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INVESTIGATION OF THE POSSIBILITY OF USING *ACIDITHIOBACILLUS FERROOXIDANS* JCM 3863 FOR BIOHYDROMETALLURGICAL RECOVERY OF RARE AND PRECIOUS METALS FROM SPENT CATALYTIC CONVERTERS

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Abstract: Precious metals like platinum, palladium, rhodium (PMG) and also copper have various industrial applications as catalysts. They play a crucial role in the automobile industry as components of the catalytic converter of vehicular tail gases. The iron oxidizing microorganisms *Acidithiobacillus ferrooxidans* demonstrate high resistance to heavy and toxic metals and has been largely implemented in biohydrometallurgy of copper, zinc, etc. Recently they have been used in the biotechnological treatment of secondary sources of metals, which make them potentially suitable for metal recovering from spent catalysts.

In this work, the experiments included 4 cycles of cultivation of *Acidithiobacillus ferrooxidans* JCM 3863 in batch in 100 ml original liquid media 9K with 1% inoculum and powder obtained from monolith formed of ceramics and metals from a spent catalytic converter, suitable for Citroen Saxo 2001 car, containing copper. Dynamics of ferrous iron oxidation were investigated in the presence of different amounts of the monolith powder in the range concentrations 10 - 30 g/l, at 28±0.5°C and 190 rpm. The average oxidation rates were estimated and compared with this one without monolith (biological control). Extension of the lag phase adaptation period and decrease of the average oxidation rate has been observed. The process wasn’t inhibited in this range of contents of monolith. The research also demonstrated the ability of *Acidithiobacillus ferrooxidans* JCM 3863 to leach copper from spent catalyst.

INTRODUCTION

XXI century is marked by significant technological progress. All new devises impact not only on human's life, but also on the environment. The global pollution and the demand for precious metals are increasing concurrently as well as many other natural materials. The main amount of wastes, whose components pollute irreversibly the environment are rich in heavy metals as Cd, Zn, Pb, Cu and hazard gases. They are a result from the burned fuels, the industries and the mining and can't be recycled. Precious metals like platinum and the other representatives of its group (PGM) can be recovered by conventional hydrometallurgical and pyrometallurgical methods, but in an insignificant amount (Rumpold and Antrekowitsch, 2012; Jha et al., 2013; Cui J.and Zhang L., 2008). Platinum and PGMs have been widely applied in medicine, in the production of electronics, space materials and especially in the automotive and chemical industries as catalyst due to its relative chemical nature, resistance and thermostability (http://www.platinum.matthey.com/). The natural sources for PGMs are not sufficient for the increasing demands (Buttler, 2011; Jha et al., 2013; http://www.cmmarket.ru/; http://www.gold.org/). The quantity of PGMs implemented in the exhaust system is about 2 g platinum, 0.5 g rhodium and less than 0.5 g palladium per kg of catalytic converter and vary by vehicle type, year and manufacturer (Ivanović et al., 2011). The automotive catalytic converter can reduce more than 99% of the gas emissions of CO, NO, hydrocarbons. Different mixtures of PGMs and other metals are like the copper built into it. They become activated after reaching 250°C. Then all burned gases are transformed by chemical reaction into less hazardous ones as CO_2, N_2 and H_2O.

As a result, the investigations are oriented towards new environmentally friendly approaches for liquidation of negative impact on the environment, including biotechnological methods using microorganisms like *Acidithiobacillus ferroxidans*, *Pseudomonas* sp, *Desulfovibrio* sp., etc. The iron oxidizing microorganisms *Acidithiobacillus ferrooxidans* demonstrate high resistance to heavy and toxic metals (Imai et al., 1975; Velkova et al., 2011; Molaei et al., 2011) and are largely implemented in biohydrometallurgy of copper, zinc, etc. (Torma, 1977; Rohwerder et al., 2003; Free, 2013). Our preliminary experiments confirmed resistance of *Acidithiobacillus ferrooxidans* to Cu, Zn and Cd ions (Doncheva, 2010; Velkova et al., 2011; Velkova, 2012). Recently, they have been used in the biotechnological treatment of secondary sources of metals (Jingwei Wang et al., 2009; Ilyas et al., 2010; Yang et al., 2013), which make them potentially suitable for recovering these metals from spent catalysts.

The aim of this work is to investigate the behaviour of *Acidithiobacillus ferrooxidans* JCM 3863 in the presence of monolith from automotive converter and its possibility to leach metals from it.

MATERIALS AND METHODS

Microorganisms. The experiments were carried out with the strain *Acidithiobacillus ferrooxidans* JCM 3863 from Japan Collection of Microorganisms.

Medium. Bacteria were cultivated in 9K liquid media (Silverman and Lundgren, 1959).

Automotive converter. The main components of the catalytic converter are presented in fig. 1 (http://www.bmcatalysts.co.uk/catalytic-converters/). Monolith (based on ceramics and catalytic metals) from a spent catalytic converter for Citroen Saxo 2001 has been used. The monolith was mechanical powdered. The initial size of a single particle is under 0.5 mm. It was placed in a different amount in liquid media.

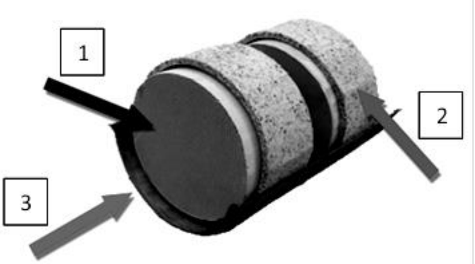

Figure 1. Components of a catalytic converter: 1. Ceramic monolith containing precious metals as the catalyst; 2. Heat resistant matting; 3. Grade 409 stainless steels (BM Catalysts, UK).

Experimental conditions. The experiments included four cycles of cultivation of Acidithiobacillus ferrooxidans JCM 3863 in batch in 100 ml mixture of original liquid media 9K, 1% inoculum and different amount of powdered monolith in range10 - 30 g/l, 28±0.5°C, pH=2 and 190 rpm. The average oxidation rates were estimated and compared with a biological control cultivated without monolith powder. The chemical oxidation without bacteria and monolith has been used as chemical control. All experiments were carried out in triplicate.

Analytical methods. Concentrations of ferrous, ferric ions and total iron were determined spectrophotometrically (Karamanev et al., 2002). The concentration of copper ions in liquid phase was determined by atomic absorbance spectrometry at the end of each cycle after filtration and centrifugation at 4000 rpm for 40 minutes.

Dynamics of Acidithiobacillus ferrooxidans JCM 3863 oxidation activity. Average oxidation rates have been calculated as follows:

$$\mathbf{r = (P_t - P_o)/t,} \qquad (1)$$

where: **r** is the average oxidation rate [g/l.h], $\mathbf{P_o}$ – initial concentration of product Fe^{3+} [g/l], $\mathbf{P_t}$ – concentration of product Fe^{3+} at the time t [g/l], t – time from the start of process to the achievement of a defined degree of oxidation of Fe^{2+} [h].

Degrees of substrate oxidation have been calculated as follows:

$$\boldsymbol{\eta = (S_o - S_t).100/S_o \text{ or } \eta = (P_t - P_o).100/S_o,} \qquad (2)$$

where: **η** is the degree of oxidation of substrate Fe^{2+} [%], $\mathbf{S_o}$ – initial concentration of substrate Fe^{2+} [g/l].

The dynamics of both bacterial and chemical controls have been obtained under the same conditions as the experiments with monolith.

Data treatment. All the results have been obtained after data treatment by means of Microsoft Excel 2010 and Origin 6.1.

RESULTS AND DISCUSSION

Dynamics of ferrous ions oxidation in presence of powered monolith. The investigations with suspended cells of *Acidithiobacillus ferrooxidans* JCM 3863 have been shown that at concentrations of powdered monolith in the range of 10 – 30 g/l dynamics of bacterial oxidation of ferrous (fig.2) wasn't inhibited. Compared with dynamics of process in biological controls it has been found a significant extension of the lag phase. After it, during the log phase, the character of the dynamics of ferrous ions oxidation has been almost similar in all experimental series. Degree of Fe^{2+} oxidation from the process beginning to 5-7 g/l Fe^{3+} has been observed to be lower (36-75%) against those in controls (85-86%). This result could be explained by sorption of iron in ceramic monolith. We observed decreasing of the Fe^{3+} and total iron in the liquid phase when the concentration of produced Fe^{3+} has been reached to these concentrations (5-7 g/l). This may lead to wrong calculations of the degree and average rate of oxidation. It has to keep in mind that we determined these quantities only for the period of ferric concentration increase in the log phase (fig. 2 and 3).

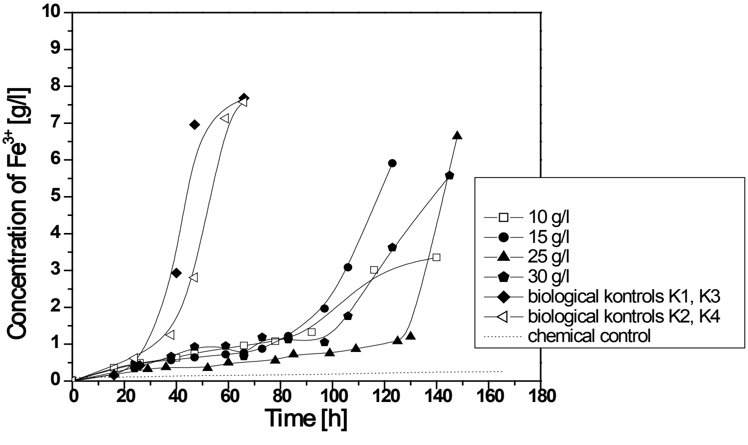

Figure 2. Dynamics of ferrous ions oxidation in presence of powered monolith.

The average oxidation rates in the presence of powered monolith have been determined to be very low – in the range 0,024 – 0,048 g/l.h. These results have been up to 3 times lower compared with those of biological controls where they have been 0,115 - 0,116 g/l.h.

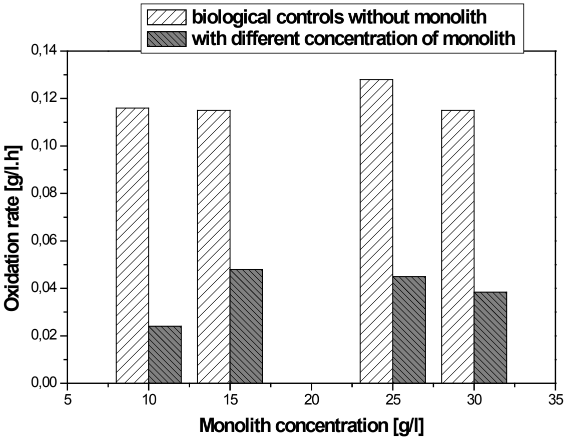

Figure 3. Apparent average oxidation rates in presence of powered monolith and in biological controls.

Bioleaching of copper from powered monolith. Some automobile converters contain copper as part of the catalyst. Because of that we have investigated the possibility of *Acidithiobacillus ferrooxidans* JCM 3863 to leach copper from monolith. After the end of each cycle of cultivation in the presence of powered monolith, the concentration of leached copper ions in liquid phase has been determined. The results are shown in table 1.

Table 1. Copper ions bioleached from monolith.

Concentration of powered monolith [g/l]	Amount of powered monolith in the flask [g]	Average amount of bioleached copper in the flask [mg]
10	1,0	0,90
15	1,5	1,10
25	2,5	1,45
30	3,0	1,55

The established ability of *Acidithiobacillus ferrooxidans* JCM 3863 to leach copper from spent catalyst is the main result of this investigation. The results obtained in this experiment can serve as a basis for the development of new biohydrometalurgical methods for leaching of copper from spent catalysts and thus to facilitate the further removal of other metals.

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REFERENCES

1. BM Catalysts, UK, http://www.bmcatalysts.co.uk/catalytic-converters/
2. Buttler J. Platinum. 2011. Johnson Matthey Publishing, (UK) http://platinum.matthey.com/uploaded_files/PT_2011/complete_publication.pdf
3. Cui J., Zhang L. 2008. Metallurgical recovery of metals from electronic waste: A review. *Journal of Hazardous Materials*, 158:228–256.
4. Doncheva V. 2010. Investigation of heavy metals influence on oxidation ability of *Acidithiobacillus ferrooxidans* JCM 3863 in biofilm. Ms. Thesis, Faculty of Biology, Sofia University “St. Kliment Ohridski”, Sofia, Bulgaria.
5. Free M., 2013. Hydrometallurgy: Fundamental and Applications. Minerals, Metals and Materials Society, pp. 137-182.
6. Ilyas S., Ruan C., Bhatti H.N., Ghauri M.A., Anwar M.A. 2010. Column bioleaching of metals from electronic scrap. *Hydrometallurgy*,101:135–140.
7. Imai K., Sugio T., Tsuchida T., Tano T. 1975. Effect of heavy metal ions on the growth amd iron-oxidizing activity of *Thiobacillus ferrooxidans*, *Agricultural Biology and Chemistry*, 39: 1349-1354.
8. Ivanović S.Z., Trujuć V.K., Gorgievski M.D., Mišić L.D., Božić D.S. 2011. Removal of platinum group metals (pgms) from the spent automobile catalyst by the pyrometallurgical process. *15th International Research/Expert Conference ”Trends in the Development of Machinery and Associated Technology” TMT 2011, Prague, Czech Republic, 12-18 September 2011*, pp.701-704. http://tmt.unze.ba/zbornik/TMT2011/167-TMT11-048.pdf.
9. Jha M.K., Lee Jae-chun, Kim Min-seuk, Jeong J., Kim B.-S., Kumar V. .2013. Hydrometallurgical recovery/recycling of platinum by the leaching of spent catalysts. *Hydrometallurgy*, 133: 23–32.
10. Johnson Matthey, Precious Metals Management, (UK) http://www.platinum.matthey.com/
11. Karamanev D., Nikolov L., Mamatarkova V. 2002. Rapid simultaneous quantitative determination of ferric and ferrous ions in drainage waters and similar solutions. *Minerals Engineering*, 15 (5): 341-346.
12. Molaei S., Yaghmaei S., Ghobadi Z. 2011. A study of Acidithiobacillus ferrooxidans DSMZ 583 adaptation to heavy metals. *Iranian Journal of Biotechnology*, 9: 133-144.
13. Rohwerder T., Gehrke T., Kinzler K., Sand W. 2003. Bioleaching Review Part A: Progress in Bioleaching: Fundamentals and Mechanisms of Bacterial Metal Sulfide Oxidation. *Applied Microbiology and Biotechnology*, 63: 239–248.
14. Rumpold R., Antrekowitsch J. 2012. Recycling of platinum group metals from automotive catalysts by an acidic leaching process, *The Southern African Institute of Mining and Metallurgy, Platinum 2012*: 695-713.

15. Silverman, M.P., Lundgren, D.G. 1959. A study on the chemoautotrophic iron bacterium *Ferrobacillus ferrooxidans*. I. An improved medium and a harvesting procedure for securing high cell yields. *Journal of Bacteriology*, 77: 642-647.
16. Torma, A.E. 1977. The role of *Thiobacillus ferrooxidans* in hidrometallurgical processes. *Advances of Biochemical Engineering*, 6: 1-37.
17. Velkova G. 2012. Dynamics of bacterial oxidation of iron ions by *Acidithiobacillus ferrooxidans* JCM 3863 in presence of copper ions. Ms. Thesis, Faculty of Biology, Sofia University "St. Kliment Ohridski", Sofia, Bulgaria.
18. Velkova G., Doneva A., Mamatarkova V. 2011. Influence of Cu^{2+} and Co^{2+} on Bacterial Oxidation of Ferrous Ions by Acidithiobacillus ferrooxidans JCM 3863 in Suspended Cells Cultures. Youth scientific conference "Kliment's Days". Conference Proceeding, Second Book: 11-14, ISSN: 1314-4960.
19. World Commodity Markets (Мировые товарные рынки), http://www.cmmarket.ru/
20. World Gold Council, http://www.gold.org/
21. Yang Y., Diao M., Liu K., Qian L., Nguyen A.V., Qui G.2013. Column bioleaching of low-grade copper ore by *Acidithiobacillus ferrooxidans* in pure and mixed cultures with a heterotrophic acidophile *Acidiphilium* sp. Hydrometallurgy, 131–132: 93–98.