



Approaching zero discharge concept in refineries by solar-assisted photo-Fenton and photo-catalysis processes

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ABSTRACT

To undertake a better water management in Oil&Gas sector, it is essential to decrease the wastewater generation by increasing the current reused water rates. Focused on this motivation, this study presents the performances of solar-assisted photo-Fenton and heterogeneous photo-catalysis on refinery wastewater treatment for reuse purposes with the aim of zero discharge. While initial tests were made on synthetic refinery wastewater, real case studies were performed with two types of refinery effluent in order to test the feasibility of using AOPs either as a secondary or tertiary treatment. Even though heterogeneous photo-catalysis and a combined process showed promising results for the treatment of the refinery effluents, photo-Fenton treatment revealed a superior effectiveness for application in both secondary and tertiary treatments, considering the improvements on TOC removal, toxicity and biodegradability. Photo-Fenton as secondary treatment resulted as efficient as the biological treatment, reaching final TOC values ca. 20 mg/L and 88% of COD removal presenting values lower than those achieved after the biological treatment. Moreover, a marked increase in the BOD_5/COD ratio from 0.38 to 0.83 was obtained. Furthermore, as a tertiary treatment, photo-Fenton process either with $H_2O_2/COD = 10$ and $H_2O_2/Fe^{2+} = 50$ or $H_2O_2/COD = 4$ and $H_2O_2/Fe^{2+} = 10$ provided a final TOC value < 4 mg/L. This result reveals the possibility to reuse the effluent in the refinery plant, thus increasing the sustainability.

1. Introduction

Petroleum refinery is one of the industrial activities, which use larger amount of water and consequently produce large amount of wastewater that contains various organic pollutants, from aromatic to aliphatic compounds [1]. Although it has a very important place in the world economy, there are too many concerns for its environmental effects [2,3]. The discharging limits determined by legislations have been decreasing, forcing the industries to develop more effective methods for the removal of these various organic recalcitrant contaminants [4].

On the other hand, depending on the refinery size and process configuration, the amount of produced wastewater is 0.4–1.6 times the amount of processed crude oil [5,6]. Recycling this water for different purposes such as process water, cooling water and fire water after treatment (depending on the quality standards) is a remarkable option to meet the water needs of the plant [7,8]. From this point of view, the treated effluent may play an important role in sustainable management of water resources through decreasing wastewater discharges, which also presents an economical advantage [9].

So far, conventional treatment techniques based on physicochemical, mechanical and biological methods have been used to remove the organic contaminants from wastewater [4]. However, these processes produce concentrated sludge, which requires further operations. Besides, they perform with limited efficiency in case of emulsified oil and small oil droplets [10]. Thus, in recent years, attentions have been directed toward advanced oxidation processes (AOPs), which generate highly reactive oxidants such as hydroxyl radicals, to transform organic compounds by means of oxidation and mineralization into harmless compounds like H_2O , CO_2 and inorganic salts [11,12].

Conventionally, treatment of refinery effluents composes of preliminary, primary and secondary treatments. In the preliminary step, crude solids and substances are removed mechanically. In the primary treatment, API (American Petroleum Institute) oil-water separators and dissolved air flotation (DAF) processes are applied in order to remove free and emulsified oils. As a secondary treatment, biological treatment is applied, which may remove up to 90% of organic materials in the effluent. Although the discharging requirements are reached after secondary treatment, reuse of this treated water can only be possible by removal of some specific compounds [9]. Apart from this, although

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