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Hexavalent chromium reduction by *Escherichia coli* in the presence of ferric iron

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ABSTRACT

The potential of Cr(VI) reduction by *Escherichia coli* in the presence of soluble Fe(III) was investigated to explore the chemo-biologically mediated reduction process under anaerobic condition. The reduction efficiency of Cr(VI) reached 95% within 24 h. The influences of experimental parameters, including initial pH, temperature, Fe(III) dosage, carbon source, and chelating agent, were also investigated. The highest efficiency of reduction was observed when pH was 5.8 and temperature was 32°C. Amendments of culture medium with Fe(III) and citric-3Na enhanced Cr(VI) reduction, while the addition of EDTA-2Na inhibited the process. Analysis showed that soluble Fe(III) enhanced the reduction process by shuttling electrons from bio-reduced Fe(II) to Cr(VI) in a coupled biotic-abiotic cycle and hence, Cr(VI) was reduced to Cr(III) followed by deposition to sludge.

Keywords: Hexavalent chromium; Microbial reduction; Optimum reduction; Ferric iron

1. Introduction

Chromium is one of the most frequently detected metal contaminant in the environment due to its wide application in industries including metal finishing, electroplating, leather tanning, water cooling, and wood preservation [1,2]. In aqueous system, chromium primarily exists as trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). In comparison of the two forms of chromium, Cr(III) is relatively innocuous due to its insolubility and bare mobility. Indeed, it is considered as an essential trace element required for glucose and lipid metabolisms [3]. However, Cr (VI) is extremely toxic, carcinogenic, and mutagenic to living organism. Thus, removal of Cr(VI) from aqueous environment is essential to protect human health and environment. The conversion of Cr(VI) to Cr(III) could be an optional strategy.

Conventional methods for Cr(VI) removal from contaminated aqueous system involve physical and chemical processes, such as membrane filtration, extraction, ion exchange, adsorption [4,5], and chemical reduction followed by precipitation [6]. Major drawbacks associated with these methods are economically expensive and ineffective in the low concentration range, and some of the methods even produce secondary pollutions that require extra remediation measures. Zero-valence iron (ZVI) has received wide attention as a useful tool for the remediation of Cr(VI) groundwater [7,8]. Nevertheless, the surface passivation of ZVI by deposition of Fe and Cr oxides inhibits the application of ZVI. Bioremediation applying micro-organisms is cost effective, sustainable, and

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environmentally compatible, which provides an attractive treatment option. However, microbial reduction of Cr(VI) has the disadvantage of low reduction rate and bacteria may be poisoned by high concentration of Cr(VI). Combination of micro-organism and ZVI provides a feasible way for Cr(VI) reduction, since it can weaken the disadvantages of treatments performed by micro-organism or ZVI alone. So far as it is known, the interaction of micro-organism and ZVI during Cr(VI) reduction process is theoretically based on microbial reduction of Fe(III) generated by reaction between Cr(VI) and Fe° or Fe(II), and Cr(VI) reduction by bio-generated Fe(II) [9]. Therefore, the understanding of mechanism of microbial Cr(VI) reduction in the presence of soluble Fe(III) is essential to figure out the potential of using micro-organism and ZVI for the remediation of Cr(VI) pollution.

Fe(III) mediated microbial reduction of Cr(VI) could be affected by numerous factors, such as initial pH, temperature, carbon source, Fe(III) dosage, and chelating agent. Initial pH is the most important factor that affects the reduction of Cr(VI) by Fe(II) [10,11]. Researchers have also reported that pH and temperature have significant effects on microbial growth and activity [12,13]. Therefore, initial pH and temperature are crucial to Cr(VI) reduction and they can affect both microbial activity and chemical reaction during the reduction process. Under anaerobic condition, microbial reduction of Fe(III) and Cr(VI) are both related to organic matter utilization and energy conservation. Thus, carbon source could be an essential factor for Fe(III) mediated microbial reduction of Cr(VI). Fe(III) dosage and chelating agent are also important to Cr(VI) transformation, since Fe(III) dosage directly affects Fe concentration in solution and chelating agents could affect Cr(VI) reduction by chelating Fe and Cr.

The main objective of this work is to characterize the Cr(VI) resistant and reduction potential of the anaerobic bacteria in the presence of ferric iron. Moreover, effects of pH, temperature, carbon source, Fe(III) dosage, and chelating agent on Cr(VI) reduction were also investigated.

2. Materials and methods

2.1. Reagents

All reagents were of analytical grade and purchased from Aladdin chemistry Co., Ltd. (Shanghai, China) and Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Chromate stock solution was prepared in deionized water using $K_2Cr_2O_7$ that was heat-dried at 120°C for 2 h. Reaction solution pH was adjusted by diluted HCl and NaOH solutions. The serum bottles were soaked in 10% HNO_3 and then rinsed with deionized water.

2.2. Microbe cultivation

Escherichia coli is a common kind of Fe(III)-reducing micro-organism, whose ability to reduce iron was described numerously by researchers. The bacteria used in this study were mainly constituted by *E. coli* FR-2 [14], which were generously provided by Professor Li (Zhejiang University, China). The bacteria were cultured in basal medium [15] containing 250 mg L^{-1} of glucose, 100 mg L^{-1} of NH_4Cl, 540 mg L^{-1} of $NaHCO_3$, 30 mg L^{-1} of KH_2PO_4, 10 mg L^{-1} of $MgCl_2{\cdot}6H_2O$, 7 mg L^{-1} of Na_2SO_3, and other trace elements, to pursue an enrichment. Glucose was added as carbon source, and $FeCl_3$ was added to acquire a 40 mg L^{-1} of Fe(III) dosage. The culture medium was adjusted to pH 6.8 and oxygen was removed by repeated vacuuming and flushing with N_2 gas. The container was then sealed with butyl rubber stopper to isolate the air. Enriched bacteria were harvested by centrifugation (4,000 rpm, 10 min) after incubated in a shaker at 150 rpm and 32°C.

Afterwards, domestication was conducted to get a higher Cr(VI) tolerance for the bacteria. The cultivation was carried out in the same culture medium for enrichment, but with Fe(III) dosage of 20 mg L^{-1} and Cr(VI) additions of 1, 3, 6, and 10 mg L^{-1} in sequence. The culture medium was adjusted to pH 6.8 followed with the exposure to N_2 gas. The bacteria were harvested by centrifugation (4,000 rpm, 10 min) after anaerobic incubation in a shaker at 150 rpm and 32°C. Furthermore, the ability of Cr(VI) reduction by domesticated bacteria was tested.

In order to monitor any abiotic Cr(VI) reduction and confirm the necessity of living bacteria for Cr(VI) reduction, control treatments without bacteria and receiving heat-killed bacteria were conducted. Heat-killed bacteria were prepared by incubating a certain amount of domesticated bacteria at 80°C for 30 min [16]. Incubations were carried out aerobically without N_2 flushing and using gauze covers instead of rubber stoppers, in order to investigate the influence of O_2 on Cr(VI) reduction.

2.3. Batch experiments

Batch experiments were conducted in 250 ml serum bottles with butyl rubber stoppers. The solution containing nutrient substances, 30 mg L^{-1} of Fe(III),

and 10 mg L^{-1} of Cr(VI) was adjusted to a certain value of pH and then transferred to serum bottles. Samples for initial Cr(VI) concentration determination were taken prior to pH adjustment. The reaction solution was continuously purged with N_2 gas and oxygen was removed. The reduction studies were started by addition of the bacteria harvested from the domestication medium and being sealed with butyl rubber stoppers. The harvested bacteria were added at concentrations of 0.136–0.148 g L^{-1}, which were measured by drying a certain amount of broth to constant weight in an oven. Incubations were conducted at 32°C on a rotary shaker at 150 rpm. The reduction process was monitored at different intervals by withdrawing 2 ml samples from the serum bottles with N_2-flushed needles and syringes.

The effects of initial pH (4.8, 5.8, 6.8, 7.8), temperature (20, 32, 40°C), and Fe(III) dosage (0–50 mg L^{-1}) were investigated to characterize the Cr(VI) reduction efficiency by bacteria in the presence of ferric iron. Moreover, glucose, sucrose, and trisodium citrate as carbon sources for Cr(VI) reduction were tested and the effects of glucose concentration (0–5,000 mg L^{-1}) on Cr(VI) reduction were further investigated. Amendments of culture medium with different types and concentrations of chelating agents (EDTA-2Na and Citric-3Na) were also conducted to investigate the effects of chelating agent on Cr(VI) reduction. The molar ratios of EDTA-2Na to Fe(III) were set to 3:4 and 3:8, while the molar ratios of cirtric-3Na to Fe(III) were set to 1:1 and 1:2. All the batch experiments were performed in triplicates. Samples were drawn from serum bottles with N_2-flushed needles and syringes at different intervals.

2.4. Analytical procedures

The concentration of Fe(II) and Cr(VI) in the samples was determined colorimetrically using UV/VIS spectrophotometer (TU-1810APC, China). Fe (II) concentration was analyzed at a wavelength of 510 nm after forming colored complexes with 1,10-phenathroline. Diphenylcarbazide was applied to react with Cr(VI) and the absorbance of their complex was measured at a wavelength of 540 nm and compared to standards prepared with $K_2Cr_2O_7$. Total soluble chromium was analyzed using atomic absorption spectrometer (AA 6300C, Shimadzu Ltd.). Cr(III) concentration in supernatant was calculated by subtracting Cr (VI) from total chromium. For all batch experiments, the means of three parallel treatments with a standard deviation were accepted as the final value. Moreover, pH meter (SG2, Mettler-Toledo Instruments (Shanghai) Co., Ltd.) was used for pH measurement.

3. Results

3.1. Microbe reduction ability

The potential of Cr(VI) reduction by bacteria was examined (shown as Fig. 1). Results indicated that living bacteria were essential for Cr(VI) reduction. The reduction efficiency of Cr(VI) in treatment receiving heat-killed bacteria was similar to treatment without bacteria, and the reductions were both negligible. Treatment receiving living bacteria had a higher efficiency of Cr(VI) reduction, which affirmed the ability of bacteria to reduce Cr(VI). Experimental results also demonstrated that the bacteria had a tolerance of 40 mg L^{-1} of Cr(VI) (data not shown). Afterwards, incubations were carried out aerobically using gauze covers instead of rubber stoppers and they reduced less Cr(VI) at a minimum rate compared to those anaerobic incubations. This observation suggested that anaerobic condition was preferred for Cr(VI) reduction rather than aerobic condition.

3.2. Determination of pH and temperature

In this study, pH and temperature have significant effects on Cr(VI) reduction by affecting both microbial activity and chemical reaction. The reduction of Cr(VI) was carried out under pH of 4.8, 5.8, 6.8, and 7.8, with the initial Cr(VI) concentration of 10 mg L^{-1}, Fe(III) dosage of 30 mg L^{-1}, and microorganism addition of 0.148 g L^{-1}, respectively. The groups were then incubated at 32°C in a shaker at 150 rpm. As shown in Fig. 2(a), the optimum pH for

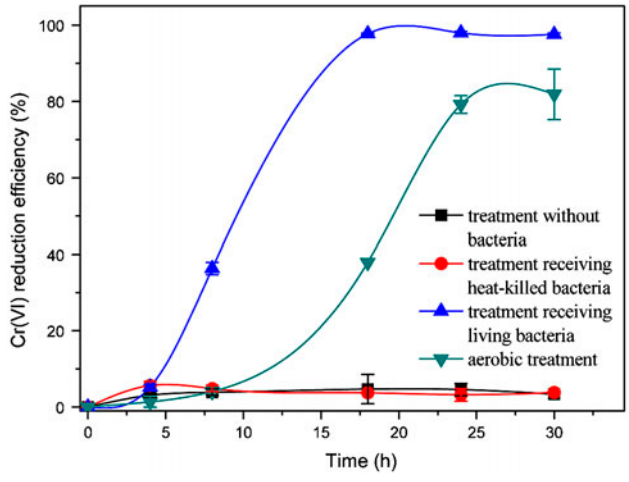

Fig. 1. Examination of Cr(VI) reduction potential by living bacteria and effects of oxygen on reduction process (pH, 5.8; initial Cr(VI) concentration, 10 mg L^{-1}; Fe(III) dosage, 30 mg L^{-1}; glucose as carbon source; incubated at 32°C and 150 rpm).

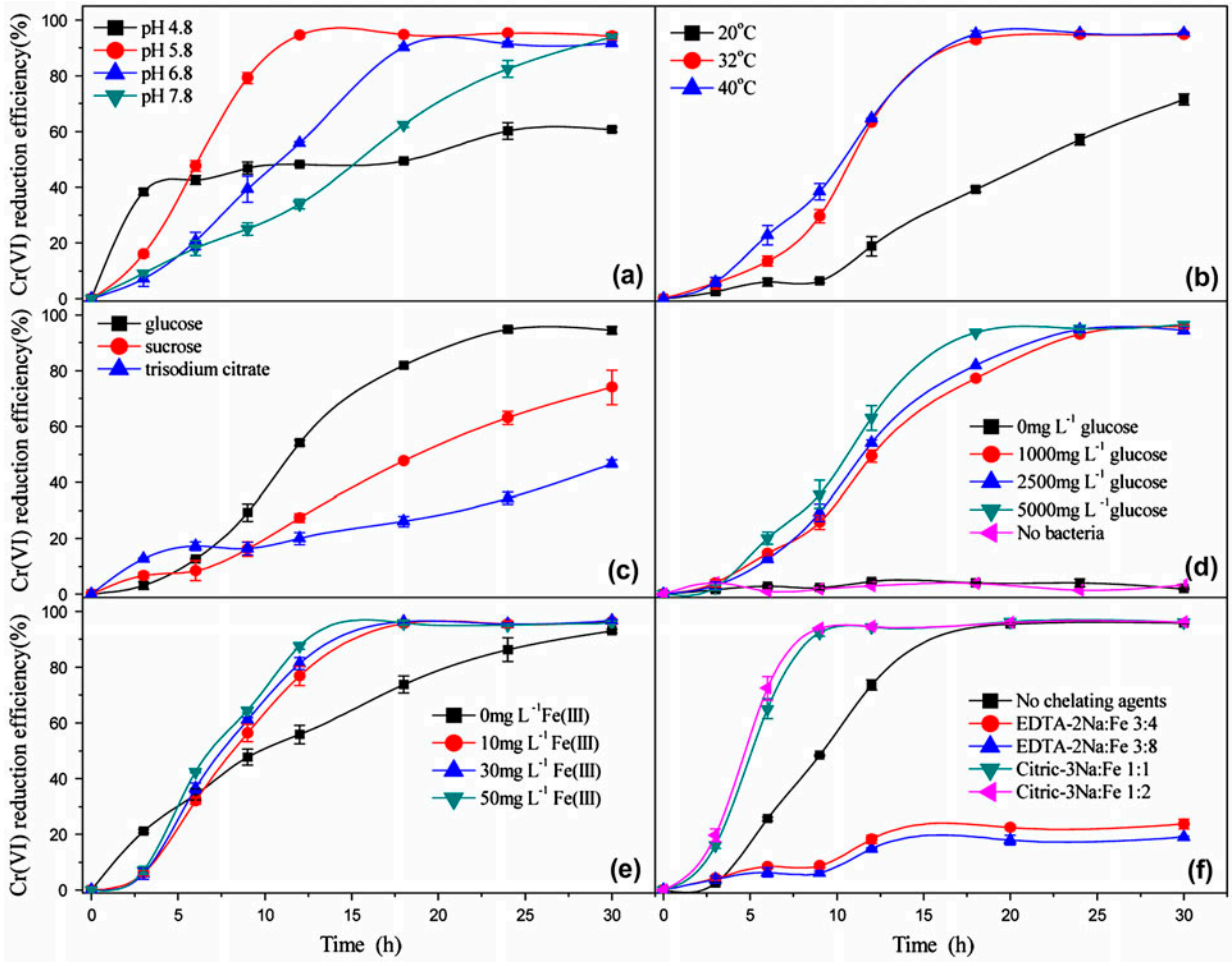

Fig. 2. Cr(VI) reduction efficiency for different (a) pHs, (b) temperatures, (c) carbon sources, (d) glucose additions, (e) Fe(III) dosages, (f) chelating agents amendments as a function of time (pH, 5.8; initial Cr(VI) concentration, 10 mg L^{-1}; Fe(III) dosage, 30 mg L^{-1}; glucose as carbon source; incubated at 32°C and 150 rpm; otherwise mentioned).

Cr(VI) reduction by bacteria in the presence of ferric iron was pH 5.8. Nonetheless, the bacteria were also capable of completely reducing Cr(VI) within 30 h at pHs of 6.8 and 7.8 with a decreasing reduction rate. Fig. 2(a) also shows that only 60% of Cr(VI) was reduced after 30 h incubation at pH 4.8, suggesting that the bacterial activity was limited when pH was 4.8. Mistry et al. [17] have studied the reduction of Cr(VI) using *Vogococcus sp*. to find out that the optimum pH occurred at 7. Pal and Paul [12] have also reported that the optimum pH and temperature for Cr(VI) reduction by bacteria isolates were 6 and 25°C. The difference in optimum pH indicated that pH modification was important for different microbe cultures to achieve the maximum Cr(VI) reduction in Cr(VI) detoxification [18].

Cr(VI) reduction by bacteria was also evaluated within a temperature range of 20–40°C. As shown in Fig. 2(b), Cr(VI) reduction at 32 and 40°C was quite synchronous and both completed in 18 h, while the reduction of Cr(VI) at 20°C was less efficient as compared to 32 and 40°C. This observation suggested that the most suitable temperature for the experimental system was 32°C considering both the efficiency and energy conservation, since lower temperature lowered the reduction rate, while higher temperature was not able to improve the rate.

Based on the experiments and analysis, the initial pH 5.8 and 32°C were applied for batch experiments below.

3.3. Effects of carbon source on chromate reduction

It has been reported that a variety of organic compounds may be utilized by micro-organisms as electron donors for Cr(VI) reduction [13]. In this study, the effects of carbon source i.e. glucose, sucrose, and trisodium citrate on Cr(VI) reduction by bacteria in

the presence of ferric iron were investigated. Fig. 2(c) presents Cr(VI) reduction efficiency of the three different carbon sources vs. time. Consequently, 94, 88, and 63% of Cr(VI) were reduced by glucose, sucrose, and trisodium citrate within 30 h of incubation, respectively. This result suggested that glucose was the optimum carbon source for Cr(VI) reduction among the three carbon sources. This result was consistent with the previous studies [19,20].

The effects of glucose concentration on Cr(VI) reduction was further investigated (Fig. 2(d)), with glucose additions of 0, 1,000, 2,500, and 5,000 mg L^{-1}, respectively. No Cr(VI) reduction was observed in the medium without glucose, while around 95% of Cr(VI) reduction was noticed in 30 h when glucose was applied. Moreover, the rate of Cr(VI) reduction slightly increased with the increase of glucose addition. This result implied that glucose was essential for bacterial Cr(VI) reduction and it significantly improved the Cr(VI) reduction.

3.4. Effects of Fe(III) dosage on chromate reduction

Different concentrations of Fe(III) were applied to investigate the effects of Fe(III) dosage on Cr(VI) reduction. As shown in Fig. 2(e), Cr(VI) reduction was significant and stable when Fe(III) was added to the medium. For all the three Fe(III) added sets, more than 95% of Cr(VI) was reduced within 18 h. However, treatment without Fe(III) reduced 73 and 92% of Cr(VI) within 18 and 30 h, respectively. This result suggested that Fe(III) played an important role during Cr(VI) reduction and could enhance the reduction. The raise of Cr(VI) reduction rate by Fe(III) loading in this study could be explained by reduction of Fe(III) to Fe(II) by micro-organisms and the product Fe(II) subsequently reduced Cr(VI) to Cr(III). Furthermore, early studies [21,22] have reported Cr(VI) reduction by Fe(II) and the reaction was ready and efficient. Mohatt et al. [23] found that sulfamethoxazole dissipation in soil microcosms was higher under Fe(III)-reduction conditions so that iron was likely to be an electron transmitter between electron donor (e.g. glucose) and sulfamethoxazole. Thus, in this study, Fe (III) increased the rate of Cr(VI) reduction by transferring electron between electron donor (e.g. glucose) and Cr(VI) with the help of bacteria.

3.5. Effects of chelating agent on chromate reduction

Fe(III) could be uniformly distributed in the solution by adding appropriate chelating agent, which contributed to the enhancement of the reduction process. In this study, we have also examined the potential of Cr(VI) reduction in culture medium amended with EDTA-2Na or citric-3Na (Fig. 2(f)). The molar ratios of EDTA-2Na to Fe(III) were set to 3:4 and 3:8, and the molar ratios of citric-3Na to Fe(III) were set to 1:1 and 1:2. As shown in Fig. 2(f), amendment with citric-3Na raised the Cr(VI) reduction rate, while the addition of EDTA-2Na inhibited Cr(VI) reduction. Comparing the two chelating agents, citric-3Na was supposed to be a useful extra carbon source and electron donor for bacteria and Cr(VI) reduction [24,25], while EDTA-2Na may inhibit bacterial growth and activity. Epelde et al. [26] have reported that EDTA had negative effects on soil respiration and dehydrogenation activity, and therefore inhibited the activity of soil microbial community. Moreover, EDTA-2Na had strong chelating capability, which could make Fe and Cr unavailable for the microbial transformation. For both chelating agents applied, however, their dosage had negligible effect on Cr(VI) reduction.

4. Discussion

Besides utilized by micro-organisms in the process, glucose may also react with chromate directly. The mechanism of the reaction was reported by Bayen et al. [27]. In the reaction, glucose serves as an electron donor, while Cr(VI) serves as a terminal electron acceptor. Nevertheless, this reaction was inconspicuous in our study due to the limited efficiency of Cr(VI) reduction in treatment with glucose but without bacteria. Results in this study suggested that Cr(VI) reduction was mainly accomplished through two mechanisms.

In the first, Cr(VI) was reduced by bacteria directly. In this process, electron donor (e.g. glucose) was essential, since the reduction of Cr(VI) almost did not occur during incubation when bacteria were not supplied with glucose or other electron donors (Fig. 2(d)). This observation suggested that Cr(VI) reduction in this study was related to glucose utilization and energy conservation in a certain way. Chris et al. [28] have found that the facultative anaerobe *Pantoea agglomerans* SP1 had the ability to couple anaerobic growth to the reduction of Cr(VI), which means Cr(VI) reduction was involved in the respiration and the process provided energy for *P. agglomerans* SP1 growth. Accordingly, in this study, Cr(VI) could possibly serve as an electron acceptor during bacteria respiration and be reduced as a result. Moreover, fermentation could be the main biological process rather than respiration. Glucose utilization via fermentation could conserve energy and co-metabolize chromate by bumping electrons to Cr(VI). Regardless the specific biological process, electrons produced during microbial metabolism were applied to Cr(VI) reduction. In a word, electron donor such as

glucose was essential for microbially mediated reduction of Cr(VI). Electrons originally provided by electron donors were received by Cr(VI) and reduced Cr(VI) to Cr(III) with the help of bacteria.

By the second mechanism, Fe(III) was enzymatically reduced to Fe(II) by bacteria. Fe(II), subsequently, shuttled its electron to Cr(VI) and was freshly oxidized to Fe(III) itself. Therefore, Cr(VI) was reduced to Cr(III) after receiving electrons from three 1-electron transfers. Thus, the second pathway of electron transfer could be described as electrons being transferred by bacteria and iron in sequence. The electrons were originally devoted by glucose and finally received by Cr(VI). Fig. 3 presents Fe(II) generation by bacteria and indicated the reduction of Cr(VI) by generated Fe(II). In the absence of Cr(VI), around 10 mg L^{-1} of Fe(II) was measured in the soluble phase within 12 h, which confirms the bacteria could reduce Fe(III) to Fe(II). On the contrary, only 4 mg L^{-1} of Fe (II) was found in the incubation with an initial Cr(VI) concentration of 10 mg L^{-1} within 12 h and Cr(VI) was reduced to around 1 mg L^{-1}. This result suggested the reduction of Cr(VI) by generated Fe(II). As shown in Fig. 3, Fe(II) concentration was maintained at 10 mg L^{-1} after 12 h incubation without Cr(VI) addition or Cr(VI) concentration was decreased to below detection limit. Overall, Fe(III) could be reduced by bacteria and hence enhanced the reduction of Cr(VI) via shuttling electrons by generated Fe(II). Improving of Cr(VI) reduction by iron-reducing bacteria in the presence of Fe(III) has also been reported by previous studies[16,29], which confirmed the second Cr(VI) reduction mechanism. Under anaerobic condition, Fe (III) was accessible to bacteria and the reduction of Fe (III) to Fe(II) appeared more facile than Cr(VI) reduction. Furthermore, chemical reaction between Fe(II) and Cr(VI) occurred rapidly, for data showing that more than 85% of Cr(VI) was reduced by Fe(II) within 1 min (data not shown; the initial concentrations of Cr (VI) and Fe(II) were 10 and 30 mg L^{-1}, respectively). The capability of iron reduction-oxidation under anaerobic condition supported the possibility and efficiency of iron application for Cr(VI) reduction by bacteria. Buerge and Hug [10] suggested that the product of Cr(VI) reduction by Fe(II) was X-ray amorphous, as no X-ray diffraction pattern was obvious. We have examined the product of our study using the same X-ray diffraction method, and found a similar result (data not shown).

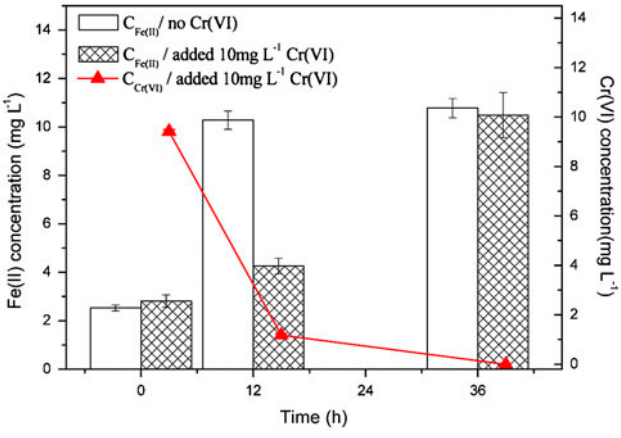

Fig. 3. Concentration of Fe(II) during reduction process with or without Cr(VI) addition (pH, 5.8; Fe(III) dosage, 30 mg L^{-1}; glucose as carbon source; incubated at 32°C and 150 rpm).

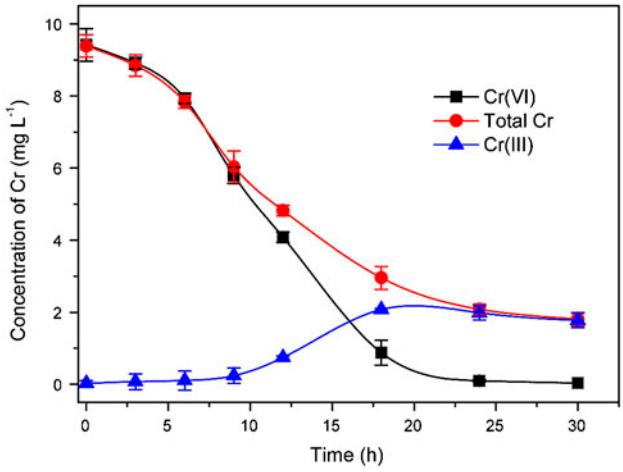

Fig. 4. Concentration of Cr(VI), Cr(III), and total Cr in soluble phase as a function of time (pH, 5.8; initial Cr(VI) concentration, 10 mg L^{-1}; Fe(III) dosage, 30 mg L^{-1}; glucose as carbon source; incubated at 32°C and 150 rpm. Samples were centrifuged at 8,000 rpm for 5 min and filtered through a 0.45 μm membrane filter before measurements).

In this study, concentrations of Cr(VI) and total chromium in soluble phase were also measured, and the Cr(III) concentration was calculated by subtracting Cr(VI) from total chromium. As demonstrated in Fig. 4, Cr(VI) concentration in soluble phase was decreased to undetectable level in 24 h, and total soluble Cr was also reduced significantly. This observation confirmed the precipitation of Cr(III) after Cr(VI) reduction.

Overall, Cr(VI) received electrons originally donated by organic compounds, such as glucose, and was reduced to Cr(III), which subsequently deposited to the sludge. Direct bacteria reduction and iron mediated bacteria reduction were the two mechanisms both taking place during Cr(VI) reduction process.

5. Conclusions

In this study, *E. coli* was applied to reduce Cr(VI) in the presence of soluble ferric iron. Results implied

that living bacteria were responsible for the decrease of Cr(VI) from solution and that anaerobic condition was preferred than the presence of O_2. Factors, including initial pH, temperature, Fe(III) dosage, carbon source, and chelating agent were discussed. Results suggested the optimum pH and temperature for Cr (VI) reduction were 5.8 and 32˚C. Organic compounds were required for the reduction of Cr(VI) and glucose supported faster reduction rate of Cr(VI) than sucrose and trisodium citrate. Increase of glucose concentration raised Cr(VI) reduction rate slightly. The reduction of Cr(VI) by bacteria was significant enhanced by soluble Fe(III), although increasing Fe(III) dosage had negligible effect on Cr(VI) reduction. Chelating agents influenced the reduction of Cr(VI) differently when different complex compounds were used. Amendments with citric-3Na enhanced the reduction of Cr(VI), while the addition of EDTA-2Na inhibited the process. Moreover, analysis of Cr(VI) reduction mechanisms showed that the soluble Fe(III) enhanced the reduction process by shuttling electrons from bio-reduced Fe(II) to Cr(VI) in a coupled biotic–abiotic cycle. Cr(VI) was reduced to Cr(III) followed by Cr (III) deposition to sludge.

Acknowledgments

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References

[1] M.Z. Alam, S. Ahmad, Toxic chromate reduction by resistant and sensitive bacteria isolated from tannery effluent contaminated soil, Ann. Microbiol. 62 (2012) 113–121.
[2] L. Liu, Y. Yuan, F.B. Li, C.H. Feng, In-situ Cr(VI) reduction with electrogenerated hydrogen peroxide driven by iron-reducing bacteria, Bioresour. Technol. 102 (2011) 2468–2473.
[3] W.T. Cefalu, F.B. Hu, Role of chromium in human health and in diabetes, Diabetes Care 27 (2004) 2741–2751.
[4] R.A.K. Rao, F. Rehman, M. Kashifuddin, Removal of Cr(VI) from electroplating wastewater using fruit peel of Leechi (*Litchi Chinensis*), Desalin. Water Treat. 49 (2012) 136–146.
[5] S.Q. Ye, S.Y. Guo, Y.G. Yu, H. Wu, R. Han, Removal of the heavy metal ion Cr(VI) by soybean hulls in dyehouse wastewater treatment, Desalin. Water Treat. 42 (2012) 197–201.
[6] M. Owlad, M.K. Aroua, W.A.W. Daud, S. Baroutian, Removal of hexavalent chromium-contaminated water and wastewater: A review, Water Air Soil Pollut. 200 (2009) 59–77.
[7] M. Gheju, Hexavalent chromium reduction with zero-valent iron (ZVI) in aquatic systems, Water Air Soil Pollut. 222 (2011) 103–148.
[8] X.S. Lv, J. Xu, G.M. Jiang, J. Tang, X.H. Xu, Highly active nanoscale zero-valent iron (nZVI)–Fe_3O_4 nanocomposites for the removal of chromium(VI) from aqueous solutions, J. Colloid Interface Sci. 369 (2012) 460–469.
[9] T. Lee, J.W. Park, Recovery of iron reactivity for removal of Cr(VI) using iron-reducing consortium, KSCE J. Civ. Eng. 10 (2006) 175–180.
[10] I.J. Buerge, S.J. Hug, Kinetics and pH dependence of chromium(VI) reduction by iron(II), Environ. Sci. Technol. 31 (1997) 1426–1432.
[11] M.G. Mitrakas, A.S. Pantazatou, R. Tzimou-Tsitouridou, C.A. Sikalidis, Influence of pH and temperature on Cr(VI) removal from a natural water using Fe(II): A pilot and full scale case study, Desalin. Water Treat. 33 (2011) 77–85.
[12] A. Pal, A.K. Paul, Aerobic chromate reduction by chromium-resistant bacteria isolated from serpentine soil, Microbiol. Res. 159 (2004) 347–354.
[13] Z.G. He, F.L. Gao, T. Sha, Y.H. Hu, C. He, Isolation and characterization of a Cr(VI)-reduction *Ochrobactrum* sp. strain CSCr-3 from chromium landfill, J. Hazard. Mater. 163 (2009) 869–873.
[14] W. Li, C.Z. Wu, S.H. Zhang, K. Shao, Y. Shi, Evaluation of microbial reduction of Fe(III)EDTA in a chemical absorption-biological reduction integrated NOx removal system, Environ. Sci. Technol. 41 (2007) 639–644.
[15] Y. Zhou, L. Gao, Y.F. Xia, W. Li, Enhanced reduction of Fe(II) EDTA-NO/Fe(III)EDTA in NO_x scrubber solution using a three-dimensional biofilm-electrode reactor, Environ. Sci. Technol. 46 (2012) 12640–12647.
[16] D.E. Cummings, S. Fendorf, N. Singh, R.K. Sani, B.M. Peyton, T.S. Magnuson, Reduction of Cr(VI) under acidic conditions by the facultative Fe(III)-reducing bacterium *Acidiphilium cryptum*, Environ. Sci. Technol. 41 (2007) 146–152.
[17] K. Mistry, C. Desai, K. Patel, Chromate reduction by *Vogococcus* sp. isolated from Cr (VI) contaminated industrial effluent, Electron. J. Biol. 6 (2010) 6–12.
[18] F. Masood, A. Malik, Hexavalent chromium reduction by *Bacillus* sp. strain FM1 isolated from heavy-metal contaminated soil, Bull. Environ. Contam. Toxicol. 86 (2011) 114–119.
[19] G.F. Liu, H. Yang, J. Wang, R.F. Jin, J.T. Zhou, H. Lv, Enhanced chromate reduction by resting *Escherichia coli* cells in the presence of quinone redox mediators, Bioresour. Technol. 101 (2010) 8127–8131.
[20] A.M.F. Orozco, E.M. Contreras, N.E. Zaritzky, Cr(VI) reduction capacity of activated sludge as affected by nitrogen and carbon sources, microbial acclimation and cell multiplication, J. Hazard. Mater. 176 (2010) 657–665.
[21] L.N. Døssing, K. Dideriksen, S.L.S. Stipp, R. Frei, Reduction of hexavalent chromium by ferrous iron: A process of chromium isotope fractionation and its relevance to natural environments, Chem. Geol. 285 (2011) 157–166.
[22] S.E. Fendorf, G. Li, Kinetics of chromate reduction by ferrous iron, Environ. Sci. Technol. 30 (1996) 1614–1617.
[23] J.L. Mohatt, L.H. Hu, K.T. Finneran, T.J. Strathmann, Microbially mediated abiotic transformation of the antimicrobial agent sulfamethoxazole under iron-reducing soil conditions, Environ. Sci. Technol. 45 (2011) 4793–4801.
[24] C. Desai, K. Jain, D. Madamwar, Hexavalent chromate reductase activity in cytosolic fractions of *Pseudomonas* sp. G1DM21 isolated from Cr(VI) contaminated industrial landfill, Process Biochem. 43 (2008) 713–721.
[25] A.M. Ferro Orozco, E.M. Contreras, N.E. Zaritzky, Cr(Vi) reduction capacity of activated sludge as affected by nitrogen and carbon sources, microbial acclimation and cell multiplication, J. Hazard. Mater. 176 (2010) 657–665.
[26] L. Epelde, J. Hernández-Allica, J.M. Becerril, F. Blanco, C. Garbisu, Effects of chelates on plants and soil microbial community: Comparison of EDTA and EDDS for lead phytoextraction, Sci. Total Environ. 401 (2008) 21–28.
[27] R. Bayen, M. Islam, B. Saha, A.K. Das, Oxidation of D-glucose in the presence of 2,2´-bipyridine by Cr(VI) in aqueous micellar media: A kinetic study, Carbohydr. Res. 340 (2005) 2163–2170.
[28] C.A. Francis, A.Y. Obraztsova, B.M. Tebo, Dissimilatory metal reduction by the facultative anaerobe *Pantoea agglomerans* SP1, Appl. Environ. Microbiol. 66 (2000) 543–548.
[29] B. Wielinga, M.M. Mizuba, C.M. Hansel, S. Fendorf, Iron promoted reduction of chromate by dissimilatory iron-reducing bacteria, Environ. Sci. Technol. 35 (2001) 522–527.