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Oxidative mineralisation of petroleum refinery effluent using Fenton-like process

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ABSTRACT

Petroleum refinery effluents (PREs) are wastewaters characterised by high values of chemical oxygen demand (COD) and total organic carbon (TOC). Mineralisation of PRE is not commonly reported. For Fenton oxidation, in particular, reported PRE mineralisation is low. In this paper, treatability of a petroleum refinery effluent using a Fenton-like oxidative reaction is described. A statistically designed experimental matrix was used to evaluate the individual and combined effects of process variables based on a five-level central composite design (CCD). Response surface methodology (RSM) was employed to optimise the parameters of interest (COD and TOC), and response surface equations were subsequently developed. These parameters were optimised from studies of the independent variables, for reaction time [t_r] = 30–240 min, molar ratio of hydrogen peroxide to the organic wastewater [H_2O_2]:[PRE] = 2–12 and mass ratio of hydrogen peroxide to catalyst [H_2O_2]:[Fe^{3+}] = 5–20. The COD and TOC of the PRE at an initial pH of 7 were 1343 mg O_2/L and 398 mg C/L, respectively. Under optimal conditions, maximal TOC and COD reduction achieved within 30 min of oxidation reaction were 70% and 98.1%, respectively. The obtained models had correlation coefficients (R^2 and R^2_{adj}) of 0.9984 and 0.9916 for TOC and 0.9636 and 0.8835 for COD. At a pH of 3, corresponding optimal oxidation conditions were found to be [H_2O_2] = 1008.0 mM and [Fe^{3+}] = 686.0 mg, that is, a molar ratio of [H_2O_2]:[PRE] = 12 and mass ratio of [H_2O_2]:[Fe^{3+}] = 5.

Keywords: Fenton-like; Petroleum refinery effluent; Response surface methodology; Mineralisation

1. Introduction

The refining process of crude oil produces over 2500 refined products (Yavuz et al., 2010) and generates large volumes of effluents containing light fractions of aliphatic and aromatic petroleum hydrocarbons. As reported by Alva-Argáez et al. (2007), the estimated average water consumption in processing a barrel of crude oil is 246–341 L of water. Approximately 0.4–1.6 times the volume of the processed crude oil is discharged as petroleum refinery wastewater (PRE) (Coelho et al., 2006).

Effluents generated from petroleum-refining industries differ from refinery to refinery due to variation in plant configuration and type of crude oil processed (Saien and Nejati, 2007). Generally, the effluents are made of numerous organic and inorganic components arising from the feedstock nature, which is composed mainly of hydrocarbons along with a wide range of other components (Santos et al., 2006b). Discharge of contaminants from the petroleum industries form residual chemical oxygen demand (COD), which has detrimental environmental consequences due to high oxygen demand and toxicity of the individual components in wastewater. Thus, strict regulations are in place in terms of minimum levels allowable for their disposal (Santos et al., 2006a; Guidelines, 2009; Ma et al., 2009).

Significant advancement has been made by several novel approaches to petroleum refinery effluent (PRE) treatment through COD reduction. Among them are crossflow membrane bioreactors (Rahman and Al-Malack, 2006), adsorption of pollutants onto date-pit activated carbon (El-Naas et al.,

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