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A biological cyanide production and accumulation system and the recovery of platinum-group metals from spent automotive catalysts by biogenic cyanide

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ABSTRACT

A system for the biological production and accumulation of cyanide was developed, which was used to recover platinum-group metals (PGMs) from spent automotive catalysts. This two-stage process was proposed to overcome drawbacks of biological cyanidation such as low cyanide production, unsuitable pH for bacterial growth and cyanidation, and difficult access of cyanide lixiviant to the surface of target resources. The batch- and continuous-type cyanide production systems achieved maximum cyanide concentrations of 954.8 and 6594.5 mg/L, respectively. The leaching of Pt, Pd, and Rh from ground spent automotive catalysts by the biogenic cyanide was compared with leaching by a chemical NaCN solution. A 1000 mg/L biogenic cyanide solution leached Pt, Pd, and Rh at efficiencies of 92.1%, 99.5%, and 96.5%, respectively, at 150 °C. The chemical NaCN solution leached these PGMs at efficiencies of 100%, 99.9%, and 100%, respectively, under the same condition. These differences might be due to the effect of dissociated anions and oxygen in the biogenic cyanide. Although the leaching efficiencies by the biogenic cyanide were a little less than those by the chemical cyanide, the feasibility of the biological cyanide production and accumulation system for PGMs leaching was demonstrated.

1. Introduction

Platinum-group metals (PGMs; platinum, palladium, rhodium) are used as catalysts in automobile catalytic converters owing to their activity, stability, and selectivity (Webb, 1958; Hoffmann, 1988). The recovery of PGMs from catalyst materials is important, because PGMs are expensive and are often present in greater concentrations in secondary resources than in ore. Recovery from spent catalysts materials in industrial scale is usually via pyrometallurgical processes (Crundwell et al., 2011; Jha et al., 2013). Pyrometallurgical processes include plasma fusion, copper collection, and addition of crushed catalysts to a copper smelter feed, with subsequent electrodissolution to recover the PGMs (Bernfeld et al., 1985; Umicore, 2006). The advantages of pyrometallurgical process are increased productivity and greater efficiency, which results in maximized metal recovery rates (Hagelüken, 2006). However, this process is energy intensive, generates atmospheric pollution, and has a lengthy overall flow sheet which results in unavoidable PGM losses (Jha et al., 2013).

Hydrometallurgical processes are also studied to leach PGMs directly from catalyst materials using suitable lixiviants such as aqua regia (Schreier and Edtmaier, 2003; Jafarifar et al., 2005; Matjie et al., 2005), inorganic acid (HCl, HNO_3, and HF) (de Sá Pinheiro et al., 2004), or sodium cyanide (Atkinson, 1992; Kuczynski et al., 1992). Comparing with the pyrometallurgical processing, the hydrometallurgical method is more exact, more predictable, and easier to control (Andrews et al., 2000), but often results to lower recovery efficiencies and tends to produce large amounts of waste solutions (Rumpold and Antrekowitsch, 2012). Recently, many studies have targeted to develop environmentally friendly method for PGMs such as electro-generated chlorine (Upadhyay et al., 2013) and hydrogen peroxide (Kizilaslan et al., 2009) to reduce harmful and toxic gas emission and the amount of waste solution. Also, high-temperature cyanide leaching, a direct hydrometallurgical process, has in trials successfully leached PGMs for recovery (Desmond et al., 1991; Atkinson, 1992; Kuczynski et al., 1992; Shams et al., 2004; Chen and Huang, 2006). The chemical reaction of PGMs cyanidation is as follows (Chen and Huang, 2006):

$$2Pt + 8NaCN + O_2 + 2H_2O \rightarrow 2Na_2[Pt(CN)_4] + 4NaOH \quad (1)$$

$$2Pd + 8NaCN + O_2 + 2H_2O \rightarrow 2Na_2[Pd(CN)_4] + 4NaOH \quad (2)$$

$$4Rh + 24NaCN + 3O_2 + 6H_2O \rightarrow 4Na_3[Rh(CN)_6] + 12NaOH. \quad (3)$$

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The advantages of this method over acid leaching include low corrosion, selective PGM extraction, and lower base metal dissolution. However, excessive use of cyanide for the dissolution of PGMs has associated environmental risks, and thus more environmental friendly biological cyanidation for PGM leaching is being investigated. It is believed that the biological method has been one of the most promising environmentally sound technologies in metallurgical processing because bacteria produce cyanide and can subsequently detoxify in a biological cyanidation system. Biological cyanidation also has the advantage of producing cyanide without requiring the transport of the chemicals to a processing site.

Cyanide-producing bacteria, such as *Chromobacterium violaceum*, *Pseudomonas fluorescens*, and *Pseudomonas plecoglossicida*, produce cyanide from glycine by oxidative decarboxylation (Knowles and Bunch, 1986; Blumer and Haas, 2000). They have been used to recover gold from low-grade gold ores (Shin et al., 2013) and the printed circuit boards of waste electronics (Brandl et al., 2001; Tran et al., 2011a, 2011b). Very few works have been published in PGM recovery by cyanide producing bacteria, in particular, from spend automotive catalysts. Brandl et al. (2008) found about 0.2% mobilization of platinum from automobile catalytic converter by using *P. plecoglossicida*, cyanide producing bacteria. However, only low concentrations (3.5–15 mg/L) of cyanide have been produced biologically (Wissing, 1974; Tran et al., 2011b), and the pH of the bacterial cultures is not generally appropriate for cyanidation, which is optimal at above pH 10.5 (Rees and Van Deventer, 1999; Shams et al., 2004). In addition, the surfaces of the target ores or secondary resources are sometimes blocked from the cyanide lixiviant by biofilms or extracellular polymeric substances from the bacteria.

In this work, a two-stage process is proposed. Cyanide is first biologically produced, and then used to recover PGMs in a separate vessel. The initial stage used an air-purged *C. violaceum* culture bottle for biological cyanide production and two NaOH traps to capture and accumulate the HCN produced in the culture bottle. The operation conditions for maximum cyanide production were optimized such as the concentration of NaOH solution in the traps and operating time. The feasibility of using the biogenic cyanide for PGM recovery from spent automotive catalysts was then evaluated by comparing it with a NaCN solution in leaching tests. Factors such as temperature and cyanide concentration were also investigated.

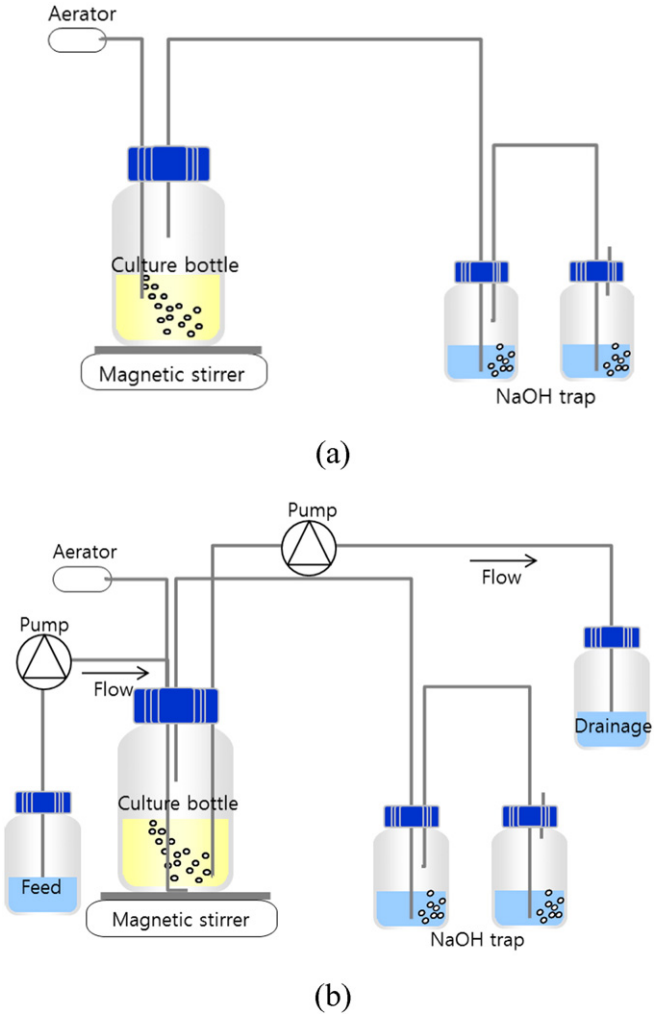

Fig. 1. Schematic diagrams of (a) the batch-type and (b) the continuous-type cyanide production and accumulation systems.

2. Experimental

2.1. Bacterial strain and culture conditions

A cyanide-producing bacterium, *C. violaceum* DSM 30191^T, from the Deutsche Sammlung von Mikroorganismen und Zellkulturen (DSMZ; Braunschweig, Germany) culture collection was maintained in yeast extract/peptone medium (YP medium; peptone 10 g, yeast extract 5 g, distilled water 1 L) (Tran et al., 2011b) at 30 °C. A non-cyanide-producing bacterium, *Bacillus megaterium* DSM 3228 (DSMZ) was also used (Castric and Castric, 1983). Bacterial viability was determined by plate counting on nutrient agar.

2.2. Operation of a cyanide production and accumulation system

A batch-type cyanide production and accumulation system employed a 2 liter Pyrex bottle and two NaOH traps with an aerator as shown in Fig. 1(a). The traps contained 50 mL NaOH solution at a concentration of 1, 5, or 10 N in a 100 mL amber Pyrex® bottle. *C. violaceum* pre-grown in the YP medium for 24 h was inoculated in the culture bottle containing 1 L YP medium at approximately 10^6 cells/mL. The glycine concentrations were varied in the YP medium to 0.5, 1, 2, 5, and 10 g/L to investigate the effect on cyanide production. The reactors were mixed with a magnetic stirrer at 300 rpm and maintained at 30 °C for 5 d. The dissolved oxygen (DO) concentration was uniformly maintained in the reactors by an aerator with a flow rate of 3 mL/s; its initial mean value in the reactor was about 5 mg/L.

A continuous-type cyanide production and accumulation system employed a reactor and trap system similar to that of the batch-type system, but the system was equipped with feed and drainage vessels and pumps to enable feed flow and drainage (Fig. 1(b)). The pre-grown *C. violaceum* in the YP medium was similarly inoculated in the culture bottle, and then cultivated under similar conditions with magnetic stirring for 1 d without feeding fresh YP medium. After 1 d, fresh YP medium containing 1 g/L glycine was fed continuously into the culture bottle at a flow rate of 1000 mL/d with a peristaltic pump. The reaction volume was constantly maintained at 1 L with a 1 d hydraulic retention time (HRT). The DO concentration was uniformly maintained by using an aerator. The reactor was operated for 11 d.

Samples were collected from the reactor and traps once a day during operation to measure the cyanide concentration and bacterial viability. After sample collection, the same volume (5 mL) and the same concentration of fresh NaOH solutions was added to the traps to maintain the total reaction volume; corrections were also made when calculating the total cyanide concentration. Bacterial viability was determined by plate counting on nutrient agar. The cyanide concentration was analyzed by titration against standard $AgNO_3$ solution (EPA_Method_9014, 1996; Clesceri et al., 1998).