 and (Cc/Fe+Cr)@pH2 were represented as pure Gp, the biocompostie (composite of Cc and Fe), pure Cc, and the biocompostie (composite of Cc

Tab. 1. Speciation of sorbed Cr on the pure algae (Gp and Cc) and biocomposites of algae and iron hydroxide (Gp/Fe and Cc/Fe) at pH 2.0 were determined by LCF analyses of adsorption samples.

Samples	Sorbed Cr	Cr(III) species		Cr(VI) species	R-factor
		Cr-hydroxide	Cr-acetate	Cr(VI)-std	
	mg g^{-1}	%			
(Gp+Cr)@pH2	0.88	39	63	0	0.003121
(Gp/Fe+Cr)@pH2	0.90	21	53	26	0.002975
(Cc+Cr)@pH2	1.76	53	48	0	0.005014
(Cc/Fe+Cr)@pH2	1.36	25	75	3	0.002071

The fitting range of XANES is between -20 and +30 eV. The weighting factors on each fit were summed to 100 ± 3% and were normalized to 100%. [a] Normalized sum of the squared residuals of the fit (*R-factor* = $\sum$(data-fit)^2/$\sum$data^2)

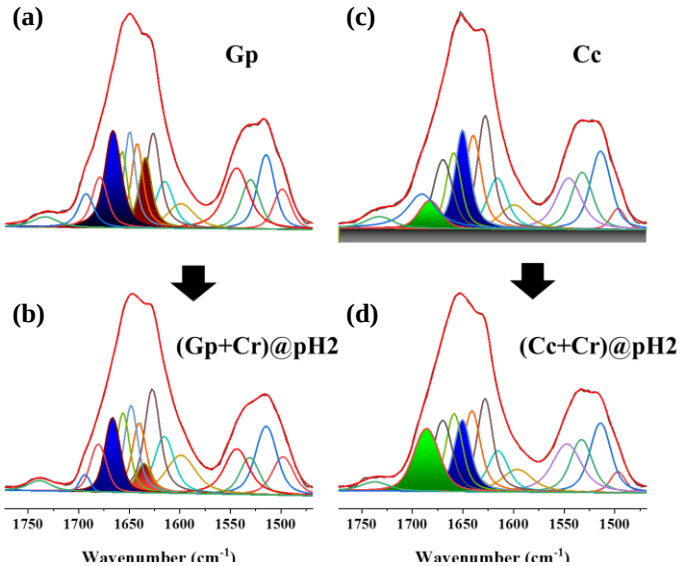

Fig 3. Representative for decomposition results with secondary structure proteins of FTIR spectra (1468-1773 cm^{-1}) for (a) the pure Gp, (b) the biocomposite (composite of Gp and Fe) after reacting with Cr at pH 2 for 6 h, (c) the pure Cc, and (d) the biocomposite (composite of Cc and Fe) after reacting with Cr at pH 2 for 6 h.

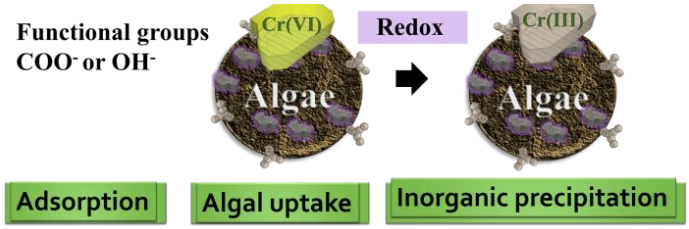

Fig 4. Accumulation mechanisms of Cr on Cyanidiales.

Acknowledgments

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References

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