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Combined AOPs for potential wastewater reuse or safe discharge based on multi-barrier treatment (microfiltration-H_2O_2/UV-catalytic wet peroxide oxidation)

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HIGHLIGHTS

- Equation for estimation of UVC dose accumulated by the water was proposed.
- Filtration, H_2O_2/UVC and H_2O_2/GAC as multiple-barrier treatment (MBT) was suggested.
- The water toxicity was increased after H_2O_2/UVC step and reduced after H_2O_2/GAC.
- Complete removal of H_2O_2 was achieved during the multiple treatments.
- The quality of the wastewater after multiple barrier treatment allows its reuse.

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ABSTRACT

The viability of a multi-barrier treatment (MBT) for safe discharge or potential reuse of synthetic industrial wastewater was evaluated in this study. The proposed MBT consists of microfiltration membrane pre-treatment (MF), followed by hydrogen peroxide photolysis (H_2O_2/UVC) using a medium pressure Hg lamp (MP) and granulate activated carbon (GAC). The synthetic wastewater (SIWW) obtained by addition of different industrial organic pollutant (orange II, phenol, 4-chlorophenol and phenanthrene) to the effluent taken from a municipal wastewater treatment plant was used in this study.

At optimal operational conditions complete degradation of added contaminants, about 85% of total mineralization and total disinfection were achieved after MBT treatment. Toxicity tests with *Vibrio fischeri* and *Paracentrotus lividus* sea-urchin (fertilization and embryo-larval development assays) were conducted with water after each treatment step and drastic decrease of toxicity was observed after applied process. However, it was demonstrated that after H_2O_2/UVC step toxicity of water significantly increased and was even higher than that of SIWW. Novel equation for estimation of UVC dose was introduced as one of the most important scaling parameter. The main operational and maintenance cost (O&M) of MBT process was evaluated in this work. Thus, the high quality of the obtained effluent suggests its suitability for water reuse or safe discharge.

1. Introduction

Due to the growing demand of population, the industry undergoes fast development. The quality of surface water has been a source of growing concern for the last decade. A major source of water pollution is municipal sewage, which poses a threat to both human health and aquatic ecosystems. Wastewater treatment plants must treat a wide variety of natural and industrial products since they receive wastewater from both domestic and industrial sources.

Many industrial enterprises such as refineries, pulp and paper mills, and pharmaceutical companies discharge wastewaters to the environment, so in addition to known chemicals classically found in municipal effluents, an emerging panel of molecules such as pharmaceuticals, personal care products and products from the nanotechnology industry makes the chemical composition of wastewater increasingly more complicated to analyze and to

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process [1]. The harmful effects of these contaminants have been tested in the field and laboratory, mainly for their endocrine disruption effects [2]. Recently, their immunotoxicological effects [3,4] showed that these effluents lead to immunosuppression in mussels, oxidative stress and neurotoxicity in polychaete *Hediste diversicolor* [5]. Therefore, new technologies are needed for industrial and municipal wastewater treatment.

According to the accepted theory, the AOPs such as Fenton (H_2O_2/Fe^{2+}), photo-Fenton (H_2O_2/Fe^{2+}/UV), photocatalysis (TiO_2/UV), H_2O_2 photolysis (H_2O_2/UVC) are based on generation of hydroxyl radicals ($OH^{\cdot}$), which are known to be responsible for organic pollutants oxidation [6]. Nevertheless, little is known about how this treatment may introduce oxidative chemical modifications that could modulate or even possibly increase the toxic potential of municipal wastewaters toward aquatic biota [7,8].

For instance, it was reported that presence of residual H_2O_2 and by-products in the effluent after H_2O_2/UV treatment increase its toxicity [9]. Hence, the toxicity of treated water should always be studied after AOP treatment. Nevertheless, the toxicity of the H_2O_2/UVC effluent can be eliminated using post filtration with granular activated carbon (GAC). The installation for drinking water production in Netherlands [10] can serve as an example of such treatment scheme.

A number of studies using different operational conditions [11–15] demonstrated that H_2O_2 in presence of activated carbon (AC) can oxidize the organic molecules (catalytic wet peroxide oxidation, CWPO), such as dyes, phenol, and different phenolic compounds. According to some studies mentioned above, the H_2O_2 can be activated by GAC or AC to generate $OH^{\cdot}$, following the reactions (A) and (B):

$$AC + H_2O_2 \rightarrow AC^+ + OH^- + OH^{\cdot} \quad (A)$$

$$AC^+ + H_2O_2 \rightarrow AC + H^+ + HO_2^{\cdot} \quad (B)$$

It was suggested that like in Fenton's oxidation reaction, graphenic layers of GAC are behaving as heterogeneous catalyst that donated delocalized π-electrons for H_2O_2 decomposition on the carbon surface [16].

In the study of Anfruns et al. [15] it was reported that H_2O_2 treatment for activated carbon regeneration is limited for non-polar and hydrophobic VOCs since these compounds remain adsorbed on the surface. On the other hand, polar and hydrophilic VOCs were found to be transferred to the bulk and react with generated oxidant species. Therefore, H_2O_2/UVC process before GAC seems to be a promising and efficient treatment to remove polar and non-polar organic pollutants from the water. Nevertheless, more research should be done in order to analyze the possible risk of this treated effluent to the ecosystem when it is discharged.

The feasibility of MBT process including micro-filtration, H_2O_2/UVC and CWPO for safe discharge of the synthetic industrial wastewater (SIWW) or reuse of it was the aim of this research. An equation to estimate the UVC irradiation intensity in desired location of the reactor and also, the dose received by wastewater was proposed. The detoxification of the effluent together with the environmental risk was assessed. The toxicity of the SIWW, effluent of H_2O_2/UV and MBT effluent was studied using two marine species, the sea urchin *Paracentrotus lividus* and the bacteria *Vibrio fischeri*.

2. Materials and methods

2.1. Water assay

The water used in this work was the effluent of municipal wastewater treatment plant in Chiclana de la Frontera (Cádiz, Spain). The treatment plant includes physical and biological processes for water purification.

In order to prepare SIWW, different compounds (phenol, 4-chlorophenol, phenanthrene, orange II) were added to the effluent of urban wastewater matrix (UWW). In the present study, pollutant concentrations were relatively low, because in the industrial wastewater effluents these are usually found at low concentrations. But even at low level, contaminants can be toxic for the receiving environment. The SIWW characterization is presented in Table 1.

Glucose was used to increase the TOC up to 40 mg L^{-1} for simulation the TOC of industrial wastewater effluent.

All these compounds were of analytical grade and purchased from Sigma Aldrich (Spain): 4-chlorophenol (CAS number 106-48-9), phenol (CAS number 108-95-2), phenanthrene (CAS number 85-01-8) and orange II, the sodium salts of the acid 4-(2-hydroxy-1-naphtalene) azo-benzene-sulphonic, (CAS number 633-96-5). Glucose was obtained from MP Biomedicals (CAS number 50-99-7). The UWW was spiked with the abovementioned contaminants before filtration (first step in MBT process).

2.2. Experimental setup

The MBT experimental set up is divided on three steps: filtration, H_2O_2/UVC and H_2O_2/GAC (CWPO) (Fig. 1A).

2.2.1. Filtration step

The UWW was subjected to the filtration as pre-treatment step. It was done in order to increase the water transmittance because it is a critical parameter for AOP processes. The fiber glass filter with a pores size of 0.7 μm was used (Watman GF/G, Spain).

2.2.2. Photolysis of H_2O_2

An immersion type photoreactor (Heraeus TQ-150 model, Germany) was used for UV–H_2O_2 photolysis experiments. The experiments were performed in discontinuous mode with recirculation. According to description of the reactor provided by the producer, the height (h) and inner diameter of Pyrex glass reactor are 25 cm and 7.6 cm, respectively. The medium pressure lamp was covered by a quartz sleeve 30 cm high and with outer diameter 2.5 cm. It was located vertically at the center of the reactor.

However, only 18.5 cm of the quartz sleeve was in contact with the water, therefore this height was used to estimate the surface of the lamp and also, to calculate the reactor volume. Hence, total irradiated volume in the system was 380 mL and SIWW was recirculated using a peristaltic pump Masterflex L/S Digital Pump

Table 1
The main characteristics of SIWW.

Parameter (unit)	Value	Parameter (unit)	Value
COD (mg O_2 L^{-1})	150	*E. coli* (CFU 100 mL^{-1})	10^4
TOC (mg C L^{-1})	40	Total coliforms (CFU 100 mL^{-1})	10^7
SS (mg L^{-1})	30	Nematodes (eggs 10 L^{-1})	<D.L.
Turbidity (NTU)	3.5	4-Chlorophenol (mg L^{-1})[a]	1.5
Transmittance (%)	40.3	Phenol (mg L^{-1})[b]	3.8
pH	7.42	Phenanthrene (mg L^{-1})[c]	0.5
Conductivity (μS cm^{-1})	1380	Orange II (mg L^{-1})[d]	5

[a] Some industrial effluents contain chlorophenol from 0.15 to 100–200 mg L^{-1} [17–19].

[b] In different wastewaters, concentration of phenol or mixture of phenols varies from 10 to 17,000 mg L^{-1}. In the effluents which are discharged to the environment, the concentration should be below or around 1.0 mg L^{-1} [20,21].

[c] The PAHs can be found in environment for instance coastal estuaries and marine sediments [22]. The concentration of PAHs in the effluent of industrial wastewater plants vary from undetectable to 4.4 mg L^{-1} [23].

[d] Most of dyes cannot be removed from natural waters by microorganisms or sunlight, thus, coloring the water even at low concentrations [24,25].