Journal of Hazardous Materials 219–220 (2012) 253–259

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Hexavalent chromium reduction in a sulfur reducing packed-bed bioreactor

Erkan Sahinkaya[a,*], Adem Kilic[b], Muslum Altun[c], Kostas Komnitsas[d], Piet N.L. Lens[e]

[a] Department of Bioengineering, Istanbul Medeniyet University, Göztepe, Istanbul, Turkey
[b] Department of Environmental Engineering, Harran University, Osmanbey Campus, 63000 Sanliurfa, Turkey
[c] Department of Chemistry, Hacettepe University, Beytepe, Ankara, Turkey
[d] Department of Mineral Resources Engineering, Technical University of Crete, 73100 Chania, Greece
[e] Unesco-IHE Institute for Water Education, Westvest 7, Delft 2611 AX, Netherlands

ARTICLE INFO

Article history:
Received 30 January 2012
Received in revised form 26 March 2012
Accepted 1 April 2012
Available online 7 April 2012

Keywords:
Chromium reduction
Sulfur reduction
Metal removal
Hydrogen sulfide

ABSTRACT

The most commonly used approach for the detoxification of hazardous industrial effluents and wastewaters containing Cr(VI) is its reduction to the much less toxic and immobile form of Cr(III). This study investigates the cleanup of Cr(VI) containing wastewaters using elemental sulfur as electron acceptor, for the production of hydrogen sulfide that induces Cr(VI) reduction. An elemental sulfur reducing packed-bed bioreactor was operated at 28–30 °C for more than 250 days under varying influent Cr(VI) concentrations (5.0–50.0 mg/L) and hydraulic retention times (HRTs, 0.36–1.0 day). Ethanol or acetate (1000 mg/L COD) was used as carbon source and electron donor. The degree of COD oxidation varied between 30% and 85%, depending on the operating conditions and the type of organic carbon source. The oxidation of organic matter was coupled with the production of hydrogen sulfide, which reached a maximum concentration of 750 mg/L. The biologically produced hydrogen sulfide reduced Cr(VI) chemically to Cr(III) that precipitated in the reactor. Reduction of Cr(VI) and removal efficiency of total chromium always exceeded 97% and 85%, respectively, implying that the reduced chromium was retained in the bioreactor. This study showed that sulfur can be used as an electron acceptor to produce hydrogen sulfide that induces efficient reduction and immobilization of Cr(VI), thus enabling decontamination of Cr(VI) polluted wastewaters.

1. Introduction

Hexavalent chromium is considered as acutely toxic, teratogenic and carcinogenic [1,2]. Contamination of soil, surface- and groundwater with chromium is a worldwide problem and is the result of its extensive use in numerous industrial processes such as production of alloys and mainly stainless steel, metal plating, leather tanning and wood treatment [3,4]. Although chromium exists in oxidation states varying between −2 and +6, Cr(VI) and Cr(III) are the most dominant ions present in industrial wastewaters [4]. In contrast to Cr(VI), the hydroxide of trivalent chromium is characterized by limited solubility at neutral pHs as well as by low availability for biological uptake. Cr(III), when present in low concentrations, is essential for human nutrition, whereas at high concentrations it is toxic to plants. Hence, the most commonly used approach to detoxify chromium containing solutions is the reduction of Cr(VI) to Cr(III) and its immobilization as amorphous hydroxide ($Cr(OH)_3$), which is either adsorbed or precipitated at slightly acidic or neutral pHs [5–9]. Chung et al. [9] reported that the maximum precipitation rate of $Cr(OH)_3$ occurs at pH around 8.0, while at a pH below 7.0 Cr(III) may not be present in solid form.

Cr(VI) can be reduced by chemical or biological means. Zero-valent iron, ferrous iron [3,5,7] and dissolved sulfide [10] are the most commonly used reagents in environmental systems for chromate reduction. Although chemical reduction of Cr(VI) with the use of zero-valent or ferrous iron is quite efficient, the main disadvantages of the process are the high cost of chemicals and the production of big volumes of sludge. Microbial reduction of Cr(VI) is one of the approaches used for the detoxification of solutions containing Cr(VI) [11]. Literature data on Cr(VI) toxicity are rather controversial. Several studies mention that Cr(VI) is toxic to activated sludge at concentrations above 5 mg/L, whereas other studies reported stimulation of bacterial growth up to 25 mg/L. However, it is mentioned that a high concentration of Cr(VI) inhibits activated sludge growth and 80 mg/L have been identified as lethal dose [12]. Several other studies reported that it is difficult to continuously remove Cr(VI) from solutions without intermittently reseeding a biological system [13]. Shen and Wang [14] studied a two-stage system where *Escherichia coli* cells grown aerobically in a completely mixed reactor (first-stage) pumped into an anaerobic plug-flow reactor to reduce Cr(VI) (second-stage) and reported that almost

* Corresponding author. Tel.: +90 216 280 32 05; fax: +90 216 602 28 05.
E-mail addresses: erkansahinkaya@yahoo.com, esahinkaya@medeniyet.edu.tr (E. Sahinkaya).

0304-3894/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jhazmat.2012.04.002

complete removal of Cr(VI) was achieved in the plug-flow reactor under specific operating conditions. The efficiency of the plug-flow reactor was significantly affected by the concentration of Cr(VI) in the feed, while the rate of Cr(VI) reduction decreased with time.

The main advantages of the use of biogenically produced hydrogen sulfide for the removal of Cr(VI) from contaminated solutions are the high reduction efficiency and the low cost of chemicals. The production of hydrogen sulfide via sulfate reduction for the biotreatment of acid mine drainage has been extensively studied (for a review, see Kaksonen and Puhakka [15]). Although the reduction of Cr(VI) under sulfidogenic conditions has been well demonstrated, only few studies are available in the literature [6,11,16]. Furthermore, it should be underlined that hydrogen sulfide, as a very effective reducing agent, is responsible for the reduction of Cr(VI) under sulfate-reducing conditions such as those prevailing in marine environments [10].

Although hydrogen sulfide is able to detoxify chromium containing solutions, other media contaminated with Cr(VI), such as groundwater, may not contain sufficient sulfate to enable its generation. In this case, elemental sulfur is used as electron acceptor to enable production of hydrogen sulfide. In the presence of an electron donor, such as acetate, elemental sulfur is reduced by *Desulfuromonas* to hydrogen sulfide, according to reaction (1) [17], which can be then used for the chemical reduction of Cr(VI) (reaction (2)) [10,11].

$$CH_3COOH + 4S^0 + 4H_2O \rightarrow 2H_2CO_3 + 4H_2S \quad (1)$$

$$2CrO_4^{2-} + 3H_2S + 4H^+ \rightarrow 2Cr(OH)_3 + 3S^0 + 2H_2O \quad (2)$$

$$CH_3COO^- + SO_4^{2-} \rightarrow 2HCO_3^- + HS^- \quad (3)$$

A major advantage of using elemental sulfur instead of sulfate as electron acceptor is that it requires four times less electron donor for the production of the same amount of hydrogen sulfide (reactions (1) and (3)). Although few studies have investigated the simultaneous Cr(VI) and sulfate reduction using sulfate reducing bacteria [6,11,16], the use of elemental sulfur as electron acceptor to generate hydrogen sulfide which is used for the reduction of Cr(VI) has not yet been studied. Elemental-sulfur is non-toxic, insoluble in water, stable under ambient conditions, and readily available. It can be also used as support material in bioreactors for sulfur reducing bacteria. Hence, the present study investigates the efficiency of biological removal of Cr(VI) in a packed-bed bioreactor in which elemental sulfur serves as electron acceptor for the production of hydrogen sulfide and the subsequent reduction of Cr(VI).

2. Materials and methods

2.1. Abiotic-chemical reduction of Cr(VI)

In order to explore the abiotic reduction of Cr(VI) with elemental sulfur, a batch experiment was carried out in the absence of biomass. In this experiment, an anaerobic reactor containing all required micro and macro nutrients, 5 g elemental sulfur, and 2 mg/L Cr(VI) was operated at 30 °C for 24 h.

In the second batch test, the chemical reduction of Cr(VI) was evaluated to confirm the stoichiometry of its reduction by hydrogen sulfide. 150 mL serum bottles were filled with 100 mL distilled water containing 100 mg/L Cr(VI) and covered with rubber septa and aluminum caps. The bottles were purged with N_2 gas for 5 min to remove oxygen. Effluent from a sulfur-reducing bioreactor (Section 2.2) containing the stoichiometric amount of hydrogen sulfide as indicated by reaction (2) (9.5 mg HS^-) was added to the bottles using a syringe. The bottles were incubated overnight at 30 °C in a shaking incubator operating at 100 rpm. Four runs were performed: two of them were controls and did not involve addition of hydrogen sulfide whereas hydrogen sulfide was added in stoichiometric amount to the other two parallel runs. The bottles were sampled at the start and the end of the incubation period in order to determine pH, and the concentration of hydrogen sulfide and Cr(VI).

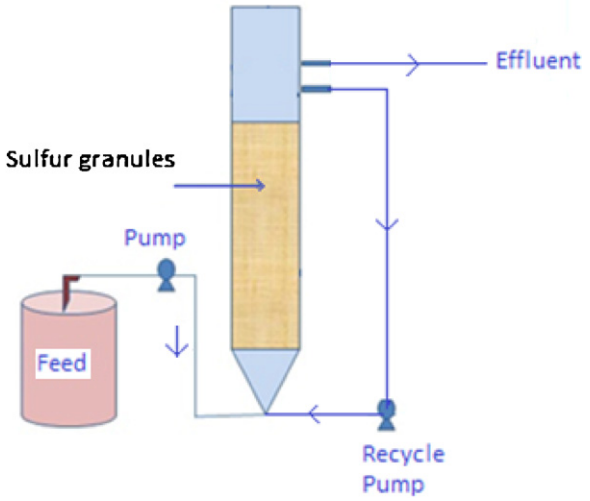

Fig. 1. Schematic representation of the column reactor used in this study.

In a third experiment, which was identical to the second one, except that biogenically produced hydrogen sulfide was added to the 1 L vessels. Sampling was done at specific time intervals and subsequent determination of the Cr(VI) reduction rate.

2.2. Bioreactor set up and operation

A laboratory glass column bioreactor with an empty bed volume of 500 mL was used (Fig. 1). The reactor was filled with commercially available elemental sulfur (3–5 mm, supplied from Microtek Ltd., Turkey) as support material and electron acceptor and covered with aluminum foil to prevent growth of phototrophic bacteria. Sulfate reducing sludge obtained from an anaerobic baffled reactor treating acid mine drainage was used as inoculum [18]. The reactor operated in batch mode for 7 days after inoculation, and then in continuous up-flow mode at 28–30 °C in a temperature controlled room. The feed contained micro and macro nutrients (56 mg/L KH_2PO_4, 110 mg/L NH_4Cl, 11 mg/L ascorbic acid and 50 mg/L yeast extract) and ethanol or acetate as electron donor and carbon source (1000 mg/L as COD). The feed was supplemented with 1000 mg/L $NaHCO_3$ to maintain the pH at neutral values, as well as with $K_2Cr_2O_7$ to obtain the desired Cr(VI) concentration (Table 1). All chemicals were purchased from Merck (Germany). The feed solution was kept refrigerated at 4 °C prior to use to prevent COD removal, sulfate reduction, and metal precipitation.

Synthetic wastewater was fed into the bioreactor (500–1400 mL/day) using a peristaltic pump to maintain the desired HRT (Table 1). The effluent was recirculated in the bioreactor at a ratio (flow rate of wastewater/flow rate of recirculated effluent) of 500 until day 142 in order to dilute feed, increase mass transfer and enable reactor operation in a completely mixed mode. HRT was calculated by considering the empty bed volume of the bioreactor and the feed flow rate without taking recirculation into account. After day 142, no recirculation took place in order to prevent loss of H_2S to the gas phase and thus increase its concentration in the liquid phase. Sampling of the reactor feed and the effluent was carried out 3 times a week to determine pH, alkalinity and COD, as well as the concentration of Cr(VI) and