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Evaluation of synergy and bacterial regrowth in photocatalytic ozonation disinfection of municipal wastewater

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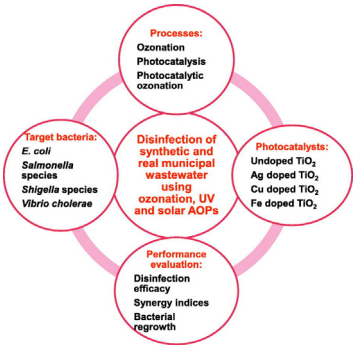
HIGHLIGHTS

- Disinfection of synthetic and real municipal wastewater was studied.
- Ozonation, photocatalysis and photocatalytic ozonation were used.
- Synergy indices of up to 1.86 were obtained during photocatalytic ozonation.
- Disinfection time was reduced by 50–75% using photocatalytic ozonation.
- There was no bacterial regrowth after UV and solar photocatalytic ozonation.

GRAPHICAL ABSTRACT



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ABSTRACT

The use of solar and ultraviolet titanium dioxide photocatalytic ozonation processes to inactivate waterborne pathogens (*Escherichia coli*, *Salmonella* species, *Shigella* species and *Vibrio cholerae*) in synthetic water and secondary municipal wastewater effluent is presented. The performance indicators were bacterial inactivation efficiency, post-disinfection regrowth and synergy effects (collaboration) between ozonation and photocatalysis (photocatalytic ozonation). Photocatalytic ozonation effectively inactivated the target bacteria and positive synergistic interactions were observed, leading to synergy indices (SI) of up to 1.86 indicating a performance much higher than that of ozonation and photocatalysis individually (SI ≤ 1, no synergy; SI > 1 shows synergy between the two processes). Furthermore, there was a substantial reduction in contact time required for complete bacterial inactivation by 50–75% compared to the individual unit processes of ozonation and photocatalysis. Moreover, no post-treatment bacterial regrowth after 24 and 48 h in the dark was observed. Therefore, the combined processes overcame the limitations of the individual unit processes in terms of the suppression of bacterial reactivation and regrowth owing to the fact that bacterial cells were irreparably damaged. The treated wastewater satisfied the bacteriological requirements in treated wastewater for South Africa.

1. Introduction

Pollution of water sources by waterborne pathogens constitutes a major public health risk. Municipal wastewater is a key source of

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pathogens (Bustos et al., 2014) and therefore disinfection of wastewater is mandatory to minimise the risk to public health and to the environment. Conventional wastewater treatment plants often employ chemical based disinfectants such as chlorine and its derivatives. However, chlorination presents limitations such as the formation of harmful disinfection by-products (DBPs), when reacting with natural organic matter present in the water (Chong et al., 2011); operational safety problems; as well as resistance of some microorganisms. To minimise and/or prevent the formation of DBPs, there is a need to explore alternative disinfection techniques such as advanced oxidation processes (AOPs). The AOPs are a very effective treatment technology since they can simultaneously degrade recalcitrant organic compounds and biological contaminants (Tsydenova et al., 2015). The AOPs, such as semiconductor photocatalysis and ozonation produce highly reactive hydroxyl (•OH) radicals which can attack and inactivate the microorganisms indiscriminately thus forming little or no DBPs by mineralizing the pollutants to harmless products such as carbon dioxide and water.

Interest in the use of AOPs for wastewater treatment has increased in recent years because of the need for wastewater reuse to address shortages of freshwater and strict requirements for wastewater discharge (Oneby et al., 2010; Paraskeva and Graham, 2002). In particular, ozonation has been applied in post-tertiary municipal wastewater treatment due to low formation of DBPs (Wert et al., 2007) compared to chlorination. The use of photocatalysis has great potential due to its advantages such as operation at ambient conditions of temperature and pressure, high efficiency in organic mineralisation and inactivation of pathogens (Chong et al., 2012). However, to date, most of the photocatalytic disinfection studies have been conducted at the laboratory scale (Venieri et al., 2017; Booshehri et al., 2017; Agulló-Barceló et al., 2013) and pilot scale (Booshehri et al., 2017; Ferro et al., 2015; Malato et al., 2016) using synthetic and sometimes real municipal wastewater samples. This is due to challenges of scale up such as mass transfer limitations.

Heterogeneous photocatalytic disinfection, using titanium dioxide (TiO_2) as photocatalyst, is limited by slow oxidation rate, which results from low quantum efficiency values (Augugliaro et al., 2006). Furthermore, TiO_2 is only active under ultraviolet (UV) light which requires the use of electricity powered UV lamps since the use of sunlight is limited by the fact UV light constitutes only 4–6% of the solar radiation. The utilization of visible light (45% of solar radiation) requires modification of TiO_2 using methods such as metal-ion doping to extend the light absorption of the photocatalysts from UV range to the visible range as shown using Ag, Cu and Fe in our previous study (Mecha et al., 2016b). Metal-ion doping introduces metal ions into a pure semiconductor to change its electronic properties and thus the photocatalytic activity (Khraisheh et al., 2015). This occurs because the dopant shifts the absorption to the visible wavelengths by substituting Ti in the substitutional sites or in the interstitial sites. Furthermore, dopant addition enhances photoreactions and modifies material properties such as particle size and crystal structure (Sahu and Biswas, 2011).

In addition, to improve the performance of the photocatalytic processes, addition of oxidant species such as hydrogen peroxide or ozone has been explored (Rajeswari and Kanmani, 2009). When photocatalysis is coupled with ozonation, the combination influences the reaction mechanisms by increasing the efficiency and decreasing the reaction time with respect to the individual processes (Augugliaro et al., 2006; Mecha et al., 2016a). This is due to synergistic effect between ozonation and photocatalysis thus maximizing the production of hydroxyl (•OH) radicals (Moreira et al., 2016; Mecha et al., 2016a). Bacterial inactivation using photocatalytic ozonation is achieved through disrupting normal cellular functions by the reactive oxygen species (ROS), especially the •OH radicals leading to loss of membrane potential (Berney et al., 2006) resulting in oxidative damage to cellular components, thereby leading to the death of the microorganisms (Pham and Lee, 2014). However, photocatalytic ozonation has not been applied yet at full-scale.

In most instances, water and wastewater treatment standards focus only on coliform bacteria such as *E. coli* (Walt et al., 2009). However, apart from *E. coli*, information regarding the behaviour of other bacteria during disinfection is very limited; yet, the bacterial content of wastewater comprises different species which exhibit variable tolerance to disinfection processes as a result of differences in cellular structure (Venieri et al., 2014). In addition, because biological contaminants have the potential to regrow, when the stress conditions imposed by the water treatment processes are relieved, microbiological indicators should be monitored during storage of the treated wastewater. It has been shown that bacterial regrowth does occur after photocatalytic disinfection (Wist et al., 2002; Rizzo, 2009) or disinfection by ozone (Sousa et al., 2017; Demir and Atguden, 2016). This is a major limitation in the application of these processes individually and consequently there is a need to investigate whether the combined process (photocatalytic ozonation) can overcome this challenge.

Therefore, in the present study, the effects of photocatalyst type (un-doped and metal-ion-doped TiO_2), source of irradiation (ultraviolet and solar light), and water matrix (synthetic and real wastewater) were investigated using individual unit processes and combined AOPs for wastewater disinfection. For this purpose, the naturally occurring *Escherichia coli*, *Salmonella* species, *Shigella* species, and *Vibrio cholerae* were tested before and throughout the different treatments to: (i) determine the inactivation kinetics of these microbial contaminants in synthetic and real wastewater effluents; (ii) assess the synergistic effects resulting from the combined ozonation and photocatalysis processes; and (iii) evaluate the durability of disinfection by determining the bacterial regrowth after 24 and 48 h post-disinfection. This is the first study to evaluate the use of UV and solar photocatalytic ozonation for the disinfection of municipal wastewater in South Africa for wastewater remediation. The study is unique in the sense that it compares the disinfection of synthetic and real wastewater samples targeting multiple bacterial contaminants (naturally occurring and spiked) using different photocatalysts and irradiation sources to enable a holistic performance evaluation. The study also addresses the challenge of bacterial regrowth that often occurs when ozonation and photocatalysis are used individually by exploring their collaborative performance in photocatalytic ozonation.

2. Materials and methods

2.1. Chemicals and materials

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 prepared under similar experimental conditions except for the addition of the respective salts of the doping metals. Titanium(III) chloride ($TiCl_3$) solution, concentrated ammonia and distilled water (volume ratio 2:1:2, respectively) were mixed using a magnetic stirrer 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 deionised 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. The resulting powder was calcined in a furnace at 500 °C for 4 h. Potassium iodide (KI), sodium thiosulphate, hydrochloric acid, and starch were obtained from Merck (Pty) Ltd. (South Africa). All chemicals used were of analytical grade and were utilized without modification. All solutions were prepared using Milli-Q water. Ozone was produced using an air-fed ozone generator (Wassertec, Light Blue ozone generator).