Characterization and Biotechnological Clean-up Process of a TiO_2 Spent Catalyst

Brenda R. Cruz-Ortiz, Lourdes Díaz-Jiménez, and Dora A. Cortés-Hernández

***Abstract*—TiO_2-based catalysts are widely used in Claus units in natural gas-processing plants, for the conversion of hydrogen sulfide to elemental sulfur. As a result of the constant reaction cycles the catalyst suffered sulfur deposition on its active sites, resulting in a decrease of its catalytic activity. In this work a biodesulfurization process on a TiO_2 spent catalyst was performed. Physicochemical characterization of the catalyst by scanning electron microscopy, X-ray diffraction, specific surface area, and elemental analysis was performed. *Thiobacillus thiooxidans* was the microorganism employed to eliminate the sulfur from the spent catalyst. A sulfur reduction of 60 wt.% was obtained following 30 days of treatment.**

***Index Terms*—*Acidithiobacillus thiooxidans*, microbial desulfurization, spent catalyst, TiO_2.**

I. Introduction

The gasification and refining processes of the petrochemical industry generate wastes by their catalytic stages. One of the impurities present in the natural gas is hydrogen sulfide (H_2S) which produces corrosion and acid rain. As per environmental regulations, the H_2S has to be removed from the natural gas. The Claus process is employed for the conversion of H_2S to elemental sulfur. This process consists of a serial of catalytic reactions that involve the use of three different catalysts. One of these catalysts is titanium dioxide (TiO_2). This TiO_2 is discarded after five years of catalytic reactions due to sulfur deposition on its surface. However, these catalytic wastes are not appropriately confined due to the dispersion of the accumulated species, leading to the risk of ecosystem contamination. Several authors have developed physicochemical methods for the reactivation or cleaning of spent catalysts [1]-[3]. Nevertheless, these methods use chemicals and generate by-products which involve high costs and environmental risks. Thus, the need of new alternatives using microbiological methods became prominent and has been widely studied. These microbiological methods have the ability to transform non-essential compounds that eventually may represent an environmental threat [1]-[3].

Biotechnological processes have attracted attention due to their low cost and high efficiency. The more common example is bioleaching, which is a novel approach for the recovery of metals from various solid industrial wastes. Bioleaching is based on the ability of some microorganisms to transform solid compounds into extractable entities. Several authors [4], [5] have studied the use of acidophilic sulfur oxidizing bacteria as *Acidithiobacillus thiooxidans*, *Leptospirillum ferroxidans*, and *Sulfolobus* to extract valuable metals such as Ni, V, and Mo from spent petroleum catalyst. *A. thiooxidans* is a chemolithotrophic acidophilic bacterium that grows on elemental sulfur as energy source and it is important in the microbial catalysis of sulfide oxidation.

The aim of this work is to develop a biodesulfurization method to transform sulfur species, occluded on the catalytic sites of a TiO_2 spent catalyst, into products of easy elimination; generating a sulfur-free catalyst that can be used as a raw material to produce new high value-added products.

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Brenda R. Cruz-Ortiz is with the Ceramics Department at Autonomous University of Coahuila, México. Blvd. V. Carranza y José Cárdenas Valdés, C.P. 25280, Saltillo, Coah, México (e-mail: b.cruz@uadec.edu.mx).

Lourdes Díaz-Jiménez and Dora A. Cortés-Hernández are with CINVESTAV-Saltillo. Av. Industria Metalúrgica No. 1062, Ramos Arizpe, Coahuila, 25900, México (e-mail: lourdes.diaz@cinvestav.edu.mx, dora.cortes@cinvestav.edu.mx).

II. Materials and Methods

A. Spent Catalyst Characterization

The spent catalyst employed in this study was supplied by Pemex-Gas refinery (Mexican Petroleum Company) localized in the southeast of México. The catalyst was powdered using a porcelain mortar and a pestle. This powder was sieved through # 100 mesh size and its characterization was performed by X-ray diffraction (XRD, Philips® Mod. X'Pert PW3040), using a current of 30 mA and a voltage of 40 kV in a 2θ range from 10° to 80°; scanning electron microscopy (SEM, Philips® , Mod. XL30 ESEM), equipped with system of microanalysis by EDS (EDAX, Mod. Genesis); specific surface area (BET Beckman Coulter, Mod. SA 3100). In addition, elemental analyses were performed by combustion (LECO Corporation CS-230) and atomic absorption spectroscopy (Thermo Electron Corporation, Mod. Solaar S4).

B. Bacteria Strain and Culturing

The strain used in the desulfurization experiments was *Acidithiobacillus thiooxidans* (ATCC-19377). The bacterium arrived frozen in a test tube. This tube was incubated at room temperature for two weeks. The culture was examined by phase contrast microscopy (Carl Zeiss®) to ensure that growth had occurred. Then, the entire tube was used to inoculate 100 mL of medium ATCC #125 (sulfur 10 g, $(NH_4)_2SO_4$ 0.2 g, $MgSO_4 \cdot 7H_2O$ 0.5 g, $CaCl_2$ 0.25 g, KH_2PO_4 3.0 g and $FeSO_4$ 5.0 mg per liter of distilled water). The medium was sterilized by autoclaving at 15 lb/in^2 for 15 min. In the previous step, the sulfur was sterilized separately using UV irradiation for 1 h. The flask was placed on a shelf at room temperature during 4

weeks until the sulfur settled to the bottom of the flask, as a signal of bacteria growth.

In order to achieve a high bacteria concentration for the desulfurization experiments, *A. thiooxidans* was cultivated aerobically at 26℃ in 100 mL of medium ATCC-125 (pH 2 adjusted with H_2SO_4). The end of the exponential growth phase was reached at ~ 200 h with an average biomass of 10^{10} cells/mL. This solution was used as the planktonic (suspended) inoculum for the biodesulfurization experiments.

C. Biodesulfurization Process

Before the biodesulfurization treatments, the SC was immersed in 75% ethanol (v/v) for 1 h in order to kill the microorganisms attached to it. The amount of catalyst employed in the experiments was 10% (w/v). This catalyst was used as sulfur source for *A. thiooxidans*. The catalyst was placed in a flask with 100 mL of medium ATCC #125 (pH 2) with 1 mL of *A. thiooxidans* solution (~10^{10} cells/mL). Furthermore, experiments with 0.1 or 0.5% (w/v) of sulfur as additional source of energy were prepared. All the flasks were incubated aerobically at 26℃ for 30 days. The biotic assays were done in triplicate. In order to compare the chemical and biological sulfur oxidation, an abiotic (without *A. thiooxidans)* control was also tested. Bacteria cell count, pH value, sulfate concentration (turbidimetric method, ASTM D-516-68/Method B), and sulfur analysis were made during the 30 days of treatment.

III. Results and Discussion

A. Spent Catalyst Composition

The chemical analysis of the spent catalyst showed the presence of sulfur (1.90 wt.%), carbon (0.06 wt.%), silicon (0.07 wt.%), aluminum (0.90 wt.%), copper (0.005 wt.%), iron (0.16 wt.%), and zirconium (0.10 wt.%). The presence of iron and copper indicates that the spent catalyst contains promoter substances, which were added to the catalyst to increase its catalytic activity and its useful life. These elements modify the structure and the acidic properties, increasing its catalytic activity in oxidation, dehydrogenation and, photocatalysis reactions, improving TiO_2 activity [6]. The BET analysis of the spent catalyst showed a specific surface area of 1.4 m^2/g. For comparison purposes, a BET analysis to one sample of TiO_2 catalyst in optimal conditions showed a specific surface area of 156 m^2/g; these results indicate that other cause of catalyst decay was the loss of active sites due to variations in reactor temperatures and sulfur condensation on the catalyst.

Fig. 1a) shows a morphology consisting of well-defined sheet flake-type particles captured by SEM, with a heterogeneous size distribution in a range between 3 and 25 μm. In Fig. 1b) the longitudinal cross-section of the spent catalyst shows sintered zones in the surface of the pellet. This observation is in agreement with the specific surface area result, confirming that the loss of surface area was an important factor in the catalyst deactivation. The corresponding EDS spectra (Fig. 2) showed the presence of titanium, oxygen, sulfur, calcium and aluminum. These results are in agreement with the XRD results (Fig. 3) that showed Al_2O_3, $CaSO_4$, $CaTiO_3$, and polymorphisms of TiO_2 (anatase and rutile).

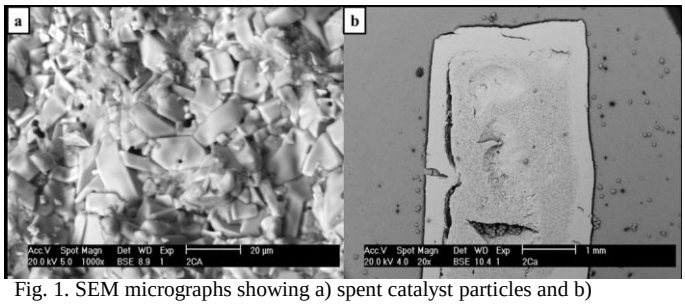

Fig. 1. SEM micrographs showing a) spent catalyst particles and b) longitudinal cross-section of spent catalyst pellet.

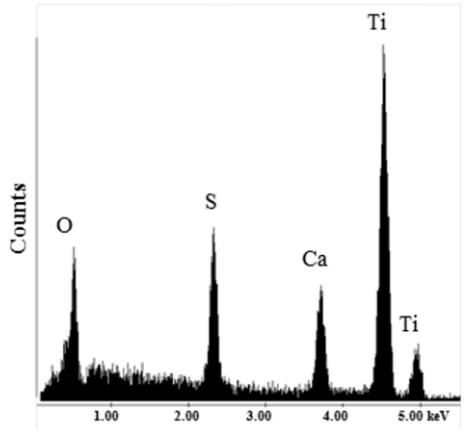

Fig. 2. EDS spectra of the spent catalyst.

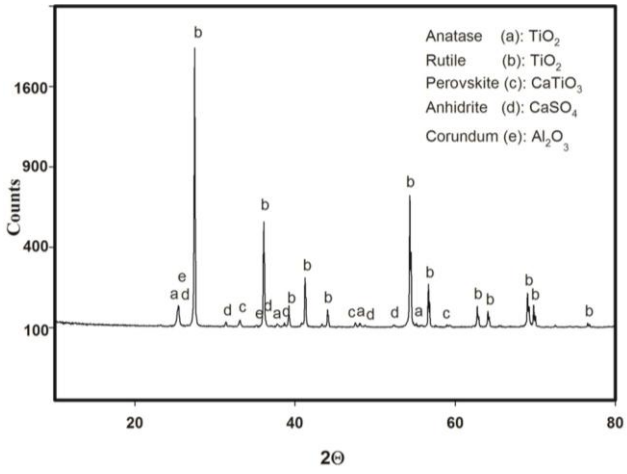

Fig. 3. DRX diffractogram of the spent catalyst.

B. A. thiooxidans Growth and TiO_2 Spent Catalyst Clean-up

A. thiooxidans demonstrated a favorable growth at pH 2. The growth of *A. thiooxidans* in presence of 0.1 or 0.5% (w/v) of sulfur (Table I) did not show significant difference in its cell concentration (~10^9 cells/mL), during the 30 days of biodesulfurization. This indicates an efficient growth in presence of the spent catalyst and demonstrates that, this bacterium is able to grow with lower sulfur concentrations than that reported in the literature (1 g/L) [7].

Table II shows the biodesulfurization results after 15 and 30 days of treatment. During the first 15 days of treatment, a decrease in the sulfur content occurred in biotic and abiotic experiments; however, this result is attributed to sulfate dissolution. From the day 15, an increase in the

biodesulfurization percentages in the experiments with *A. thiooxidans* was observed. Similar results were obtained in presence of 0.1 % (w/v) and absence of sulfur, avoiding the necessity of additional sulfur and making the process simpler. The chemical analysis from the day 30 showed sulfur reduction up to 59.5% ± 0.05 for the experiment performed in absence of additional sulfur.

TABLE I: AVERAGE CELL DENSITY, PH AND SULFATES DURING 30 DAYS OF BIODESULFURIZATION PROCESS

Sulfur (%, w/v) added	*A. thiooxidans* (cells/mL)	pH	SO_4^{-2} (mg/L)
0.5	$5.8 – 8.0 \times 10^9$	2.3-1.7	2680-4000
0.1	$4.0 - 4.6 \times 10^9$	2.3-1.9	2700-3700
0	$3.8 - 4.5 \times 10^9$	2.3-2.0	2750-1400

In Fig. 4 the average sulfate concentration during 30 days of treatment is shown. It is observed that in presence of the spent catalyst the bacterium *A. thiooxidans* is capable of produce ≈ 3000 mg/L of sulfates and in absence of catalyst only is detected the sulfates from the liquid medium, this indicates a conversion from elemental sulfur to sulfate. The pH values were in the range between 2 to 1.8 during the experiments.

TABLE II: SULFUR CONTENT AFTER 15 AND 30 DAYS OF BIODESULFURIZATION

Experiment (Biotic or abiotic conditions)	Sulfur added (%, w/v)	Sulfur reduction 15 days (%, w/w)	Sulfur reduction 30 days (%, w/w)
Biotic	0.5	33 ± 0.8	57.5 ± 0.3
Abiotic	0.5	26.3 ± 0.7	28 ± 1.4
Biotic	0.1	37.4 ± 0.6	60 ± 0.6
Abiotic	0.1	31 ± 0.4	32.5 ± 0.5
Biotic	0	36.3 ± 0.07	59.5 ± 0.05
Abiotic	0	30.4 ± 0.1	31.5 ± 0.6

According to the reported by Jiang *et al*. [8] a sulfur reduction of 16% was achieved in rubber in 20 days using *Thiobacillus ferrooxidans* cells. Other related publications such as [9] and [10] showed 35-40% of sulfur removal from carbon using the microorganism *Acidianus brierleyi* in 8 days and 91% of sulfur removal using *Acidithiobacillus sp*. in 30 days, respectively.

Various options such as minimizing spent catalyst waste generation, utilization to produce new catalysts and other useful materials, recycling through recovery of metals and treatment of spent catalysts for safe disposal, are available to refiners to handle the spent catalyst problem. However, due to the high loss of specific surface area, crystallographic phase transformation from anatase, which is more active catalytically, but less thermodynamic stable than rutile, the reactivation is not a suitable alternative for this spent catalyst. In this sense, we have worked in the recycling of this spent catalyst to produce materials with antibacterial properties [11].

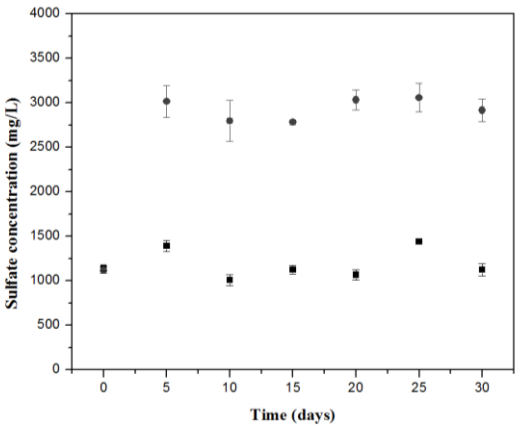

Fig. 4. Sulfate concentration during the 30 days of biodesulfurization: ● spent catalyst with *A. thiooxidans;* ■ *A. thiooxidans* control.

IV. CONCLUSION

It was possible to develop an efficient microbiological method to eliminate sulfur species from a spent catalyst. The spent catalyst did not show toxicity against *A. thiooxidans* during the biodesulfurization. *A. thiooxidans* has the ability of employ the sulfur present in the spent catalyst as an energy source. This method is low-cost and environmentally friendly, since no toxic by-products were generated. Additionally, due to the high percentage of TiO_2 in the spent catalyst, is possible to use this waste as a potential raw material to produce value-added materials.

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Brenda R. Cruz-Ortiz was born in México and received her B.Sc. in chemistry (2008) and her M.Sc. in biotechnology (2010) from the Autonomous University of Coahuila, México. In 2015 she obtained her Ph.D. in metallurgic and ceramic engineering from CINVESTAV, México. She has been a visitor research assistant during her Ph.D. in the Nanotechnology and Integrated Bioengineering Centre, U.K. At present, she is working as a lecturer in the Faculty of Chemistry of the Autonomous University of Coahuila, México. Her research interests are biotechnology, ceramic materials, catalysis and photocatalysis. Dr. Cruz has received several awards and recognitions for her academic and research work.

Lourdes Díaz-Jiménez was born in México and received her B.Sc. in chemistry (1994) and her M.Sc. in chemistry (1997) from the Meritorious Autonomous University of Puebla, México. In 2000 she obtained her Ph.D. in chemical sciences from the University of Malaga, Spain. At present, she is a full-time professor in CINVESTAV-Saltillo, México. Her research interests are catalysis, management and reuse of waste material, biotechnology and development of new chromatographic techniques. Dr. Díaz is a member of the National System of Researchers (SNI) at level I, which is a distinction that awards for Mexican researchers.

Dora A. Cortés-Hernández was born in México and received her B.Sc. in chemical engineering (1986) from the Autonomous University of Coahuila, México. In 2001 she obtained her Ph.D. in biomedical sciences from the Queen Mary University of London, U.K. At present, she is a full-time professor in CINVESTAV-Saltillo, México. Her research interests are bioceramics, bioactive composites and biomimetic coatings in ceramic and metallic substrates. Dr. Cortés is a member of the National System of Researchers (SNI) at level II.