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Toxicity and genotoxicity of hospital laundry wastewaters treated with photocatalytic ozonation

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HIGHLIGHTS

► Study refers to hospital laundry wastewater treatment with wastewater.
► The photocatalytic properties were studied upon ozone and iron catalyzer.
► Genotoxic effects were also detected for *A. cepa*.
► The $UV/O_3/Fe^{2+}$ 150 mg L^{-1} method was more efficient in reducing COD (59.1%), BOD (50.3%) and TKN (86.8%).

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ABSTRACT

The aim of the present study was to assess the efficiency of advanced oxidative processes based on photocatalytic ozonation (O_3, UV, UV/O_3, $UV/O_3/Fe^{2+}$ 50 mg L^{-1} and 150 mg L^{-1}) in the treatment of hospital laundry wastewaters. The analysis of the investigated wastewater revealed high chemical oxygen demand (COD — 3343.8 mg L^{-1}), biochemical oxygen demand (BOD_5 — 1906.4 mg L^{-1}), total Kjeldahl nitrogen (TKN — 79.8 mg L^{-1}) and *Daphnia magna* toxicity (EC50 = 1.73). Genotoxic effects were also detected for *Allium cepa*. Reductions of some parameters occurred after photocatalytic ozonation. The $UV/O_3/Fe^{2+}$ 150 mg L^{-1} method was more efficient in reducing COD (59.1%), BOD_5 (50.3%) and TKN (86.8%). There was significant reduction ($p<0.05$) in *D. magna* toxicity, O_3 (EC50 = 47.3%), UV (EC50 = 50.6%) and $UV/O_3/Fe^{2+}$ 150 mg L^{-1} (EC50 = 45.4%) processes. Normalization of the mitotic index and reduction of micronucleated cells were observed in *A. cepa* after the treatments. Results demonstrate that these methods were efficient in the degradation of hospital laundry wastewaters, representing a thriving alternative for the removal of pollutants that cause toxicity and genotoxicity.

1. Introduction

Hospital wastewaters contain a wide variety of persistent chemical substances and complex mixtures of organic matter, detergents, surfactants, antibiotics, antiseptics, solvents, medical drugs and radioactive substances, often disposed into local sewage systems without any previous treatment (Emmanuel et al., 2005; Verlicchi et al., 2012). Depending on the activities involved, hospital wastewaters can be generated in different sectors of a hospital and thus have a quite variable composition. This composition usually results in high levels of toxicity, genotoxicity and organic load, thus causing a considerable impact on the ecosystem and inherent hazard to human health.

Among the major sectors implicated in the generation of hospital wastewaters, we have the divisions of clinical analyses, divisions of radiation therapy and chemotherapy, laundries, ICUs and hospital rooms in different wards (Kist et al., 2008; Machado et al., 2012). Hospital laundry wastewaters are characterized by high COD and BOD_5 depending on the washing stage (Machado et al., 2012). When the washing stages were not subdivided, COD and BOD_5 concentrations were 477 and 305 mg L^{-1}, respectively, but when they were subdivided into rinsing, washing, and softening, the most critical stages (e.g., first rinsing) yielded COD and BOD_5 concentrations as high as 3343 and 1906 mg L^{-1}, respectively. In addition, they have a large concentration of particulate material, proteins, starch, fat, oils and greases, detergents, disinfectants and pharmaceutical products (Kümmerer, 2011; Verlicchi et al., 2010a). These substances are highly hazardous as their

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levels of toxicity are very high for aquatic organisms, requiring in loco treatment.

Many of the pollutants found in these wastewaters belong to the category of non-regulated "emerging pollutants," but can be the object of future regulations depending on their effects on the environment and on human health (Verlicchi et al., 2012). The contact of this type of wastewater with the environment can produce negative effects on the biological balance of aquatic ecosystems, causing imbalance at different trophic levels by the action of toxic and genotoxic agents and indirectly by eutrophication (Kümmerer et al., 2002; Berto et al., 2009; Coelho et al., 2009; Michael et al., 2012).

In Brazil, in general, hospital wastewaters are not properly treated and are discharged into water BOD_5 that supplies towns, industries, and primary production. For instance, medical drugs not metabolized by patients reach surface waters and, consequently, the surrounding environment (Vecchia et al., 2009). Studies show that hospitals, clinics and similar establishments generate wastewaters with high genotoxic potential due to the chemical and pharmaceutical products they contain (Kümmerer et al., 2002).

Currently, several studies have been conducted to assess the presence of general and emerging pollutants, to find out about their potentially harmful effects using different toxicological and microbiological assays, and to find different ways to mitigate and reduce their impacts by different treatments (Verlicchi et al., 2010b, 2012). In the literature, numerous studies report satisfactory results for the degradation of medical drugs in aqueous solutions by oxidative processes; however, few of them are based on real wastewater samples (Vasconcelos et al., 2009).

Among some studies, we can mention those on the characterization of emerging pollutants such as pharmaceutical drugs (Larsson et al., 2007; Vasconcelos et al., 2009; Chong and Jin, 2012; Verlicchi et al., 2012); assessment of toxicity at different trophic levels (Emmanuel et al., 2004, 2005; Boillot and Perrodin, 2008; Boillot et al., 2008); cytotoxicity and genotoxicity (Bagatini et al., 2009; Gupta et al., 2009); presence of resistant bacteria (Fuentefria et al., 2008); and investigation and application of different pre-treatment methods, such as physicochemical processes based on coagulation/flocculation (Suarez et al., 2009), use of membrane bioreactors (Kovalova et al., 2012), or advanced oxidative processes such as Fenton and photo-Fenton (Kajitvichyanukul and Suntronvipart, 2006), $UV/TiO_2/O_3$ (Machado et al., 2007; Kist et al., 2008; Molnar et al., 2012), ozone-based electrochemical methods (Machado et al., 2012) and heterogeneous photocatalytic methods compared with the combination of H_2O_2/O_3 and isolated ozonation (Vasconcelos et al., 2009). These methods were developed in an attempt to reduce adverse characteristics and to enable conventional treatments and to make them compliant with the legislation of each location concerning the discharge of pollutants into receiving BOD_5.

In advanced oxidative processes, highly reactive free radicals such as hydroxyl radicals ($HO\cdot$) are generated in aqueous solution and are responsible for the oxidation and mineralization of organic chemical compounds. Hydroxyl radicals are strong oxidizing agents with an oxidation potential of 2.80 V, poorly selective, and capable of acting upon a large number of organic compounds, many of which cannot be easily degraded by conventional biological systems (Vogelphol and Kim, 2004; Movahedyan et al., 2009; Oller et al., 2011). The redox potential of these radicals is high compared to that of several other radicals often used in the treatment of waters and wastewaters, such as atomic oxygen, ozone, and chlorine (Pera-Titus et al., 2004).

Given these aspects, the present study aimed to evaluate the toxicity and genotoxicity related to the efficiency of advanced oxidative processes (AOPs), to photocatalytic ozonation, used for the detoxification and reduction of load parameters in the laundry wastewaters of a hospital located in the Rio Pardo valley region, state of Rio Grande do Sul, Brazil.

2. Materials and methods

2.1. Description of the study site

Wastewater samples were collected from a 180-bed regional hospital located in Santa Cruz do Sul, central region of the state of Rio Grande do Sul, Brazil.

Approximately 150 $m^3\ day^{-1}$ of wastewater is generated by the hospital unit and is discharged into the local sewage system without any treatment. The hospital laundry produces 48 to 50 $m^3\ day^{-1}$ of wastewater from the washing of 970 kg day^{-1} of textile items, thus accounting for 33% of the hospital wastewaters.

2.2. Reactor configuration and operation and description of treatment assays

A rectangular, column-type acrylic reactor measuring $12 \times 12 \times 42$ cm was used. The reactor had a space at the center for attachment of a 15-watt germicidal lamp with a wavelength of 254 nm, activated in photocatalytic assays. Ozone was generated by the corona effect using a RADAST 2C OzoOxi ozonizer, with maximum generating capacity of 2000 mg h^{-1}. Gas was transferred to the reactor by an air compressor, and diffused into the reactor by four air stones, placed on each corner and coupled to the base. The ozone dose used corresponded to 1222 mg h^{-1} considering total transfer. UV radiation dose was equal to 0.980 mW cm^{-2}.

The efficiency of AOPs was assessed using photoirradiation: UV, O_3, UV/O_3 and two variants of the $UV/O_3/Fe^{2+}$ method, using ferrous sulfate to obtain Fe^{2+} at two different concentrations: 50 mg L^{-1} of Fe^{2+}, adapted from the COD: Oxidant: Kajitvichyanukul and Suntronvipart (2006) catalyzer ratios, and 150 mg L^{-1} of Fe^{2+}.

A ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) produced by nuclear was used in the experiments. The assays were carried out in acid media at adjusted pH ranges (3–3.5), given that this pH range is widely recommended in the literature for the solubility of ferrous ion (Kajitvichyanukul and Suntronvipart, 2006). The reaction time of 180 min, and aliquots were obtained every 30 min for kinetic assessment. At the end of the treatments, the matrix of pollutants was neutralized to pH 7 to 7.4 and prepared for biological evaluation.

2.3. Methods for wastewater analysis

The raw and treated wastewater samples in the five treatment methods were investigated as to changes in some analytical variables, such as: COD, BOD_5, TKN, total phosphorus (total P), surfactants, pH, turbidity, conductivity, total coliforms, *Escherichia coli*, toxicity and genotoxicity. Detoxification was assessed by toxicity assays with different test organisms. Six samples were collected for each sampling period. The physicochemical variables were evaluated following the guidelines of the methods used by AWWA-APHA-WEF (2005).

2.4. Toxicity assays

Acute toxicity was assessed by the immobility or mortality of *Daphnia magna* Straus, 1820, following the guidelines of the Brazilian ABNT — Associação Brasileira de Normas Técnicas (2004). The tested samples were prepared with volumetric accuracy and geometric progression of 1/2. The raw wastewater was assessed by eight dilutions in a range between 0.39 and 50%; treated wastewaters were assessed by five dilutions, from 6.25 to 100%. The assays were done in sextuplicate and EC50 was estimated using the nonparametric statistical method of Trimmed Spearman-Karber (Hamilton et al., 1979).