Accepted Manuscript



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 PII:
 \$0304-3894(17)30298-4

 DOI:
 http://dx.doi.org/doi:10.1016/j.jhazmat.2017.04.049

 Reference:
 HAZMAT 18532

To appear in: Journal of Hazardous Materials

 Received date:
 26-1-2017

 Revised date:
 18-4-2017

 Accepted date:
 19-4-2017

Please cite this article as: G.Lytras, C.Lytras, D.Argyropoulou, N.Dimopoulos, G.Malavetas. G.Lyberatos, Α novel two-phase bioreactor for microbial chromium removal from of Hazardous hexavalent wastewater. Journal Materialshttp://dx.doi.org/10.1016/j.jhazmat.2017.04.049

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ACCEPTED MANUSCRIPT

A novel two-phase bioreactor for microbial hexavalent chromium removal from wastewater

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²Institute of Chemical Engineering Sciences, Foundation of Research and Technology (ICEHT/FORTH), Stadiou 10, Platani, Patras, GR 26504, *Highlights*

- Two-Phase Bioreactor for treatment of wastewater containing up to 1350 ppm Cr(VI)
- Use of Closite[®] 30B as a solid adsorbent for the reversible adsorption of Cr(VI)
- Pediococcus acidilactici prevailed and proved to be efficient in Cr(VI) reduction
- Under optimal conditions, 550 ppm Cr(VI) are completely reduced within 48 hours
- Extracellular reduction of Cr(VI) mediated by the microbially produced lactate

Abstract

A novel two-phase bioreactor for the microbial removal of Cr(VI) from wastewater with high chromium concentration (up to 1350 ppm) is developed.

Among several potential solid-phase adsorbents tested, $Cloisite^{\circ}$ 30B, a natural montmorillonite modified with a quaternary ammonium salt that absorbs Cr(VI) in a reversible manner proved to be optimal as the solid phase of the bioreactor. $Cloisite^{\circ}$ 30B has no toxicity to the acclimated biomass and keeps the concentration of Cr(VI) ions at sub-inhibitory levels that ensure the efficient microbial removal of Cr(VI). The microbial removal of Cr(VI) was achieved using an acclimated mixed culture developed from anaerobic sludge.

The novel bioreactor was operated as a Sequencing Batch Reactor (SBR) under anaerobic and mesophilic conditions for over 200 cycles, without further addition of the solid adsorbent, and led to even 100% removal of Cr(VI) with high removal rates for concentrations ranging from 900-1350 mg/L Cr(VI).

The reduction of Cr(VI) to the less toxic Cr(III) was proved to be mediated by lactate, generated by a lactic acid bacterium, 99% similar to *Pediococcus acidilactici* as demonstrated by molecular methods. The reduction of Cr(VI) took place extracellularly where it reacts with the lactic acid produced during the process of glycolysis.

Keywords: Hexavalent Chromium; Two-phase; Solid adsorbent; Cloisite[®] 30B; lactic acid bacteria; *Pediococcus acidilactici*

1. Introduction

Many industrial processes, such as leather tanning, electroplating, paint processing and wood preservation, lead to the production of wastewater streams with high chromium concentration. Nearly 170.000 tons of wastewater containing chromium are discharged to the environment annually worldwide [1]. Chromium exhibits a wide range of possible oxidation states ranging from Cr(II) to Cr(VI). Cr(II), Cr(III) and Cr(VI) are the most common and stable [2]. In aquatic systems, trivalent [Cr(III)] and hexavalent [Cr(VI)] are the most stable oxidation states.

Cr(VI) occurs as an anion in water, either chromate (HCrO₄⁻/ CrO₄²⁻) or dichromate (Cr₂O₇²/ HCr₂O₇⁻) depending on the pH and the concentration of Cr(VI). Cr₂O₇²⁻ dominates in acidic aqueous environments, while CrO₄²⁻ prevails in basic or slightly acidic ones. Moreover, Cr₂O₇²⁻ is transformed to HCrO₄⁻ in acidic aqueous solution at a total Cr (VI) concentration below 1.26–1.74 × 10⁻² mol/L [3]. All anionic forms are very soluble in water. Cr(VI) is a strong oxidizing agent with a proven cytotoxic, mutagenic and carcinogenic effect [4] and is considered toxic to humans and the environment even at ppb levels.

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