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Ultraviolet and solar photocatalytic ozonation of municipal wastewater: Catalyst reuse, energy requirements and toxicity assessment

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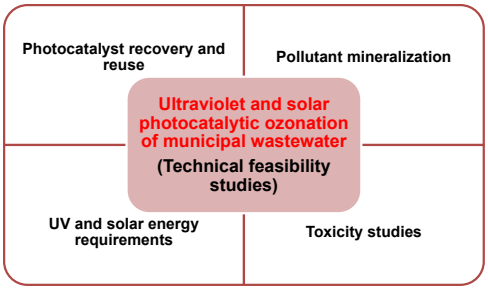
HIGHLIGHTS

- Bare TiO_2 and metal ion (Ag, Cu & Fe) doped TiO_2 were used for wastewater treatment.
- Photocatalysts were used three times without significant reduction in performance.
- Photocatalytic ozonation reduced the energy expenditure by 46–81%.
- Wastewater toxicity decreased after treatment by photocatalytic ozonation.

GRAPHICAL ABSTRACT



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ABSTRACT

The present study evaluated the treatment of municipal wastewater containing phenol using solar and ultraviolet (UV) light photocatalytic ozonation processes to explore comparative performance. Important aspects such as catalyst reuse, mineralization of pollutants, energy requirements, and toxicity of treated wastewater which are crucial for practical implementation of the processes were explored. The activity of the photocatalysts did not change significantly even after three consecutive uses despite approximately 2% of the initial quantity of catalyst being lost in each run. Analysis of the change in average oxidation state (AOS) demonstrated the formation of more oxidized degradation products (ΔAOS values of 1.0–1.7) due to mineralization. The energy requirements were determined in terms of electrical energy per order (E_{EO}) and the collector area per order (A_{CO}). The E_{EO} (kWh m^{-3} $Order^{-1}$) values were 26.2 for ozonation, 38–47 for UV photocatalysis and 7–22 for UV photocatalytic ozonation processes. On the other hand, A_{CO} (m^2 m^{-3} $order^{-1}$) values were 31–69 for solar photocatalysis and 8–13 for solar photocatalytic ozonation. Thus photocatalytic ozonation processes required less energy input compared to the individual processes. The cytotoxicity of the wastewater was analysed using the 3-(4, 5-dimethylthiazol-2-yl)-2, 5-diphenyltetrazolium bromide (MTT) assay with Vero cells. The cell viability increased from 28.7% in untreated wastewater to 80% in treated wastewater; thus showing that the treated wastewater was less toxic. The effectiveness of photocatalytic ozonation, recovery and reusability of the photocatalysts, as well as detoxification of the wastewater make this low energy consumption process attractive for wastewater remediation.

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1. Introduction

The increasingly stringent standards for wastewater discharge coupled with the shortage of freshwater sources have triggered the exploration of effective technologies for the treatment of municipal wastewater for reuse purposes (Puspita et al., 2015). Conventional wastewater treatment though widespread and generally effective, is inefficient especially in the degradation of contaminants such as bio-recalcitrant organic compounds (Lee et al., 2015; Park et al., 2016). This is due to the fact that biological oxidation systems are not specifically designed for this role and therefore, a high portion of these organic micro pollutants and their metabolites may avoid elimination in the municipal wastewater treatment plant (MWWTP) and enter the aquatic environment via effluents and pose significant risk to humans and the environment (Kositzi et al., 2004; Shon et al., 2006; Espejo et al., 2014). Consequently, there has been a dramatic surge in interest in the development of new wastewater remediation approaches to protect the environment and human health (Cardoso et al., 2016). Among the options that have received keen interest is the use of advanced oxidation processes (AOPs) such as ozonation and photocatalysis to polish wastewater effluents to the required standards for discharge or reuse. However, before any technology can be deemed suitable for use, there is need to perform technical and economic feasibility studies (Chong et al., 2012) to facilitate up scaling.

Energy requirement is one of the main factors to be considered when evaluating wastewater treatment processes. Specifically for the case of AOPs, which are often characterized by high energy consumption (Esplugas et al., 2002), this is a key issue of concern. Most AOPs are electric-energy-intensive, therefore, electricity tends to account for the main operating cost (Bolton et al., 2001). Based on this need, the International Union of Pure and Applied Chemistry (IUPAC) proposed the use of figures-of-merit for evaluation of AOPs on the use of electrical and solar energy and for the comparison of energy consumption regardless of the nature of the system (Bolton et al., 2001). For instance, ultraviolet (UV) light driven photodegradation is effective in the mineralization of organic pollutants; however, this comes with a high consumption electrical energy, thus making the process costly. In fact, Oller and colleagues (Oller et al., 2011) estimate that electrical energy represents approximately 60% of the total cost of operating a UV photocatalytic reactor. Based on this limitation of using UV lamps, there have been accelerated research efforts to explore the use of the renewable and free solar energy through the development of visible light active photocatalysts. This can substantially reduce treatment costs and furthermore, solar energy is more favourable from an environmental perspective (Tsydenova et al., 2015).

Apart from the minimization of energy requirements for AOPs, a potential avenue of sustainability especially for photocatalytic processes is the recovery and reuse of the photocatalysts in slurry reactors. Surprisingly, from the literature, not many studies have addressed the recovery and reuse of the catalysts or studied catalyst activity after repeated uses. This makes it important to evaluate catalyst recovery and reuse as a way of making the process sustainable especially when treating real wastewater that has numerous constituents that may affect the catalyst life (van Grieken et al., 2009). Nevertheless, the few studies that have investigated this aspect have reported positive results, with some achieving good catalytic activity even after reusing the catalyst three to five times (Rupa et al., 2007; Miranda-García et al., 2011).

Another important aspect is that since the operation of AOPs is based on the production of non-selective and highly reactive hydroxyl (•OH) radicals, they are capable of oxidising many wastewater constituents indiscriminately (Sievers, 2011). This may inadvertently result in the formation of oxidation by-products that may be toxic. To determine the safety of the treated wastewater for reuse or even discharge, the toxicity of the wastewater samples before and after treatment needs to be evaluated. The determination of potential toxicity of treated wastewater is a major research thrust for AOPs to help inform their implementation in wastewater remediation (Linden and Mohseni, 2014). The use of physico-chemical analyses may not be sufficient to determine the toxicity of these products. Therefore, biological tests are a suitable alternative methodology to characterise the toxicity of these complex water samples without the need to determine the composition of the mixture or its chemical properties (Žegura et al., 2009). This is because, it is almost impossible to identify all the toxic oxidation by-products that have been formed when the wastewater contains different types of micro pollutants.

The effectiveness of UV and solar photocatalytic ozonation processes for municipal wastewater decontamination was demonstrated in our previous study (Mecha et al., 2016a). Based on the promising results that were obtained, it was necessary to investigate the technical feasibility aspects of this technology to facilitate practical application. The objectives of this study were: (i) to use figures-of-merit to estimate the energy requirements of UV and solar photocatalytic ozonation; (ii) to evaluate the durability of the photocatalysts by performing catalyst reuse studies; and (iii) to assess the cytotoxicity of the treated wastewater to determine its safety for reuse.

2. Materials and methods

2.1. Chemicals and materials

Bare Titanium dioxide (TiO_2) and metal-ion (Ag, Cu and Fe) doped TiO_2 were synthesized as explained in our previous study (Mecha et al., 2016b). In summary, the photocatalysts (un-doped TiO_2, silver-doped TiO_2, copper-doped TiO_2, and iron-doped TiO_2) were synthesized under similar conditions except for the addition of the respective doping metals. Titanium(III) chloride ($TiCl_3$) solution, ammonia and distilled water (volume ratio 2:1:2, respectively) were thoroughly mixed using magnetic stirring at room temperature. For the doped photocatalysts, the appropriate amounts of silver, copper and iron nitrates (2.0 wt %) were added and the mixture was stirred for 20 h, after which the suspension was washed three times using deionized water and then centrifuged three times at 3000 r/min to remove the resulting ammonium chloride. The precipitate was then dried at 100 °C for 10 h in an oven and the resulting powder calcined in a furnace at 500 °C for 4 h (Mecha et al., 2016b). Ozone was produced using an air fed ozone generator (Wassertec, Light Blue ozone generator). Methanol, potassium iodide (KI), sodium thiosulphate, hydrochloric acid, and starch were obtained from Merck (Pty) Ltd (South Africa). Cytotoxicity analysis reagents, 3-(4, 5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT), phosphate buffered saline (PBS) and acidic isopropanol (0.1N HCl in absolute isopropanol) were sourced from Sigma-Aldrich (South Africa). All chemicals used were of analytical grade and were utilized without modification. All solutions were prepared using Milli-Q water.

2.2. Water samples

Synthetic water (SW) and secondary wastewater (SWW) effluent were used in this study. The SW was prepared by spiking deionized water with phenol (5000 μg/L). The SWW effluent was obtained from Daspoort wastewater treatment plant in Pretoria, South Africa. The samples were collected after the biological treatment stage and transported to the laboratory and analysed for