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Post-treatment of refinery wastewater effluent using a combination of AOPs (H_2O_2 photolysis and catalytic wet peroxide oxidation) for possible water reuse. Comparison of low and medium pressure lamp performance

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ABSTRACT

The main aim of this work was to study the feasibility of multi-barrier treatment (MBT) consisting of filtration, hydrogen peroxide photolysis (H_2O_2/UVC) and catalytic wet peroxide oxidation (CWPO) for post-treatment of petroleum refinery effluent. Also the possibility of water reuse or safe discharge was considered. The performance of MBT using medium (MP) and low (LP) pressure lamps was compared as well as operation and maintenance (O&M) cost. Decomposition of organic compounds was followed by means of gas chromatography–mass spectrometry (GC–MS), total organic carbon (TOC) and chemical oxygen demand (COD) analysis.

After filtration step (25 μm) turbidity and concentration of suspended solids decreased by 92% and 80%, respectively. During H_2O_2/UVC process with LP lamp at optimal conditions (H_2O_2:TOC ratio 8 and UVC dose received by water 5.28 W_{UVC} s cm^{-2}) removal of phenolic compounds, TOC and COD was 100%, 52.3% and 84.3%, respectively. Complete elimination of phenolic compounds, 47.6% of TOC and 91% of COD was achieved during H_2O_2/UVC process with MP lamp at optimal conditions (H_2O_2:TOC ratio 5, UVC dose received by water 6.57 W_{UVC} s cm^{-2}). In order to compare performance of H_2O_2/UVC treatment with different experimental set up, the UVC dose required for removal of mg L^{-1} of COD was suggested as a parameter and successfully applied.

The hydrophilicity of H_2O_2/UVC effluent significantly increased which in turn enhanced the oxidation of organic compounds during CWPO step. After H_2O_2/UVC treatment with LP and MP lamps residual H_2O_2 concentration was 160 mg L^{-1} and 96.5 mg L^{-1}, respectively. Remaining H_2O_2 was fully consumed during subsequent CWPO step (6 and 3.5 min of contact time for LP and MP, respectively). Total TOC and COD removal after MBT was 94.7% and 92.2% (using LP lamp) and 89.6% and 95%, (using MP lamp), respectively. The O&M cost for MBT with LP lamp was estimated to be 0.44 € m^{-3} while with MP lamp it was nearly five times higher. Toxicity assessment was performed using two marine species (*Vibrio fischeri* and *Paracentrotus lividus* sea-urchin) after each treatment step. The highest toxicity was attributed to H_2O_2/UVC effluent for both tested species. After MBT a drastic decrease of toxicity was achieved.

1. Introduction

While a huge amount of freshwater is consumed by industries, about 700 million people are living under water scarcity nowadays (United Nations, 2014). A petroleum refinery consumes from 10 to 20 gallon (37.8–75.7 L) to 50–60 gallon (189.3–227.1 L) for processing a barrel of crude oil (C.H. Guernsey and Company, 2009). Generated wastewater constitutes about 41% of consumed water (C.H. Guernsey and Company, 2009). Conventional treatment of highly polluted petroleum wastewater usually consists of physico-chemical and mechanical methods followed by biological

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processing (Oller et al., 2011). However, aliphatic and aromatic hydrocarbons, which can be toxic for the receiving environment (Hoshina et al., 2008), are still present in petroleum wastewater effluent (Oller et al., 2011). Hence, additional treatment leading to safe water discharge or reuse is needed.

Significant interest regarding Advanced Oxidation Processes (AOPs) as promising methods for water reuse or safe discharge emerged in last decades. The AOPs were studied for the degradation of numerous organic contaminants in aquatic environment (Levchuk et al., 2015; Maillard et al., 1992; Černá et al., 2013; Pozan and Kambur, 2013; Bertelli and Selli, 2006; García-Molina et al., 2005; Gumy et al., 2005). Non-selectivity and high oxidizing capacity of AOPs lead to degradation and partial or full mineralization of nearly all organic compounds. Thus, application of AOPs for water and/or wastewater treatment allows to remove organic pollutants by transforming them into other organic compounds with the final objective of forming innocuous inorganic substances (Bertelli and Selli, 2006).

Combination of AOPs reported earlier as Multi-Barrier Treatment (MBT) demonstrated an excellent performance for post-treatment of synthetic industrial wastewater effluents (Rueda-Márquez et al., 2015a, 2015b). Proposed MBT includes three main steps: filtration, photolysis of hydrogen peroxide (H_2O_2/UVC) and catalytic wet peroxide oxidation (CWPO) with granular activated carbon (GAC) as catalyst. It is well accepted that hydroxyl radicals generated during the H_2O_2/UVC process (according to reaction 1) are responsible for the oxidation of organic compounds. Moreover, as it was demonstrated in some studies (Rey et al., 2011; Santos et al., 2009), hydroxyl radicals can also be formed by H_2O_2 in presence of activated carbon (CWPO, reaction 2, 3).

$$H_2O_2 + h\nu \rightarrow 2\ {}^\bullet OH \quad (1)$$

$$AC + H_2O_2 \rightarrow {}^\bullet OH + OH^- + AC^+ \quad (2)$$

$$AC^+ + H_2O_2 \rightarrow AC + {}^\bullet OOH + H^+ \quad (3)$$

Such combination of AOPs (H_2O_2/UVC followed by CWPO) is beneficial since all hydrogen peroxide remaining after H_2O_2/UVC step is consumed during subsequent filtration through the GAC column. As it was reported elsewhere (Heringa et al., 2011) some genotoxic by-products, which may be generated during the H_2O_2/UVC process, are removed after GAC filtration. Hence, the possibility to remove residual H_2O_2 and some by-products after H_2O_2/UVC significantly decreases toxicity of the treated water as it was shown in earlier studies (Rueda-Márquez et al., 2015a, 2015b). It should be mentioned that most of the publications devoted to H_2O_2/UVC water purification are not dealing with water toxicity assessment. Yet this parameter is of high importance if the studied AOP is suggested as polishing treatment method. Moreover, after H_2O_2/UVC treatment, hydrophilicity of organic molecules present in effluent is increasing as does the oxidation state of organic carbon (Gurganus et al., 2015; Kroll et al., 2011). As stated in the literature (Anfruns et al., 2013), during H_2O_2 treatment for activated carbon regeneration hydrophilic compounds are transferred to the bulk and react with oxidizing species, while hydrophobic compounds were reported to be adsorbed on the surface of AC. Thus, operation and maintenance (O&M) costs for CWPO step can be decreased by around 90% (GAC regeneration). However, the O&M cost of MBT is strongly influenced by performance of H_2O_2/UVC step, especially electricity consumption of lamps. Therefore, it is vital to find optimal operational conditions of the H_2O_2/UVC process (high performance, relatively low electricity consumption by lamps). In spite of numerous studies conducted in the field of H_2O_2/UVC water treatment, it is still challenging to compare results of different works. In most of the studies such parameter as contact time of the H_2O_2/UVC is used, which does not seem to be representative when various reactors of different geometrical configuration, lamps and types of water are utilized.

Evaluation of MBT feasibility for post-treatment of petroleum refinery wastewater effluent was the main goal of this work. The possibility of safe discharge and water reuse was studied. An attempt to address the issue of comparison of H_2O_2/UVC treatment performance was made.

2. Materials and methods

2.1. Wastewater

The effluent of industrial wastewater (RWW) was received from the local petroleum refinery. The refinery wastewater was treated by physical, chemical and biological methods before discharge. The main physico-chemical and biological characteristics of refinery effluent used in this study are shown in Table 1.

2.2. Experimental set up

The MBT train consists of filtration, H_2O_2/UVC (with MP and LP lamps) and H_2O_2/GAC (CWPO).

Microfiber filters (25 µm, Aquapro, Spain) were used to reduce water turbidity and suspended solid concentration, which in turn increases the transmittance of the effluent.

The comparison of H_2O_2/UVC process performance using two different UVC lamps (MP and LP) was one of the main objectives of this work. Experiments with both types of lamp were conducted in discontinuous mode with recirculation (Masterflex L/S Digital Pump System, 600 mL min^{-1}). For experiments with a MP lamp (Heraeus TQ-150 model, Germany) an immersion type annular photoreactor was used. The lamp was covered by a quartz sleeve and located vertically at the center of the reactor. According to the manufacturer, the lamp power was 150 W from which only 5.7 W was attributed to UVC (active for H_2O_2/UVC). The irradiated volume was 380 mL. For experiments with LP lamp (Philips TLV-8W, emission peak at 254 nm, 2 W_{UVC}) annular photoreactor in discontinuous mode with recirculation (Selecta - Percom N-M, 600 mL min^{-1}) was used. The illuminated volume of the reactor was 260 mL. More detailed description of both experimental set-ups (irradiated surface, range UVC Watts, *etc.*) can be found in Table 2.

The H_2O_2/UVC effluent was pumped through a granular activated carbon column (GAC, Hidrowater coconut shell) using recirculation (Selecta - Percom N-M, 500 mL min^{-1}) under ambient conditions (20 ± 2 °C). The length and diameter of the column were 25.4 cm and 5.1 cm, respectively. The residual H_2O_2 from H_2O_2/UVC was used for oxidation in this step. The amount, the average particle density, BET surface area and mesh size of GAC were 144.1 g, 0.47 g cm^{-3}, 900–1000 m^2 g^{-1} and 4–8 mm, respectively.

Table 1
Characteristics of petroleum refinery wastewater effluent (RWW).

Parameter (unit)	Value	Parameter (unit)	Value
COD (mg O_2 L^{-1})	128	*E. coli* (CFU 100 mL^{-1})	<D.L
TOC (mg C L^{-1})	35	Total coliforms (CFU 100 mL^{-1})	10^3
SS (mg L^{-1})	20	Nematode (CFU 100 mL^{-1})	<D.L
Turbidity (NTU)	10.90	Iron (µg L^{-1})	56
Transmittance (254 nm, %)	17.50	Phenol (µg L^{-1})	570
pH	7.14	2,4,5-trichlorophenol (µg L^{-1})	0.10
Conductivity (µS cm^{-1})	2400	Bisphenol A (µg L^{-1})	0.60