Application of an autocatalytic fenton process for the pre-treatment of an oily sludge: A sustainable approach for valorisation of refinery wastes.

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Introduction

Nowadays, the refinery industry generates huge amounts of hazardous wastes during the petroleum refining processes (especially oily sludge) (Hu et al., 2013). The environmental risks associated with the inadequate disposal of these wastes makes necessary the development of technologies to treat and valorize them properly within the framework of circular economy and sustainability.

Oily sludge is usually composed of three different phases: oily, aqueous, and solid. The oily phase presents a high percentage of carbon content, due to the presence of petroleum hydrocarbons (PHC). The solid phase contains organic and inorganic material, with a high concentration of metals (principally iron), and the aqueous phase evidences the presence of nutrients (ammonia and phosphate) and low organic carbon concentration. According to this composition, different valorization strategies can be addressed (Jerez et al., 2021).

Fenton oxidation treatment is a well-known advanced oxidation process for the removal of harnessing pollutants, especially those which are difficult to degrade by microorganisms (Pourehie and Saien, 2020). Fenton oxidation treatment shows lower energy requirements, reaction time and operational costs, as compared to other oxidation processes. The process consists in the decomposition of H_2O_2 into •OH radicals, in the presence of an iron catalyst, performing the non-selective oxidation of organic compounds, such as PHC present in refinery oily sludge, in more biodegradable compounds (Sivagami et al., 2019).

According to the characterization results of the oily sludge, an assessment of autocatalytic Fenton oxidation treatment has been performed in this work. The oily sludge presents a high concentration of iron which makes unnecessary the addition of a catalyst to promote Fenton reactions. The purpose of this pre-treatment is the decrease in the concentration of solids, and consequently a reduction of volume, of the sludge, generating a biodegradable aqueous effluent with higher loading of soluble carbon.

Materials and methods

The oily sludge used in this work was collected from an API separator in a petroleum refinery wastewater plant located in Spain and immediately stored at 4 ºC to keep at adequate conditions.

Different analytical methods were used to determine the percentage and composition of each phase of oily sludge. Thermogravimetric Analysis (TGA) was performed on a simultaneous TGA-DSC thermobalance (TGA-DCS1, Mettler-Toledo, S.A.E). Total Organic Carbon (TOC) in the aqueous phase was measured using a combustion/nondispersive infrared gas analyzer model TOC-V CSH (Shimadzu). The content of metals was measured with an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) using a Varian Vista AX spectrometer. The oily phase was analyzed by GC-MS (Gas Chromatography coupled to Mass Spectrometry).

Fenton experiments were carried out at different hydrogen peroxide concentrations (90, 45 and 20 g/L) and temperatures (25, 40, 60 and 80 ºC). The oxidant to sludge volume ratio varied from 1:5 1:10 and 1:20. The reaction time, for all experiments, was two hours without the addition of an iron catalyst. After the reaction, the solubilization of TOC and the excess of H_2O_2 in the aqueous phase were analyzed. Moreover, effluent biodegradability and toxicity were addressed by respirometry assays (Vasiliadou et al., 2018).

Results

The fractional characterization of the oily sludge phases allows settling their composition. TG-DSC analysis gave the following percentage of each phase: oily (34%), aqueous (25%) and solid (39%). From these results , can be concluded that oily sludge presents a great concentration of oil and therefore PHCs (26%wt) can susceptible to being degraded towards less complex and more biodegradable molecules with a Fenton oxidative treatment (Jerez et al., 2021).

Metals content in the solid phase was determined by ICP-AES analysis. Fe (77 g/kg), Ca (27 g/kg) and Al (26 g/kg) are the predominant metals with others in much less concentration. This significant concentration of iron makes possible the autocatalytic Fenton process and hence reducing the operation cost associated with the addition of the catalyst.

TOC concentration of the aqueous phase, before and after the Fenton experiments was measured to evaluate the carbon solubilization (Figure 1). TOC value increased progressively ($[TOC]_0$=400 ± 0,1 ppm) with the addition of higher concentration of H_2O_2, reaching 1624 ± 11, 1329 ± 10 and 910 ± 4 ppm for the studied hydrogen peroxide initial concentrations (90, 45 y 20 g/L, respectively) at the higher temperature (80 ºC). Data in Figure 1 also evidence that the increase in the working temperature has a positive effect on the TOC solubilization. Blank experiments in absence of oxidant yielded negligible carbon solubilization. In all the experiments, oxidant conversion was higher than 98 % and the average solid destruction was ca. 50 % for the higher oxidant loading.

Also, the composition of the oily phase after Fenton treatment was analyzed by GC-MS. Data shows a high degradation of hydrocarbons, especially those with high molecular weight (> C_{15}) and the progressive formation of low molecular carboxylic acids, under the working conditions which maximizes the carbon solubilization (90 g/L of oxidant and 80 ºC). Under better conditions an aqueous effluent without toxicity and 50 ± 10% of biodegradability can be achieved.

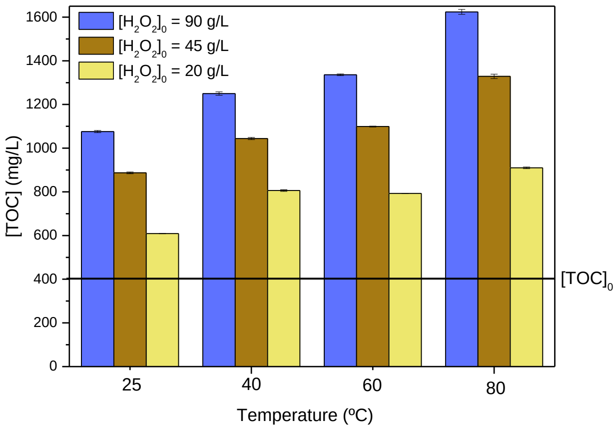

Figure 1. [TOC] in the aqueous effluent after Fenton pre-treatment under different [H_2O_2] loadings and working temperatures. Initial TOC in the aqueous phase is 400 mg/L.

Conclusions

Fenton treatment was able to degrade the organic compounds present in oily sludge under moderate temperatures, allowing their solubilization into the aqueous phase (50 % of solid destruction) and using the iron content present within the sludge. Respirometry assays demonstrates the enhancement of biodegradability and lowering of toxicity when the oily sludge is pre-treated with the autocatalytic Fenton system under optimized conditions.

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