

MICROBIOLOGICAL OXIDATION OF SULFIDES PRESENT IN REFINERY SOUR WATERS BY FIXED BED REACTORS

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A group of native bacteria with a sulfide oxidation capacity was isolated at the Instituto Colombiano del Petróleo (ICP). The bacteria were immobilized in an inert inorganic support of sintered glass that was used to evaluate a fixed packed column system working in batches as well as in a continuous mode. The experiments carried out in real wastewater and in refinery sour water show high sulfide removal percentages (over 90%) both in low and high sulfide concentrations. The appropriate operation pH is in the alkaline range (8.0 to 9.0) and it decreases as the reaction proceeds. The ability of the microbial consortium to take in the ammonia nitrogen required for their metabolic activity and a possible heterotrophic nitrification, and the phenol present in the stream as a carbon source for some of the formulated strains, is demonstrated. Sulfur mass balances are carried out quantifying it as sulfates, tiosulfates, sulfide, and elementary sulfur. The effect of operational changes on the sulfide removal percentage is evaluated obtaining a quick response of the system. A kinetic analysis was carried out and the corresponding constants derived from the Michaelis-Menten equation were calculated. The maximum removal velocity and the saturation constant are $V_m = 6.03 \cdot 10^{-8}$ kg S/m³s and $K_s = 2.1325 \cdot 10^{-4}$ kg S/m³.

En el Instituto Colombiano del Petróleo (ICP) se aisló un grupo de bacterias nativas con capacidad biooxidadora de sulfuros. Dichas bacterias fueron inmovilizadas en un soporte inorgánico inerte de vidrio sinterizado, con el cual se evaluó un dispositivo de columna empacada de lecho fijo funcionando por lotes y en continuo. Ensayos realizados en matriz real, agua agria de refinería muestran altos porcentajes de remoción de sulfuro (mayor del 90% tanto a bajas como a altas concentraciones de este compuesto). El pH óptimo de operación se encuentra en el rango alcalino (8.0 - 9.0) y se produce una disminución del mismo al tiempo que se remueve el sulfuro. de igual manera se demuestra la capacidad, por parte del consorcio microbiano, de tomar el nitrógeno amoniacal y el fenol presente en la corriente, el primero, para su actividad metabólica y posible nitrificación heterotrófica y el segundo como fuente de carbono para algunas de las cepas formuladas. Se realizan balances de masa del azufre cuantificándolo como sulfatos, tiosulfatos, sulfuro y azufre elemental. Se evalúa el efecto de cambios operacionales sobre el porcentaje de remoción de sulfuros obteniéndose una respuesta rápida del sistema. Se realiza un análisis cinético y se calculan las respectivas constantes derivadas de la ecuación de Michaelis - Menten. La máxima velocidad de remoción y la constante de saturación son $V_m = 6.03 \cdot 10^{-8}$ kg S/m³s y $K_s = 2.1325 \cdot 10^{-4}$ kg S/m³

Keywords: bioxidation, sulfides, immobilization, waste water treatment

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INTRODUCTION

Liquid wastewater streams contaminated with reduced sulfur compounds from petrochemical facilities, paper mills, and photo processing industries are serious environmental hazards due to their toxicity, corrosiveness, bad smell and high oxygen demand. There is hence a great need for the development of removal processes for wastewater sulfides. The most commonly used conventional treatment technologies by physicochemical methods are aeration (catalyzed and non-catalyzed), chlorination, ozonation, and treatments with potassium permanganate and hydrogen peroxide. All these treatments produce sulfates and tiosulfates as final products and are of a complex nature with a high energetic requirement and expensive due to the costs generated by the disposal of the produced wastes, consequently, attention has been drawn to biological alternatives during the past years.

There are reports of autotrophic and heterotrophic microorganisms (Buisman, 1989) capable of oxidizing sulfide into less toxic compounds i.e. sulfate, tiosulfate and elementary sulfur. The final products depend mainly on the nutritious demands and on the microbial ability to catalyze specific reactions. For the present case, the biotechnology laboratory of the Instituto Colombiano del Petróleo (ICP) was able to structure a consortium of native bacteria identified as BOX-9. The bacteria were isolated from different wastewater streams (Colcultidos - a tannery-, Cartagena's Refinery and Barrancabermeja's Industrial Complex). Their chemolithoheterotrophic characteristics were increased in order to enable them to use carbon molecules from organic and inorganic carbon molecules as carbon and energy sources. Some of these sulfide oxidizer bacteria produce elementary sulfur and may eventually store it in their cells (Nelson, 1990).

From the thermodynamic point of view, the sulfur biological oxidation paths are directed towards the formation of sulfides and elementary sulfur; nonetheless, the tiosulfate formation reaction is also spontaneous under oxygen saturation conditions. For some researchers, the formation of tiosulfates during the sulfide biological oxidation is caused mainly by the chemical oxidation of the sulfur, favored by a low sulfur/oxygen ratio fed to the bioreactor. On the other hand, it has been demonstrated that not all the sulfide present in bioreactor feedstocks with high sulfide concentrations

can be transformed into sulfates and elementary sulfur due mainly to limitations in biological activity (Janssen, 1995). Likewise, a high oxygen limitation (O_2 feed velocity/sulfide feed velocity [= 0.7]) produces large tiosulfate quantities (Polanco, 1997).

Wastewater process treatments with immobilized cells have showed important advantages, such as an increase in the global productivity of the system caused by the increase in cellular concentration that acts as a biocatalyst, operation under high dilution rates and under more stable conditions (Huang, 1996; Chien 1997).

In this study, the technical feasibility of using sulfur-biooxidizing native microorganisms immobilized in a sintered glass carries arranged in fixed packed columns with a rising flow from the process streams was evaluated and demonstrated. Evaluations were carried out under continuous and batch operations with a real matrix (sour water from Barrancabermeja's Industrial Complex Refinery (GCB)). The results obtained show high sulfide removal percentages even at concentrations above the average value for the sour water from the GCB.

MATERIALS AND METHODS

Immobilization of the BOX-9 bacterial consortium

The geometry of the carrier used to immobilize the group of biooxidizing bacteria was the Raschig Ring traditionally used in the chemical industry for its acceptable efficiency in separation operations and low cost. The nominal diameter of the gasket was 0,015 m and the highly porous sintered glass offered a large surface area and an adequate pore structure for microorganism adherence.

Before starting the immobilization process, the physicochemical resistance of the carrier against the sour water from the GCB was evaluated by filling a $1.25 \cdot 10^{-4} \text{ m}^3$ flask with $5.0 \cdot 10^{-5} \text{ m}^3$ of sour water. Ten other rings were added and left in constant agitation at 305 K for 45 days.

A cylindrical glass column (0.04 m internal diameter, 0.34 mm packed height and $4.27 \cdot 10^{-4} \text{ m}^3$ packed volume) with a distributing plate located at the bottom was placed before starting the immobilization process. The vacuum fraction for the bed was 0,73.

The following was the methodology applied to

immobilize and adapt the BOX-9 group to the sour waters:

- The free biomass was reactivated in a modified MTH synthetic medium (Wilmot, 1988) containing: Na_2HPO_4 (1.2 kg/m^3), KH_2PO_4 (1.8 kg/m^3), MgCl (0.1 kg/m^3), NH_4Cl (0.1 kg/m^3), CaCl_2 (0.03 kg/m^3), NaHCO_3 (0.5 kg/m^3), $\text{NaC}_2\text{H}_3\text{O}_2$ (0.8 kg/m^3), $1 \cdot 10^{-6} \text{ m}^3$ of micronutrient solution, agitated for 48 hours, 305 K and pH 8.0. It was centrifuged afterwards at 4,400 rpm for 0.33 h and left again in suspension in a MTH medium.
- After being sterilized in autoclave, the Rasching rings were appropriately charged to the column so as to minimize the empty spaces and reach an even distribution of the liquid. An aqueous solution containing modified MTH medium plus a 20% volume/volume sour water biomass was added.
- Air was slowly supplied through the lower lateral side of the column. Temperature was kept at 303 K.

Analytical Techniques

The sulfide concentration in the aqueous matrix was quantified by the selective ion electrode (ISE) using the 9616 Sure-flow electrode (Orion Research USA). The sampling volume was $5 \cdot 10^{-6} \text{ m}^3$, with the addition of an equal volume of an anti-oxidant buffer.

The analysis of sulfates and tiosulfates was carried out by High Pressure Liquid Chromatography (HPLC). An initial elimination of sulfides was carried out by precipitation with the addition of $1 \cdot 10^{-5} \text{ kg}$ cobalt acetate to the sample since this compound generates interference in the sulfate measurements. The sample was subsequently filtered and 2 to $20 \cdot 10^{-9} \text{ m}^3$ were injected into the liquid chromatographer. All tests were carried out under the following conditions: Hewlett Packard HP-1050 liquid chromatographer with a $5 \mu\text{SV}$ conductivity detector, 214 nm WD, $4.6 \text{ cm} \cdot 50 \text{ mm} \cdot 5 \mu\text{m}$ IC-Pak-Anion (Waters) anion column, and a borate/gluconate effluent with a $1.67 \cdot 10^{-8} \text{ m}^3/\text{s}$.

Samples for (UFC/cm^3) chemiolitoheterotrophic microorganisms counts were taken for all tests in an Agar-MTH medium plate and these remained in incubation during 48 hours.

Evaluation methods for the immobilization of the BOX-9 consortium in ascending flow batch systems

The column was filled with 100% sour water and

doped with Na_2S until a sulfur concentration between 0.3 and 0.4 kg/m^3 , was reached. These values correspond to the average concentrations present at the sour waters from Barrancabermeja's Industrial Complex. pH was adjusted at an initial 8.3 average to decrease the desorption of sulfur and nitrogen present as NH_3 (Restrepo, 1998). Air was supplied through the lower section at a $1 \cdot 10^{-6} \text{ m}^3/\text{s}$ flow rate. The air stream at the outlet of the column went through a 15% w/w NaOH trap to collect the sulfide stripped with the air. The work volume loaded into the column was $1.77 \cdot 10^{-4} \text{ m}^3$. The sampling volume never surpassed 15% of the total loaded volume.

Methods for the evaluation of the immobilized system under continuous ascending flows

Prior to the tests, the system was kept hours in total recirculation for 72 hours and the sour water stream in ascending flow was doped with Na_2S as to reactivate the immobilized microorganisms. After-wards, the continuous system (Figure 1) was set up according to the following procedure:

- In order to reach a concentration close to 0.3 kg/m^3 , two liters of sour water doped with Na_2S were taken

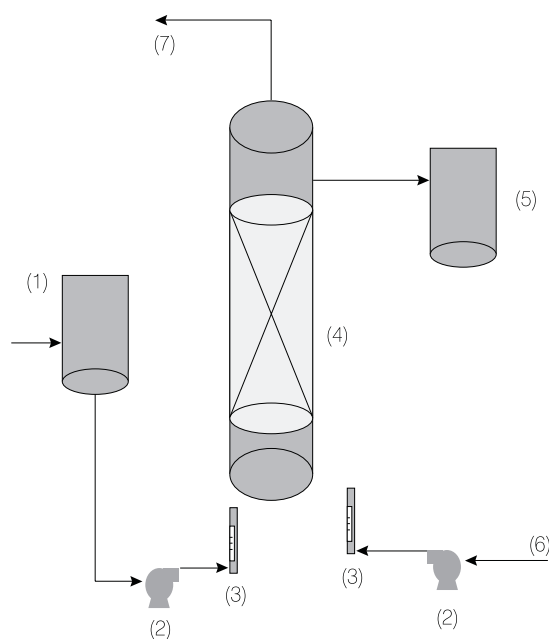


Figure 1. Diagram of the biological oxidation process under continuous operation.

- (1) Sour water feed tank, (2) Peristaltic pump, (3) Flowmeter, (4) Packed column, (5) Collecting tank (treated effluent) (6) Air supply, (7) Gas outlet

and loaded into the feeder tank which was later placed over an agitation plate and hermetically sealed.

- The column was filled with the sour water load through the peristaltic pump with a $1.33 \cdot 10^{-8} \text{ m}^3/\text{s}$ flow rate.
- Air was supplied through the lower lateral section.

Once the system stabilized i.e. after reaching the corresponding hydraulic residence time (8 hours), the feeding and air supply streams were modified in order to evaluate the sensitivity of the set up subject to common operational changes as follows:

- The air flow rate was modified from $8.33 \cdot 10^{-6}$ to $5 \cdot 10^{-6} \text{ m}^3/\text{s}$ to observe the change in the O_2 /sulfide feed velocities.
- With the above mentioned airflow, the concentration of doped sulfides in the affluent was increased (from 0.3 to $1.2 \text{ kg}/\text{m}^3$) and a 0.5% w/v trace solution was added (0.2% volume trace solution/volume reactor), in order to evaluate its effect on the removal velocity after increasing the feeding concentration levels.
- The same conditions stated in number 2, but with no trace solution added.

The set up was kept at 303 K at atmospheric pressure.

Kinetic Analysis

The sulfide removal expression when the reactor worked in continuous mode was obtained from a mathematical treatment of the Michaelis-Menten equation:

$$\frac{1}{R_s} = \left(\frac{K_s}{V_m} \right) \frac{1}{C(\ln)} + \frac{1}{V_m}$$

Where, R_s (kg of Sulfide/ m^3s) is the removal velocity, $C(\ln)$ (kg of Sulfide/ m^3s) is the average logarithmic concentration of sulfide at the inlet and outlet of the column, V_m (kg of Sulfide/ m^3s) is the maximum removal velocity and K_s (kg of Sulfide/ m^3s) is the saturation constant or substratum affinity (sulfide). These constants were calculated from a linear correlation between R_s and $C(\ln)$. The $C(\ln)$ concentration parameter was selected as a way to express the average concentration of sulfides present in the column.

RESULTS AND DISCUSSION

Immobilization of the BOX-9 microbial consortium

After charging the column for 32 days, aleatory samples of the bed were taken for analysis by electronic microscopy. Figure 2 shows the presence of the consortium microorganisms on the holder as well as inside the pores of the carrier. The formation of small monticules or cell aggregates, which indicate biofilm formation, can also be observed. The previous criteria were enough to accept a good immobilization stage and a high cellular density to start the corresponding tests.

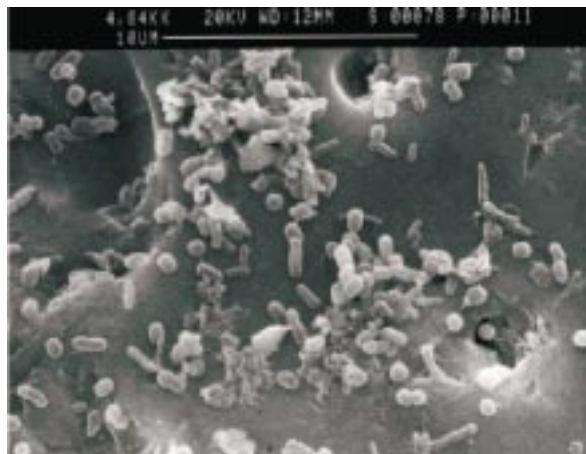


Figure 2. Microscopic photograph of the BOX-9 consortium immobilized on sintered glass rings.

Evaluation of the immobilization of the BOX-9 consortium in ascending batch flow systems

Figure 3 presents the results of the first evaluation of the batch immobilization system that show the sulfide removal percentage increase against time.

It was possible to obtain an elementary mass analysis for the sulfur with the concentration and volume data from the samples. Sulfide, sulfate, and tiosulfate were the only possible sulfur compounds considered. Table 1 shows this balance where it can be observed that the interconversion of the compounds during the course of the process keeps the initial mass of the sulfur that was fed into the system. The chosen residence time was 21 hours according to the minimal requirement for the industrial scale and, in this time, the several forms of sulfur were quantified. But the data obtained sugges-

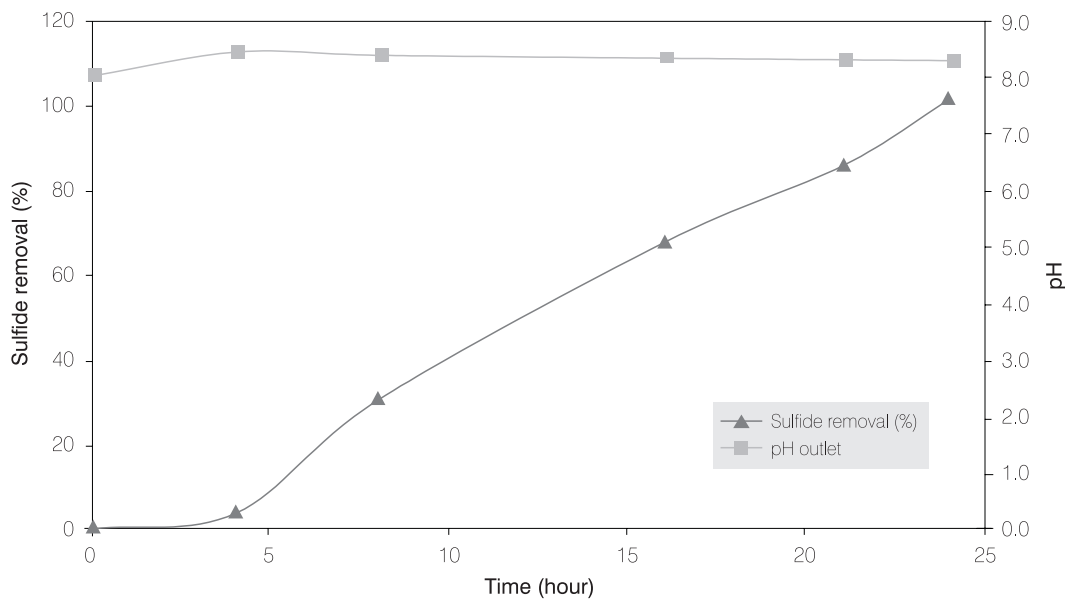


Figure 3. Removal of sulfides present in the GCB sour water in a fixed packed bioreactor under batch operation.

Tabla 1. Sulfur mass balance

	Concentration * 10 ⁻⁶	Quantity in weight * 10 ⁻⁶
	kg of S/m ³	kg
Sulfur as initial sulfur	305.2	36.6
Sulfur as initial tiosulfate	32.6	3.9
Sulfur as initial sulfide	441.7	53.0
Total initial Sulfur	779.5	93.5
Sulfur as sulfur 21 hours	47.6	5.2
Sulfur as tiosulfate 21 hours	142.8	15.7
Sulfur as sulfate 21 hours	639.5	70.3
Total sulfur 21 hours	829.9	91.3

ted selecting a longer time.

Previous evaluations demonstrated that 5% is the maximum sulfide retention percentage of the NaOH trap caused by the desorption action under pH conditions close to 8.0 and a loaded liquid/air flow volume ratio from 0.8 to 3. This value reached 1.5% during this study, a fact that explains the values obtained in the balance.

Table 2 shows the analytical results of a second batch experiment. This work was intended to analyze

the possible phenol removal during the experiment and hence, the initial and final concentrations of this compound were measured. As expected there was excellent sulfide removal as can be observed in this case after a 24 hour-operation of the column.

Results indicate a 20% phenol removal probably caused by the activity of microorganisms with high phenol affinity (*Pseudomonas*) that are present in the immobilized BOX-9 pool, or that may arrive as native biota together with the sour water.

Table 2. Evaluation of the immobilization of the BOX-9 pool in ascending batch flows during a 24 hour operation.

Pressure	Phenol *10 ³	Phenol	N-NH ₄ *10 ³	N-NH ₄	S ⁼ *10 ³	Sulfides
	kg/m ³	removal %	kg/m ³	removal %	kg/m ³	removal %
Initial load	436.47		205.0		218.00	
Final load	349.20	19.99	204.2	0.39	1.78	99.18

There was no removal of ammonia nitrogen, probably caused by the initial nitrogen concentration at levels too low to favor an heterotrophic nitrification or the air desorption of the ammonia in balance with the ammonium ion.

Evaluation of the immobilized system under continuous ascending flows

A preliminary continuous evaluation was carried out for eight hours. The analytical monitoring of the sulfur was carried out in compounds such as sulfates, tiosulfates, and sulfides to establish the corresponding mass balance. Table 3 shows the balance for the first eight hours of operation. There was a comparatively higher conversion of sulfur as tiosulfates instead of as sulfates, during the first and third hours. According to the literature, this fact could show a low sulfide/oxygen ratio and evidence of the biological oxidation process. During

the second hour there is a high percentage of sulfate formation, a fact associated to the transitory stage of the bioreactor, and consequently, there is a larger proportion of the chemical oxidation of the sulfides. On the other hand, the difference between the grams of sulfur quantified at the inlet and at the outlet increases with time. This fact could explain the possible formation of a different compound, e.g. elementary sulfur probably stored inside the cells, in addition to the small losses of sulfide (5%) towards the atmosphere.

The concentration of sulfide loaded into the column was below that expected after doping the water. This was caused by the high hydrating capacity of the Na₂S. After five hours, an additional sample of the outlet was taken to analyze the elementary sulfur concentrations using the spectrophotometric technique (Restrepo, 1998) obtaining a 20.79·10⁻³ kg/m³ value.

Table 3. Sulfur mass balance of a fixed packed reactor under continuous operation for the biological removal of sulfides.

Time	Sulfur as Sulfide	S ₂ S ⁼	Sulfur as Sulfide	Sulfide converted into S ₂ SO ₄	Sulfur as Tiosulfate	Sulfur converted into S ₂ S ₂ O ₃ ⁼	Sulfur elementary balance	Difference
h	kg/m ³	removal %	kg/m ³	%	kg/m ³	%		
1 inlet	222.00		35.96		147.99		405.95	
1 outlet	122.80	44.68	55.77	20.00	217.70	70.0	396.00	9.68
2 inlet	202.30		39.62		155.42		397.34	
2 outlet	119.80	40.78	57.75	22.00	160.56	6.2	338.11	59.23
3 inlet	249.00		38.61		161.70		449.31	
3 outlet	95.97	61.45	54.12	10.10	178.84	11.2	328.93	120.38
8 inlet	269.00		44.88		446.88		794.76	
8 outlet	2.71	99.00	62.04	6.44	645.81	74.7	710.88	50.20

The following equation expresses the material balance:

$$F_l(S_{inlet} - S_{outlet}) - F_g S_{losses} - r^* = \frac{dS}{dt}$$

where,

r^* = net velocity of the reaction in kg S/s. A negative sign accompanies this reactive because it is of a consumption nature.

F_l = Volumetric flow of the liquid. Identical at the inlet and at the outlet for the present case, dm³/min.

F_g = Flow of the gaseous stream, m³/s.

dS/dt = Term that expresses the variation in the concentration of sulfur versus time, i.e. its accumulation inside the reactor, kg S/m³s.

S_{inlet} = quantity of sulfur that enters the system quantified as sulfides, sulfates and tiosulfates, kg/m³.

S_{outlet} = quantity of sulfur that leaves the system quantified as sulfides, sulfates and tiosulfates, kg/m³.

S_{losses} = quantity of sulfur that volatilizes as sulfide and is dragged in the gaseous stream, kg/m³.

V_c = Volume of liquid loaded into the column, m³.

For a second evaluation after a 26 hour-operation,

the concentration of ammoniacal nitrogen and phenol in the feeder tank of the column was quantified. The corresponding values were 1.37 kg/m³ and 0.34 kg/m³. The affluent was collected for 15 hours for a subsequent quantification of the ammoniacal nitrogen and phenol obtaining 0.917 and 0.31 kg/m³ values. This result indicates an average removal percentage of 33.17% for nitrogen and 8.13% for phenol.

During the last evaluation, besides evaluating the disturbances mentioned in the methodology, the changes in time of the number of cells belonging to the consortium were analyzed. Figure 4 shows the difference between the number of microorganisms in the outlet and the reactor's affluent. These data were used to have an idea of the retention efficiency or the adherence of the microorganisms to the carriers. During the first hours, microorganisms were found both at the inlet and outlet of the system, with increments and decrements. However, the microorganism difference was kept at zero after 17 hours thus indicating an adequate operation of the system. When the microorganism difference is zero, it shows that the porosity of the system allows the microorganism to adhere and increase the biofilm and therefore, the support saturates more and more with microorganisms.

According to the scale in Figure 4, a considerable stability in sulfide removal can be observed after hour

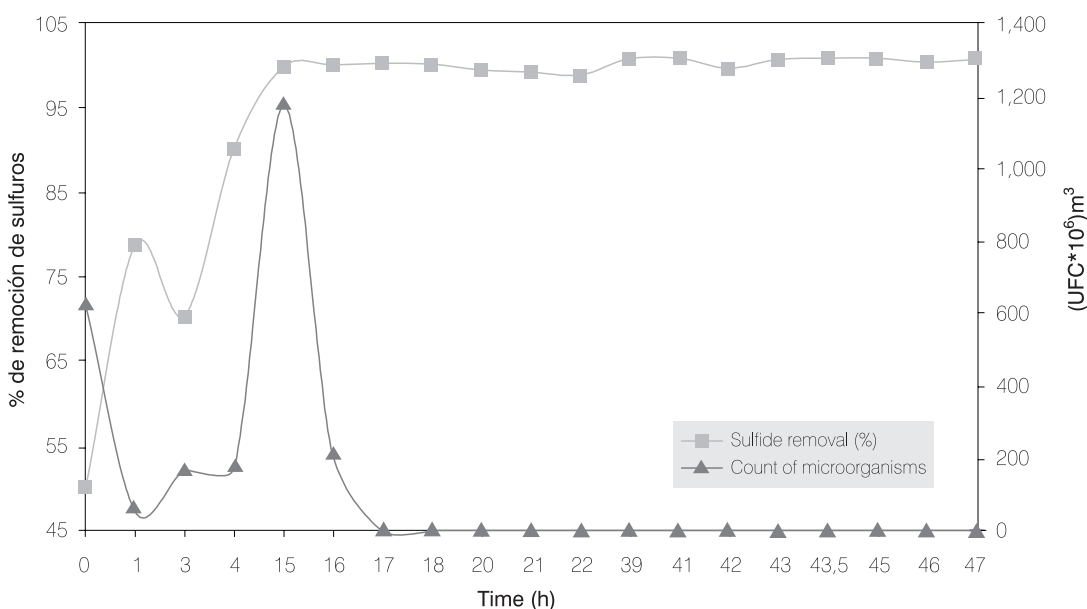


Figure 4. Sulfide removal and microorganisms count in (UFC*10⁶m³) during the evaluation of the immobilized system under continuous operation.

five, following the occurrence of a destabilization incident of the setup at hour four. The sulfide removal percentages are above 95%.

Figure 5 shows the effects on the removal of sulfide produced by the disturbances suffered by the system under continuous operation. Between hours 15 and 17 while the provision of water (at sulfide concentrations of 0.3 kg/m^3) and air (at a $8.33 \cdot 10^{-6} \text{ m}^3/\text{s}$ flow rate) remained constant, the removal percentage remained above a 99% stability interval.

- A decrease in the removal rate can be observed after the first disturbance, which consisted of decreasing the airflow to $5 \cdot 10^{-6} \text{ m}^3/\text{s}$, was introduced. Nevertheless, this rate never reached values under 90%. The sensitivity of the system to this variable can be observed and hence conclude that there is no significant effect as far as the removal capacity. Taking into account that the system did not operate for a longer period under such changes, it was not possible to determine the final removal percentage decrease nor the moment when the system would have reached a stable state.
- For the second disturbance (21 hours), the concentration of sulfide in the affluent was increased for maintaining the initial concentration, 0,5% trace solutions were added and the air flow rate was kept at $5 \cdot 10^{-6} \text{ m}^3/\text{s}$. Some minutes later, a black precipi-

tation in the feed tank and the formation of a whitish suspension inside the column were observed. These physical changes indicated a possible precipitation of sulfide as metallic salts due to the presence of ions such as cobalt and zinc that form part of the formulation of the trace solution. The data corresponding to the concentration of sulfide at the reactor's inlet reached a value much lower than that expected, thus confirming the sulfide precipitation hypothesis.

Some studies on biological oxidation of sulfides report the addition of trace solutions and nutrients i.e., nitrogen and phosphorous as ammonium and phosphates indicating the presence of sulfides under the metallic salt shape. Nonetheless, the reports indicate that such a phenomenon only represents a small percentage of the sulfide that enters the treatment system. In this work, the expected sulfide concentration was 1.2 kg/m^3 , we obtained 0.163 kg/m^3 , which represents an 86.41% decrease.

These results state the need to reformulate the trace solution in order to eliminate or decrease the metallic ions that favor the precipitation of sulfide as much as possible. This means that a cost-benefit balance between the quantity of the precipitate and the need to introduce trace solutions as a stimulus for growth of microorganisms must be undertaken.

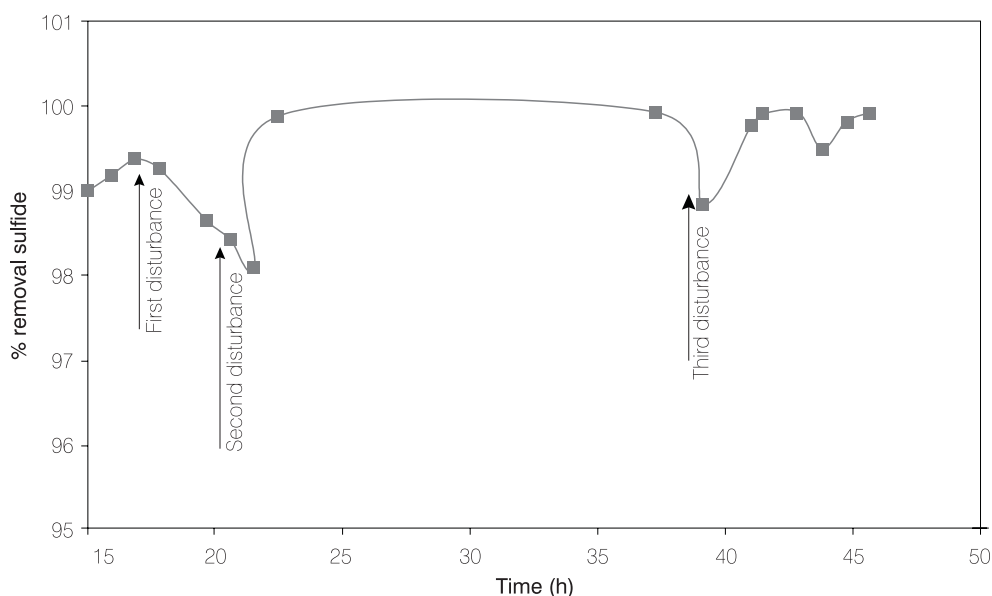


Figure 5. Sulfide removal during the evaluation of the immobilized system under continuous operation. The arrows indicate the perturbations introduced into the system.

The system showed sensitivity towards these changes, but it was not possible to monitor the reduction in the sulfide removal rate due to technical problems that destabilized the column. However, it was possible to operate the system during the subsequent 15 hours observing that between hours 39 and 40, the reactor worked under a relatively stationary state with a sulfide removal rate close to 100%.

The last disturbance consisted of the addition of water with a high concentration of sulfides, no trace solutions and, a $5 \cdot 10^{-6} \text{ m}^3/\text{s}$ air flow rate. The removal rate suddenly dropped from 100% to 98.5% but it started to oscillate at a fixed interval after one hour. If the effect of the disturbances over the removal percentage of sulfides is compared, it can be observed that the last disturbance accounts for the greatest change. In spite of this fact, the system quickly responds and remains in the 90% - 100% range.

As far as ammonium, there is a similar tendency concerning the distance between the inlet and the outlet that provides a 15% average removal rate between hours 16 and 21. The removal rate reaches a value above 40 between hours 44 and 45 in spite of the increase in the concentration of the ammoniacal nitrogen at the inlet of the column (Figure 6).

A synthetic MTH medium containing ammonium ion

as a nitrogen source for the biological activity of the microorganisms was utilized for BOX-9 pool. It is then valid to consider that there was a consumption of the previously mentioned compound present in the water in the quantities required by the pool. It is also valid to consider a possible heterotrophic nitrification mainly favored by high concentrations of ammoniacal nitrogen as it occurred after the third disturbance(s). At was previously stated, the purpose of these evaluations was to learn the flexibility of the system under possible operational disturbances that may arise at the industrial scale since the development of a system tolerant to any operational eventuality is vital whether a preliminary homogenization stage of the reactor's feedstock is carried out or not.

Kinetic Analysis

Figure 7 shows the correlation obtained in the $1/R_s$ against $1/C(\ln)$ graphic. The regression equation obtained a 0.9163 regression coefficient. The calculations of maximum sulfide removal velocity and the saturation constant were $V_m = 6.03 \cdot 10^{-8} \text{ kg S/m}^3 \cdot \text{s}$ and $K_s = 2.13 \cdot 10^{-4} \text{ kg S/m}^3$. In the present study, the saturation constant was much greater than the one reported by Chien (1996). The high concentration levels of the sulfides evaluated explain this difference.

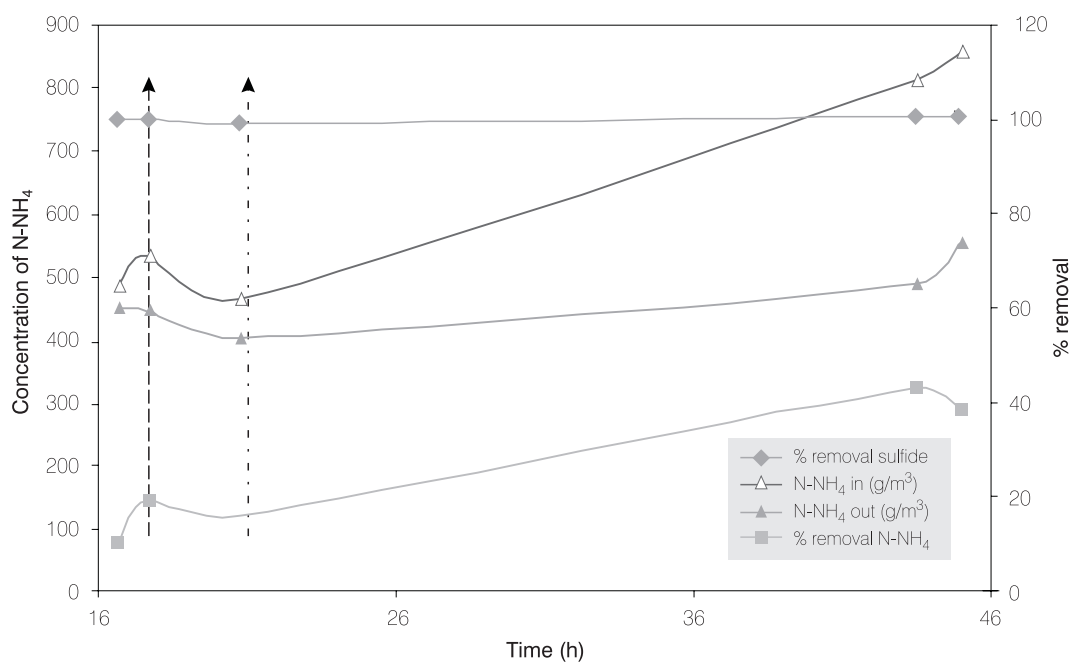


Figure 6. Ammonia nitrogen and sulfide behavior at the inlet and outlet of the column vs time.

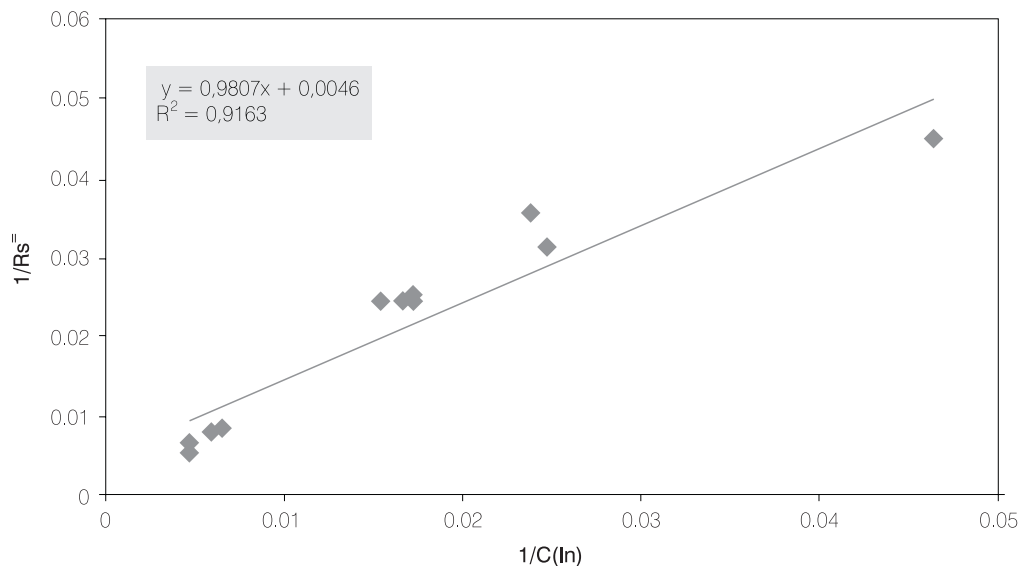


Figure 7. Correlation between sulfur removal and the average logarithmic concentration in the bioreactor.

CONCLUSIONS

- The treatment process proposed for the removal of sulfides present in refinery sour water was efficient and produced a high yield. A 99.18% sulfide removal was obtained in the batch evaluation with a 24-hour residence time. A 20% removal of phenol was also obtained.
- The evaluations of the immobilization system under continuous operation showed lack of biomass with draw indicating that the selected carriers provide an efficient capability to retain the microorganisms. The system quickly reached important removal levels (>85%) i.e. three or four after starting the setup.
- When the reactor worked in continuous mode, the three disturbances introduced into the system affected its normal operation but failed to destabilize it for long periods. The bioreactor responds few hours after having introduced the operational changes.
- The consumption of ammoniacal nitrogen by the immobilized BOX-9 pool was evidenced and accounted for a 40% removal of this contaminating compound. For the next experiments, it is necessary to consider nitrite/nitrate ratio for justifying the biological nitrification.

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