

Biological Treatment of Hexavalent (VI) Chromium Contaminated Wastewater Under Sulfate-rich Conditions

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Introduction

Large quantities of wastewater containing heavy metals are generated from industries, including textile, leather tanning, electroplating and metal finishing, as well as in the mine tailings. Heavy metals are released into the environment either in treated wastewater discharged to surface water or as sludges applied to landfills (1). They are generally toxic and cannot be degraded. However, remediation of metal contaminated water can be achieved by sorption or precipitation. Metal removal by biological sorption is achieved mainly with metal cations during the activated sludge process (2). Some bacterial species also uptake and accumulate a significant amount of certain metal ions, resulting in the transfer of metals from a contaminated matrix to biomass (3). Metal cations are precipitated biologically and typically seen in anaerobic systems containing sulfate where sulfidogens metabolically reduce sulfate to sulfide, resulting in precipitates of metal sulfides (4).

Wastewater from electroplating processes contains high concentrations of heavy metals (5). The heavy metal composition in the wastewater depends on the final products. Because the process requires strongly acidic conditions, electroplating wastewater has a low pH with high concentrations of anions such as sulfate, chloride and nitrate since metal ions are readily soluble at low pHs. Chromium (Cr) is a general contaminant in electroplating wastewater. It is a strong oxidant with mutagenic and carcinogenic activities (1). Because of its high toxicity, its release is a serious environmental concern. Chemical precipitation by pH adjustment and addition of reducing agents are the most widely used methods for treatment of Cr contaminated wastewaters (6, 7). However, these methods are expensive due to the requirement of large amounts of chemicals. In addition, a significant amount of sludge is produced, which is generally disposed of in a landfill (1). Therefore, alternative treatment methods have to be explored.

Generally, Cr exists in two oxidative states: hexavalent chromium [Cr(VI)] and trivalent chromium [Cr(III)] (8). Since Cr(VI) is much more toxic, soluble and mobile than Cr(III), the reduction of Cr(VI) to Cr(III) represents a prevalent treatment of Cr(VI) contaminated wastewaters.

This study was conducted to determine the major factors affecting biological treatment of Cr(VI) contaminated EW under sulfate-rich conditions. Basically, this study was carried out focussing on the stoichiometry of the electron. It also shows an economically feasible process for the treatment of Cr(VI)-rich wastewater from an electroplating process.

Materials and Methods

Materials

The electroplating wastewater (EW) was obtained from a local electroplating plant (Ansan, Korea), while wastewater having a high concentration of heavy metal contamination due to electroplating (HEW) was collected from an 'etching process' done at the same site. The organic wastewater (SPW) from a starch making process was used as a source of an easily degradable electron donor. Its organics and sulfate concentrations were 1500 mg COD_{Cr}/L and 150 mg sulfate/L, respectively. Limestone was obtained from a local mining area, and crushed to an average size of 1 cm in diameter. Spent oak from shiitake (SOS) was obtained from a local farm. SOS is a crushed waste oak log (1-2 cm in diameter) from the cultivation of shiitake mushrooms (*Lentinus edodes*). Sludge from a waste paper recycling plant (SWP) was collected from Hansol Paper Co. (Chonju, Korea) where waste paper is recycled.

Reactors and Their Operation

Up-flow packed-bed reactors were used. The system consisted of two column reactors. Acidic wastewater was initially fed into an alkaline reactor (acrylic cylinder, 1.8 L) with a working volume of 1.4 L where limestone (1000 g) was packed. Acidic wastewater was allowed to react with limestone during its passage through the reactor. The neutralized wastewater was pumped into a settling tank to remove solid particles, and then fed into the bioreactor. The bioreactor was initially-packed with 65.6 g of solid mixture [SOS:SWP (1:1)], and had a total volume of 0.5 L. The bioreactor was inoculated with anaerobic digester fluid (ADF, 180 mL) collected from Jungryang Municipal Wastewater Treatment Plant (Seoul, Korea) and pre-incubated at 30 for 7 days to remove organic matter. The pre-incubated ADF contained 6.8 g/L volatile suspended solids (VSS). After inoculation of ADF, the bioreactor was filled with neutralized EW (pH 6.2, 180 mL) to a working volume of 360 mL. The inoculated bioreactor was incubated for 9 days before feeding with the neutralized EW continuously in an up-flow mode using a peristaltic pump (505S, Watson-Marlow, Falmouth, Cornwall, UK) at a feeding rate of 25 mL/day. When the reactor reached steady state, the hydraulic retention time (HRT) was changed. Under the given HRT, the steady state was decided when the sulfate and heavy metals concentrations of the effluent were constant. A separate pump was used to feed the SPW. The chemical oxygen demand (COD_{Cr}) and total organic carbon (TOC) were measured to determine the consumption rate of the organics. During the operation, the flow rates of the liquid stream were confirmed every week. The temperature of the bioreactor was maintained at 37°C.

Analytical Methods

Metal concentrations were quantified using an atomic absorption spectrometer (Z-8200, Hitachi, Tokyo, Japan) after pre-treatment with nitric acid-hydrochloric acid using a standard method (3030F, 9). Sulfate concentrations were determined by the turbidimetric method (4500-SO₄²⁻ E, 9) using a spectrometer (UVIDEC-610, Jasco, Tokyo, Japan) at 420 nm. COD_{Cr} (5220 D, 9) was also analyzed using a standard method. The TOC was quantified by a TOC analyzer (TOC-5000A, Shimadzu, Tokyo, Japan). Volatile fatty acids were determined by gas chromatography (Varian 3400, Varian, San Francisco, CA, USA) as described previously (10). Nonvolatile fatty acids were measured by HPLC (M 930, Young Lin, Seoul, Korea) using a UV detector (M 720, Young Lin, Seoul, Korea) at 215 nm. Ion chromatography (Dionex DX-300, Dionex Co., Sunnyvale, CA, USA) was used to analyze anions, such as nitrate, nitrite, phosphate and chloride ions, using a conductivity detector.

Enumeration of Sulfidogens

Sulfidogens were counted using the most probable number (MPN) method (11).

Organics Consumption and Electron Recovery

Electrons available from the reduction of glucose and COD_{Cr} or TOC were calculated using the following equation: $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$, and compared with the electron consumption needed for the reduction of the electron acceptors, including SO_4^{2-}/HS^- , Cr(VI)/Cr(III), NO_3^-/NH_4^+ and NO_2^-/NH_4^+ .

Results and Discussion

Electroplating wastewater (EW) containing heavy metals was treated by a two-stage packed-bed reactor system. The acidic EW was effectively neutralized in an alkaline reactor where limestone had been packed. The neutralized wastewater together with wastewater from a starch processing factory (SPW) was fed to a sulfidogenic reactor packed with waste biomass. SPW was used to supplement the electron donor. The removal rates of sulfate and heavy metals were dependent on the electron consumption rate during the whole stage. About 67% of electrons from organics consumption were dynamically used to reduce sulfate. When the electron production rate by sulfide oxidation was higher than that required for Cr(VI) reduction, Cr(VI) was removed.

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