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Oil refinery wastewater treatment using coupled electrocoagulation and fixed film biological processes

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ABSTRACT

Oil refinery wastewater was treated using a coupled treatment process including electrocoagulation (EC) and a fixed film aerobic bioreactor. Different variables were tested to identify the best conditions using this procedure. After EC, the effluent was treated in an aerobic biofilter. EC was capable to remove over 88% of the overall chemical oxygen demand (COD) in the wastewater under the best working conditions (6.5 V, 0.1 M NaCl, 4 electrodes without initial pH adjustment) with total petroleum hydrocarbon (TPH) removal slightly higher than 80%. Aluminum release from the electrodes to the wastewater was found an important factor for the EC efficiency and closely related with several operational factors. Application of EC allowed to increase the biodegradability of the sample from 0.015, rated as non-biodegradable, up to 0.5 widely considered as biodegradable. The effluent was further treated using an aerobic biofilter inoculated with a bacterial consortium including gram positive and gram negative strains and tested for COD and TPH removal from the EC treated effluent during 30 days. Cell count showed the typical bacteria growth starting at day three and increasing up to a maximum after eight days. After day eight, cell growth showed a plateau which agreed with the highest decrease on contaminant concentration. Final TPHs concentration was found about 600 mgL^{-1} after 30 days whereas COD concentration after biological treatment was as low as 933 mgL^{-1}. The coupled EC-aerobic biofilter was capable to remove up to 98% of the total TPH amount and over 95% of the COD load in the oil refinery wastewater.

1. Introduction

Industrial wastewater treatment is a critical issue if the effects of climate change on fresh water availability worldwide are considered. This is particularly true for developing countries where raw materials transformation to elaborate products usually generates wastewater with high amounts of hazardous pollutants (Dimoglo et al., 2004; Diaz et al., 2007). In many of the cases, industrial wastewater effluents are released with few or no treatment to the natural streams. In Mexico, for example, it is estimated that only 20% of the total amount of industrial wastewater generated (6 km^3 $year^{-1}$) are treated removing the same proportion of contaminants (measured as biological oxygen demand -BOD_5-) from the total amount produced (6.95 million of tons BOD_5 per year) (CNA, 2011). Refining crude oil is a process with a high hydric footprint. Particularly in our country, petrochemical wastewater is among the main contributor to environmental contamination with large volumes of wastewater generated and high amount of diverse pollutants involved. Only during 2011, the amount of petrochemical wastewater generated by Petroleos Mexicanos (PEMEX), the Mexican oil company, was over 22 thousand millions of cubic meters (TMm^3) releasing 560 tons of pollutants (PEMEX, 2011).

Due to the nature of the pollutants included in petrochemical wastewater, its treatment is a challenging issue and several different physical-chemical, mechanical and even biological conventional treatment processes have been tested for its restoration in the past (Dimoglo et al., 2004). A wide diversity of procedures, from API separators to specific biological systems have been attempted for the reduction of chemical oxygen demand (COD), total petroleum hydrocarbon (TPH), biochemical oxygen demand (BOD_5) and many other in the effluent with some success (Diya'uddeen et al., 2011). Nevertheless, novel approach are required if cost-efficient processes are aimed to be achieved for effective removal of pollutants in the effluents.

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One interesting alternative for the treatment of complex effluents such petrochemical wastewater is electrocoagulation (EC). This non-conventional procedure takes advance of metallic anodes to form active coagulant species used for the removal of pollutants by precipitation *in situ* (Abdelwahab et al., 2009). Chemical coagulation usually presents several disadvantages when compared against EC, for example it usually generates chloride and sulfide ions, unwanted anions that may compete with cations formed by the chemical substances, minimizing the treatment efficiency, and the lack of pH variation regulation. EC, on the other side, has been reported capable to remove smaller particles, produce low amount of sludge, requires smaller room and avoids chemical storage (Zhu et al., 2007).

Moreover, in the pursuit of improving water quality of effluent, sequential coupled water treatments have been studied in order to minimize the pollution load of the effluent. Bani-Melhem and Smith (2012) reported the use of aerobic process (using a biological membrane) simultaneously with the EC, they found that applied voltage kill the bacteria when the electrode and the cells are operate at the same time. Another disadvantage described was related with adding chemicals inside the biological reactor since it could produce undesirable sub products and/or increase the sludge volume in the reactor.

Beccari et al. (1999) suggested performing physical-chemical pre-treatment following by the biological treatment. In this work EC process was selected as pre-treatment because it has been reported not needing an external chemical substance, able minimize the toxicity and decreasing the degradation inhibition (Khoufi et al., 2006). To our knowledge, relatively few works on the application of EC for refinery wastewater are currently available. The use of sequentially coupled conventional and non-conventional treatment processes appears as emerging technology for the improvement of the quality of wastewater released to the environment and, no others works are reported devoted to the application of this technology coupled with biological processes for the treatment of effluents with high pollutants concentration have been reported. The aim of this work is to show our results on the application of sequentially coupled EC and aerobic biodegradation for the removal of pollutants in refinery wastewater and demonstrate this sequential procedure able to eliminate the main pollutants included.

2. Experimental

2.1. Reagents

Sodium Chloride (NaCl) was acquired at Chemical Meyer. All the other chemical reagents used in this work were J.T Baker. All of them were A.C.S. reagent grade and used as received without any further purification.

2.2. Wastewater sample characterization

Hydrocarbon-rich wastewater (HRWW) from a petrochemical industry was obtained from a refinery effluent at eastern Mexico. The sample was analyzed for determination of pH, electric conductivity, total petroleum hydrocarbon (TPH), chemical oxygen demand (COD), turbidity, biochemical oxygen demand (BOD), total solids, hardness as $CaCO_3$, concentration of Cd, Co, Hg, Ni, Pb, Zn, Fe and Al using standard methods procedures (APHA, 1995).

2.3. Electrocoagulation (EC) procedure

The reactor used in this study for EC assessments was a 500 mL PYREX beaker used to test the performance of the cell in batch mode. The experimental setup is schemed in Fig. 1. Test were run at three pH initial values (3.0, 6.0 and 9.0) measured with a potentiometer (OAKTON Ion 510). Four voltages (3.0, 6.5, 12.0 and 15 V), three electrolyte concentrations (0.0, 0.01, and 0.1 NaCl) and two or four 12.0 × 2.50 × 0.25 cm aluminum electrodes were tested for every pH value. The electrodes were separated by a distance of 0.5 cm. During electrocoagulation process, the potential was maintained constant by using a voltage regulator (STEREN model MUL-050). For every experimental run, 500 mL of the wastewater was placed into the cell. The pH was adjusted by adding 0.1 M H_2SO_4 or NaOH depending on the required initial pH value. The electrolyte, NaCl, weighted with an analytical balance (Ohaus Analytical Plus), was added to the wastewater sample at the required concentration and then the voltage was adjusted (established with a power supply STEREN Model PRL-25) to the desired value and the EC process was carried out for 50 min. Samples, 5 mL, were drawn every 5 min during the experiment (in total, 50 mL, 10% of total reactor volume, were taken out from the reactor), settled to separate the sludge (or foam) and analyzed for COD (HACH DR/4000U spectrophotometer with a wavelength accuracy of ±1 nm) at the end of the experimental runs, throughout standard methods procedures (APHA, 1995). Additionally, pH, current density and temperature were also determined for the samples at different experimental times. Before every run, impurities on electrode surface were removed by washing with acetone and 1 M HNO_3 solution and then washed with de-ionizer water prior to use. Each run was done in duplicate. Data analysis was made with a multivariable regression in order to analyze the COD behavior with different values of pH, voltage, number of electrodes and ionic strength. In order to know the significance of the parameters, the p-test was used based with the following criteria using the MINITAB® software (Romero-Suarez, 2012):

- P value > 0.2: Not significant.
- P value < 0.05: Significant (95% confidence interval).

2.4. Bacterial strains isolation

In order to isolate bacteria present in the wastewater, 2%

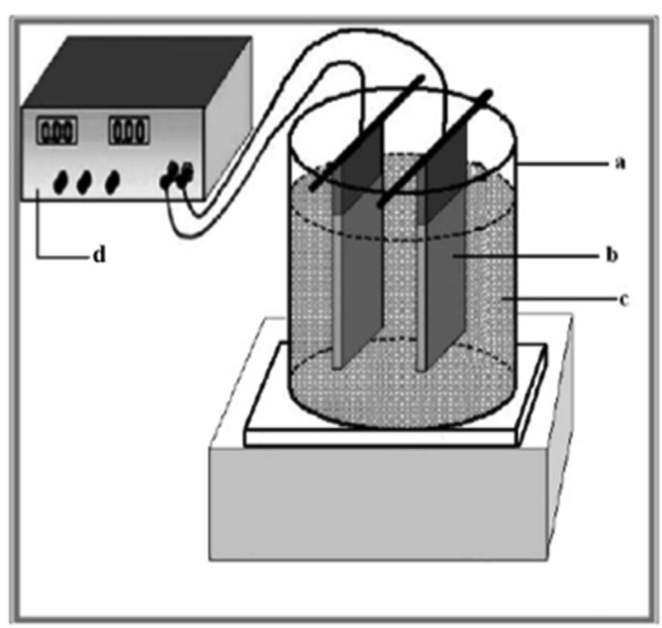

Fig. 1. Schematic representation of the EC experimental setup: a. 500 mL beaker; b. Aluminum electrodes; c. wastewater sample; d. Power supply.