Assessing chromate reduction by dissimilatory iron reducing bacteria using mathematical modeling

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HIGHLIGHTS

- Three models were proposed to evaluate Cr (VI) reduction by IRB.
- Two-pathway rather single-pathway model could describe the experimental data.
- Both chemical and microbial pathways contributed to Cr reduction by IRB.
- The electron donor availability and HRT regulated the abiotic and microbial pathways.

ARTICLE INFO

ABSTRACT

Chromate (Cr (VI)) is a ubiquitous contaminant in aquifers and soils, which can be reduced to its trivalent counterpart (Cr (III)), with the hazard being relieved. The coupling microbial and chemical reduction by dissimilatory iron reducing bacteria (IRB) is a promising approach for the reduction of Cr (VI) to Cr (III). In this work, three mathematical models with different Cr (VI) reduction pathways were proposed and compared based on their ability to predict the performance of an IRB-based stirred-flow reactor treating Cr (VI) contaminated medium and to provide insights into the possible chemical or microbial pathways for Cr (VI) reduction in the system. The Cr (VI) reduction was considered as chemical reaction between Fe (II) and Cr (VI), direct microbial reduction by IRB and combined biotic–abiotic reduction in these three models, respectively. Model evaluation results indicated that the model incorporating both chemical and microbial Cr (VI) reductions could well describe the system performance. In contrast, the other two single-pathway models were not capable of predicting the experimental data, suggesting that both chemical and microbial pathways contributed to Cr (VI) reduction by IRB. The validity of the two-pathway model was further confirmed by an independent experimental data set with different conditions. The results further revealed that the organic carbon availability and Cr (VI) loading rates for the IRB in the system determined the relative contributions of chemical and microbial pathways to overall Cr (VI) reduction.

1. Introduction

Chromium is a ubiquitous chemical contaminant in soil and groundwater, which can be produced by numerous industries including electroplating, wood preservation, and leather tanning. Among the wide range of valency states of chromium (from −4 to +6), hexavalent chromium (Cr (VI)) prevails in natural aquifer, whilst it is trivalent counterpart (Cr (III)) is dominant in municipal wastewater rich in organics (Cheung and Gu, 2007). Cr (VI) is highly soluble in water and tends to be very mobile in ecosystem (Somasundaram et al., 2011). Due to the acute toxicity, mutagenicity and carcinogenicity, Cr (VI) has been recognized as one of the seventeen chemicals that pose greatest threat to human beings (Marsh and McInerney, 2001). In comparison to Cr (VI), Cr (III) is less toxic and mobile. Consequently, a full understanding of the potential transformation pathways from Cr (VI) to Cr (III) is of great significance towards effective detoxification of Cr (VI).

A variety of physic-chemical processes have been applied to reduce Cr (VI). Traditional treatment processes using reduction–precipitation, ion exchange and reverse osmosis are not proper for large-scale application due to the high cost for set up, operation

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and maintenance (Cheung and Gu, 2007). The chemical treatment involves reduction of Cr (VI) to Cr (III) by a strong reducing agent and subsequent precipitation of Cr (III). However, this treatment process could produce large amount of environmentally hazardous sludges that need to be further treated (Somasundaram et al., 2009). The biotransformation of Cr (VI) to Cr (III) has received increasing attentions in the last two decades and been used as an alternative treatment process for Cr (VI) contaminated waste (Cervantes et al., 2001).

Many microbes have been found to be able to reduce Cr (VI) aerobically and anaerobically (Gopalan and Veeramani, 1994; Fude et al., 1994; Campos et al., 1995; Philip et al., 1998; Smith and Gadd, 2000; Woo-Chul, 2000; Guha, 2004). Chromium reducing bacteria (CRB) may utilize different organic compounds such as carbohydrates, amino acids and fatty acids as electron donors for chromium reduction (Wang and Shen, 1995). In the absence of external electron donors, the soluble reductase activity necessitates the utilization of endogenous reserves by CRB. In the absence of oxygen, the soluble reductase activity can also tunnel electron transport to Cr (VI). Sulphate reducing bacteria (SRB) have been extensively studied for the reduction of Cr (VI) (Fude et al., 1994; Tebo and Obraztsova, 1998; Smith and Gadd, 2000). The produced sulphide has been shown to be preferably combined with heavy metal such as Cr (VI) and thus form insoluble metal sulphide (Smillie et al., 1981; Fude et al., 1994). The sulphide generated by SRB can also chemically reduce Cr (VI) to Cr (III). However, the release of hydrogen sulphide would result in secondary environmental pollution and the accumulation of sulphide would inhibit the SRB activity (O'Flaherty et al., 1998).

Iron reducing bacteria (IRB) can use ferric iron (Fe (III)) as an electron acceptor to oxidize organic matters (Somasundaram et al., 2011). The ferrous iron (Fe (II)), produced by IRB, is a stronger reactant for chromate reduction than sulphide from SRB (Khérici-Bousnoubra et al., 2009). Increasing evidence shows that IRB is also capable of biological reducing Cr (VI) (Lovley et al., 1993; Parmar et al., 2000). Hydrogen or organic carbon can be served as electron donor for metal reduction by IRB. Parmar et al. (2000) reported concomitantly microbial reduction of Cr (VI) to Cr (III) and Fe (III) to Fe (II) by *Shewanella alga* strain BrY (IRB). Wielinga et al. (2001) demonstrated that the biologically produced Fe (II) by *S. alga* strain BrY could reduce Cr (VI) to Cr (III) via chemical reaction, which was coupled to biotic reduction of Cr (VI) in a stirred-flow reactor. However, the fundamental mechanisms of Cr (VI) reduction as well as the microbial and chemical interactions in IRB-based Cr (VI) reduction system are still not fully understood.

In this study, the potential pathways of Cr (VI) reduction by IRB were assessed using mathematical modeling approach. Three mathematical models with different Cr (VI) reduction pathways were proposed and compared to evaluate the system performance of a stirred-flow reactor containing *S. alga* strain BrY continuously fed with Cr (VI) contaminated medium and to provide insights into the possible Cr (VI) reduction pathways under iron reducing conditions. The evaluations of the three models were conducted based on the same set of experimental data. Model-based simulation was further performed to assess the key affecting factors that determined the Cr (VI) reduction pathways by IRB.

2. Materials and methods

2.1. Mathematical modeling of Cr (VI) reduction by IRB

The chromate reduction mechanism (chemical, biological or combined pathways) cannot be readily uncovered based on the comparison of abiotic and biological experimental data. As a result, we propose three mathematical models based on chemical pathway, biological pathway and combined pathways in order to provide insights into the involved mechanism. The nomenclatures for concentration employed in the three models are provided in Table 1. The kinetic and stoichiometric matrices for the proposed three models are shown in Table 2. In all of the three models, three types of biological and chemical processes are considered, namely hydrous ferric oxide (HFO) corrosion, microbial reduction of Fe (III) to Fe (II) by IRB with lactate as the electron donor and IRB decay. However, in Model A (Table 2) chemical reaction between Fe (II) and Cr (VI) is considered as the only pathway for chromate reduction. In contrast, Model B (Table 2) excludes the chemical reductions of Cr (VI) and is developed based on microbial reduction of Cr (VI) by IRB. Model C (Table 2) incorporates both chemical and microbial reduction of Cr (VI) by IRB. Kinetic control of all the enzymatic reaction rates is described by Michaelis–Menten equation. The kinetic rate of $k_1 X_{Fe(III)}/(K_{Fe,1} + X_{Fe(III)})$, as described in Liu et al. (2015a) is used to simulate the process of HFO corrosion. The chemical reaction between Cr (VI) and Fe (II) is described by the kinetic rate of $k_2 S_{Cr(VI)} S_{Fe(II)}$. In addition, the inhibitory effect of chromium on microbial growth is also included by implementing a Monod inhibiting kinetics. Table 3 lists the definitions, values, and units of the parameters used in the three models.

2.2. Experimental data for model evaluation

Experimental data from a stirred-flow reactor containing *S. alga* strain BrY previously reported in Wielinga et al. (2001) was used for the model evaluation. *S. alga* strain BrY is a model dissimilatory IRB, which is well characterized and demonstrated to be able to couple the oxidation of organic acids and hydrogen gas (H_2) to the reduction of varying metals. The seed culture was initiated from frozen stocks of BrY in late log and grown for 8 h at 32 °C (150 rpm). Cell suspensions were obtained by centrifugation and transferred to sterile and anaerobic pressure tubes. Heat-killed cells were prepared by holding the cell suspension at 80 °C for 20 min. A sealed stirred-flow reactor with 100 mL working volume was used to conduct Iron/chromate reduction reactions. Lactate (as sodium lactate) was added as electron donor at a final concentration of 5 mM or 10 mM. Cell suspension and HFO were added to the reactor to initiate the reactions. A 0.2 μm pore-size filter and filter-backing disk were placed at the top of the chamber to retain the cells and the iron solids in the reactor. Media containing 0.1 mM chromate was pumped into the bottom of the reactor at 4 h in each batch test, and effluent was forced out through the filter to the fraction collector. The flow rate varied from about 1.5 mL/h to 4.5 mL/h at steady-state conditions resulting in retention times that ranged from 22 to 67 h.

Two sets of batch tests were carried out to evaluate the Cr (VI) reduction in the system: (1) Batch test I was conducted using the continuous feeding reactor containing HFO and an initial lactate concentration of 5 mM during experimental period of 60 h.

Table 1
The definition and units of the model components.

Variable	Definition	Unit
$S_{Fe(III)}$	Fe (III)	g Fe/m³
$S_{Fe(II)}$	Fe (III)	g Fe/m³
S_S	Lactate	g COD/m³
$S_{Cr(VI)}$	Cr (VI)	mol/m³
$S_{Cr(III)}$	Cr (III)	mol/m³
S_{Cr}	The sum of Cr (VI) and Cr (III)	mol/m³
$X_{Fe(III)}$	Hydrous ferric oxide	g Fe/m³
X_{IR}	Biomass of IRB	g COD/m³
X_S	Readily biodegradable COD	g COD/m³
X_I	Inert particular COD	g COD/m³