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# A review of pathogen removal from municipal wastewater using advanced oxidation processes: Agricultural application, regrowth risks, and new perspectives

Barnabas Oluoch<sup>a,\*</sup>, Takudzwa Mandizvo<sup>a</sup>, William Musazura<sup>a</sup>, Taruvinga Badza<sup>a</sup>, Benton Otieno<sup>b</sup>, Stephen Ojwach<sup>c</sup>, Alfred Odindo<sup>a</sup>

<sup>a</sup> *Crop Science Discipline, University of KwaZulu-Natal, Private BagX01, Scottsville, Pietermaritzburg, 3209, South Africa* <sup>b</sup> *Water, Sanitation & Hygiene Research & Development Centre (WASH R&D Centre), University of KwaZulu-Natal, Howard College, 4041, Durban, South Africa*

<sup>c</sup> *Chemistry Department, University of KwaZulu-Natal, Private BagX01, Scottsville, Pietermaritzburg, 3209, South Africa*

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#### ABSTRACT

Pathogen removal in wastewater offers a chance to recover water and nutrients for crop production, reducing environmental contamination and public health risks. However, the risk of pathogens regrowing in treated effluents can endanger public health if reused in agriculture, attracting stringent reuse standards. While advanced oxidation processes (AOPs) promise to reduce pathogens, eliminating regrowth potential in AOP-treated effluents requires further scrutiny. This review aimed to summarize the available evidence on understanding pathogen reduction and regrowth potential in AOP-treated effluents, following best practices for scoping reviews like the preferred reporting items for systematic reviews and meta-analysis (PRISMA). It covers recent pathogen studies under AOPs, current AOP investigations, the impact of AOP dosage and retention time on pathogen control, and challenges in reusing AOP-treated effluents for crop production. Additionally, it identifies areas needing improvement or complementary treatments for pathogen-free effluents with no regrowth potential. The review concludes by summarizing key findings and suggesting research areas for further exploration.

# **1. Introduction**

Municipal wastewater treatment for reuse is a crucial strategy in mitigating water scarcity challenges  $[1,2]$  $[1,2]$ . As global populations expand and urbanize, the demand for freshwater resources intensifies, placing immense pressure on water supplies [[3\]](#page-10-0). By implementing efficient wastewater treatment processes at the municipal level, we can transform what was once considered a waste product into a valuable resource. When properly treated, wastewater can be safely reused for various non-potable purposes such as crop irrigation, industrial processes, and even replenishing aquifers [[4,5\]](#page-10-0). This approach helps alleviate the strain on freshwater sources and promotes sustainability by reducing pollution and enhancing water resource management practices [\[6,7](#page-10-0)].

Conventional wastewater treatment methods currently used by the municipalities are reported as not fully amenable to emerging contaminants such as antibacterial drugs [[8,9\]](#page-10-0) and pathogens like *E. coli* [[10\]](#page-10-0). The inadequacy of these methods in eliminating

Corresponding author. *E-mail address:* [boluoch2015@gmail.com](mailto:boluoch2015@gmail.com) (B. Oluoch).

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pathogens and preventing their regrowth threatens public health and the environment [[7,11,12](#page-10-0)]. Pathogens, including bacteria, viruses, and protozoa, can persist in treated wastewater, potentially contaminating receiving waters and endangering human health when used for irrigation or recreational purposes  $[13,14]$  $[13,14]$  $[13,14]$ . The persistence and potential regrowth of pathogens in the treated effluents are significant concerns that warrant a solution and further research, especially given the limited studies reporting on this issue.

Unlike conventional wastewater treatment methods, advanced oxidation processes (AOPs) employ various mechanisms that have been considered an alternative area of exploration as polishing steps for potentially eliminating pathogens in wastewater treatment [\[15](#page-10-0)–17]. Advanced oxidation processes employ highly reactive oxygen species (ROS) like hydroxyl radicals (•OH) to degrade organic matter, including pathogens, by attacking their cell membranes, DNA, and proteins [18–[21\]](#page-10-0). These processes also generate reactive intermediates like  $Fe^{3+}$  and  $Fe^{2+}$  species through mechanisms such as Fenton reactions, further contributing to pathogen inactivation [\[22](#page-11-0)–24]. Additionally, AOPs can produce disinfection by-products (DBPs) with antimicrobial properties, enhancing pathogen elimination [25–[27\]](#page-11-0). Furthermore, AOPs can facilitate indirect pathogen degradation mechanisms like generating secondary oxidants such as sulfate radicals (SO4⋅− ) through persulfate activation [\[28](#page-11-0)–30]. These secondary oxidants participate in radical chain reactions, increasing AOPs' oxidative potential for increased pathogen inactivation [[30\]](#page-11-0). Moreover, the synergistic effects of ROS, reactive intermediates, and DBPs contribute to comprehensive pathogen elimination, making AOPs valuable tools for ensuring safe wastewater effluent [30–[32\]](#page-11-0).

While pathogen-free effluents can be used effectively in urban landscaping [\[33\]](#page-11-0), industrial processes [\[34](#page-11-0)], and recreational water bodies [\[35](#page-11-0)], their primary importance lies in agriculture due to water and nutrient demand for crop production [\[36,37\]](#page-11-0). Prioritizing the use of pathogen-free effluents from AOPs in agriculture aligns with broader goals of promoting sustainable water management, enhancing food production, and safeguarding public health [38–[42](#page-11-0)] in line with the United Nations' Sustainable Development Goals 6, 2, and 3, respectively. This strategic allocation of treated effluents emphasizes the importance of technological advancements to address pressing challenges in key sectors such as agriculture, where water quality and availability are crucial for food production, environmental and human health, and ecological balance [43–[45\]](#page-11-0).

Despite the potential of AOPs in reducing the initial pathogen concentrations and recalcitrant organics, there is a lack of comprehensive, up-to-date studies that assess AOPs' effectiveness in eliminating regrowth in the context of agricultural application standards [\[46,47](#page-11-0)]. Existing studies have reported varying outcomes and methodologies, making it almost impossible to make unwavering decisions on the overall efficacy of AOPs in suppressing pathogen regrowth [\[48](#page-11-0)–50]. Therefore, an evidence-based approach is necessary to evaluate the potential and efficacy of AOPs in this critical area of water resources recovery through wastewater treatment.

This study presents a state-of-the-art review focusing on the application of AOPs for pathogen elimination in effluents from conventional wastewater treatment methods. A special focus has been placed on evaluating the AOPs in terms of bacterial regrowth following treatment. A comprehensive analysis of existing literature over the past five years of research allowed the consolidation and synthesis of the latest available evidence, providing a clear and unbiased assessment of AOPs' effectiveness in pathogen removal. By merging data from multiple studies and applying rigorous statistical techniques, this review aimed to uncover prospective opportunities for current AOP studies by clarifying the true impact of AOPs on pathogens across diverse wastewater treatment scenarios.

The findings from this review can be beneficial in informing wastewater treatment practices to adopt more effective technologies, increasing regulatory focus on issues like persistent pathogens, and guiding future studies regarding wastewater standards and reuse alternatives. This review has offered insights into (i) pathogens of focus, (ii) types of AOPs, (iii) the effects of process parameters on pathogen reduction and regrowth, and (iv) challenges regarding the reuse of AOP-treated effluents for crop production. Additionally, it has highlighted stages where improvements or complementary treatments may be necessary to ensure pathogen-free effluents with zero regrowth. Ultimately, this review endeavors to serve as a significant step toward enhancing the safety and sustainability of wastewater treatment processes, safeguarding both public and environmental health.

# **2. Methodology**

The existing published material supporting the broad research question was organized using a systematic review technique. Five proposed stages were observed, including (i) identifying the research objective, (ii) search method, (iii) study choice, (iv) processing, and (iv) reporting findings [[51\]](#page-11-0).

#### *2.1. Research question(s)*

To ensure that the studies selected were relevant, rigorous, and aligned with the research objectives, the population, interventions, context, outcomes, and study design (**PICOS**) technique was used to establish the objective of the current study [[52\]](#page-11-0). The **"population"** was defined as wastewater pathogens (bacteria, viruses, protozoans, and helminths). The **"intervention"** compared the application and efficiency of different AOPs in the **"context"** of wastewater treatment. Pathogen reduction and regrowth were defined as the **"outcomes."** The **"research designs"** were classified as quantitative or hybrid (mixed qualitative and quantitative).

### *2.2. Sources of data and search strategy*

The search was conducted using both the Web of Science, including all its databases, and the Scopus databases. These databases were chosen to be comprehensive and cover all aspects of wastewater treatment. **"Title-Abstract-Keyword"** search was employed in Scopus while **"all fields"** for Web of Science databases. The review was confined to peer-reviewed publications published in English between January 1, 2018, and August 24, 2023. The time confinement enabled this study to retrieve all the most recent studies on advanced oxidation of wastewater. The search strategy included broad keywords to ensure no articles were left out (Table 1).

## *2.3. Citations management, screening, and eligibility criteria*

In the **"RIS"** format, the downloaded citations were exported into a group library in the Endnote [\(https://endnote.com/](https://endnote.com/downloads) [downloads](https://endnote.com/downloads)). With the help of **"find duplicates"** within the Endnote library, duplicates were detected and deleted. The remaining citations were then title-screened manually to eliminate irrelevant citations. The product of the Endnote screening was converted from **"**●**enlx"** to **"XML"** format, saved, and then exported to Covidence [\(www.covidence.org](http://www.covidence.org)), a web-based software where abstract screening, full-text screening, and data extraction of complete articles were performed [\[53](#page-11-0),[54\]](#page-11-0). Studies with **"Restricted Access"**  during full-text screening were requested through the University of KwaZulu Natal's library and later incorporated into the review process. Generally, studies were eligible for data extraction only if written in English, peer-reviewed, focused on pathogen reduction or regrowth in municipal wastewater, explicitly addressing the advanced oxidation processes, had quantitative data on pathogens, and were original research papers and not review articles. Related citations were then combined as a study with the help of the **"Merge as study"** icon in Covidence.

#### *2.4. Data classification, summary, and reporting*

The present review employed a quantitative-analytical technique in extracting data from the articles that met the inclusion criteria [\[55](#page-11-0)]. The extracted data from the reviewed studies included (a) the type of AOP used, (b) the AOP operating conditions (dosage, retention time, and temperature), (c) the number of pathogens eliminated or regrown after treatment, (d) the type of pathogen studied, (e) the treatment scale based on the reactor volume, (f) author, (g) DOI number, and (h) year of publication. The quantitative data in the graphs were extracted using the **"web plot digitizer"** ([https://automeris.io/WebPlotDigitizer\)](https://automeris.io/WebPlotDigitizer), a web-based tool for extracting data from plots, images, and maps. The extracted data were compiled in the **"data extraction template"** within the Covidence software, and then using the **"Export"** icon, it was sent into Microsoft Excel 2016.

### *2.5. Data standardization and presentation*

In the diverse nature of research, different scientists present their results in various ways. During data extraction in this review, it was observed that pathogen data were reported in CFU/100 mL, MPN/100 mL, CFU/mL, and MPN/mL, which made it difficult to compare the findings. All extracted data was then standardized into MPN/mL units to enhance suitable data comparison.

## **3. Results and discussions**

# *3.1. Summary of the identified studies*

Following the search criteria (Table 1), 98148 articles were identified, 28 in Scopus and 98120 in Web of Science. The **"find duplicates"** function in EndNote identified and eliminated 21 duplicates. The remaining 98127 articles were manually title-screened within the Endnote following the eligibility criteria in section (**2.3**). A total of 97926 articles didn't meet the eligibility criteria and were thus deemed irrelevant and excluded from the study. As a result, 201 articles were considered eligible for abstract and full-text screening and were exported to **"covidence" (**[www.covidence.org](http://www.covidence.org)**)**. Subsequently, 135 articles did not meet the abstract inclusion criteria, leaving only 66 articles for further screening. Only 17 of the 66 full-text screened articles fulfilled the inclusion criteria ([Fig. 1](#page-3-0)).

During data extraction, it was observed that many articles included multiple AOP studies, with each study treated independently during the review process. Thus, in total, 67 AOP studies were extracted from the 17 articles ([Table 2](#page-4-0)).

# *3.2. Characteristics of the included studies*

#### *3.2.1. Widely applied AOPs*

The analysis of the extracted literature revealed a predominant focus on three main AOP-based effluent treatments: ozone-based

## **Table 1**

Keyword-driven database search technique with Boolean operators.



<span id="page-3-0"></span>

**Fig. 1.** The flow chart summary of search results, screening, and study inclusion.

AOPs, photo-based (photolysis and photocatalysis) AOPs, and combined/hybrid AOPs. Among the 67 studies analyzed, 11 were identified as ozone-based AOPs, 20 focused on photolysis-based AOPs, and 21 delved into combined/hybrid AOPs, showcasing the extensive research attention directed toward these treatment methods. The remaining 15 studies, categorized as "other AOPs" ([Fig. 2](#page-4-0)), contained diverse AOP studies with low entries that could not be scientifically comparable. They included peroxidation, peroxyfenton, electrocoagulation, and iron-activated persulfate. These findings suggest that ozone-based, photo -based, and combined/hybrid AOPs

### <span id="page-4-0"></span>**Table 2**





**SE;** Studies extracted, **PY;** Publication year.





**Fig. 2.** Grouped data of the AOPs studied.

were explored more than the other AOPs. Their operational parameters, treatment mechanisms, and environmental impacts have been extensively studied in the past five years, making them suitable candidates for detailed analysis and comparisons. This level of scrutiny and research focus underscores the significance of these AOPs in contemporary wastewater treatment strategies, highlighting their potential for further advancements and optimization in sustainable effluent treatment practices.

#### *3.2.2. Pathogens commonly studied*

A comprehensive analysis of pathogen data revealed a total of 113 data points. *Escherichia coli* and total coliforms stood out with 35 and 60 data entries, respectively, indicating a significant emphasis on these pathogens. Additionally, *Enterococcus* spp was examined in 10 data points, with *Salmonella* spp and *Pseudomonas aeruginosa* scoring 2 entries each, suggesting less attention than *E. coli* and total coliforms. Notably, some pathogens were relatively under-studied, such as *S. enterica, S. aureus, E. faecalis,* and *Listeria monocytogenes*, each represented by a single entry in the data (Fig. 3). Only pathogens with large data entries above 10 (*E. coli* and total coliforms) were used in the study to draw unbiased comparisons.

The extensive focus on *E. coli* and total coliforms in wastewater management reflects their role as reliable indicators of fecal contamination and potential health risks [\[56,57](#page-11-0)]. These organisms are crucial markers for assessing the microbiological quality of effluents and the efficacy of wastewater treatment processes [[57,58](#page-11-0)]. Regulatory standards, such as those set by the United States of America's Environmental Protection Agency (USEPA), mandate limits on *E. coli* and *Total coliform* levels in treated wastewater, driving the need for thorough monitoring and compliance [59–[61\]](#page-11-0). Beyond regulatory requirements, the presence of these bacteria in untreated or inadequately treated wastewater poses notorious significant health concerns, including gastrointestinal illnesses and infections, necessitating comprehensive research and mitigation strategies [[62,63\]](#page-11-0).

## *3.2.3. Pathogen regrowth study*

Out of the 67 extracted datasets, only 3 studies provided additional information regarding the pathogen regrowth [\(Fig. 4](#page-6-0)). Pathogen removal in wastewater has often been done to meet discharge standards [\[64](#page-11-0),[65\]](#page-11-0). However, the increased demand for agricultural water and nutrients has recently resulted in treated effluents being considered for irrigation [[37\]](#page-11-0). In arid and semi-arid regions, storing surplus AOP-treated effluents can be ideal as a water management strategy. Because wastewater storage and reuse are gaining momentum [\[66](#page-11-0)], monitoring pathogen resurgence in stored AOP-treated effluents is advisable. This ensures the effectiveness and reliability of AOPs in eliminating pathogens from wastewater [\[31](#page-11-0)], which is important in safeguarding public health and environmental safety. Additionally, assessing regrowth potential provides insights into the stability and microbial dynamics of treated effluents during storage and distribution, helping to identify potential risks of pathogen resurgence in reclaimed water systems [\[67](#page-11-0)]. Moreover, it aids in developing targeted mitigation strategies and optimizing treatment processes to minimize health hazards associated with effluent reuse, particularly in agricultural irrigation, where exposure to pathogens can directly impact food safety and human health [\[31](#page-11-0),[68\]](#page-11-0).

#### *3.3. Scrutiny of the potential of studied AOPs in pathogen removal*

## *3.3.1. Ozone-based AOPs*

Ozone-based AOPs offer various mechanisms for pathogen elimination in wastewater treatment. Their ability to directly oxidize pathogens, generate ROS, and induce secondary reactions makes them valuable tools in ensuring water safety and meeting regulatory standards for microbial quality. [Table 3](#page-6-0) presents the potential of various ozone-based AOPs in reducing microbial contaminants (*E. coli*  and total coliforms). Among these processes, ozone combined with adsorption (Granular Activated Carbon) ( $O_3$ -GAC- $O_3$ ) at a dosage of 24.5 mg/L O3 with a retention time of 60 min showed moderate potential, reducing *E. coli* by 6.31E+03 MPN/mL and total coliforms by 6.17E+03 MPN/mL [\[69](#page-11-0)]. Another promising approach was  $O_3/H_2O_2/MnO_2$  treatment at 13 mg/L  $O_3$ , 50 mg/L MnO<sub>2</sub> and 10 mg/L



**Fig. 3.** Number of research studies extracted corresponding to pathogen species.

<span id="page-6-0"></span>

**Fig. 4.** Reported studies on pathogen reduction and regrowth information.

**Table 3**  Summary of the studied ozone-based AOPs on log reduction of pathogens (MPN/mL).

Ozone-based AOPs	Dosage	Retention time	Pathogens log reduction	
			E. coli	Total coliforms
$O_3$ -GAC- $O_3$	24.5 mg/L $O_3$	$60$ min	$6.31E + 03$	$6.17E + 03$
$O_3$	$13 \text{ mg/L O}_3$	$40$ min	$\overline{\phantom{a}}$	$1.95E + 05$
O <sub>3</sub>	13 mg/L $O_3$	$60$ min	$\qquad \qquad$	$6.17E + 04$
$O_3$	24.5 mg/L $O_3$	$26 \text{ min}$	$6.31E + 03$	$6.31E + 03$
$O_3/PMS$	13 mg/L $O_3$ , 3 mg/L PMS	$60$ min	$\overline{\phantom{a}}$	$1.00E + 05$
$O_3/PS$	13 mg/L $O_3$ , 1 mg/L PS	$60 \text{ min}$		$3.98E + 05$
$O_3/Fe_2O_3$	13 mg/L O <sub>3</sub> , 25 mg/L Fe <sub>2</sub> O <sub>3</sub>	$30 \text{ min}$	$\overline{\phantom{a}}$	$1.17E + 04$
$O_3/H_2O_2/Fe^{2+}$	13 mg/L O <sub>3</sub> + 10 mg/L Fe <sup>2+</sup> + 10 mg/L H <sub>2</sub> O <sub>2</sub>	$10$ min	$\overline{\phantom{a}}$	$3.98E + 04$
$O_3/H_2O_2/Fe_2O_3$	13 mg/L O <sub>3</sub> + 50 mg/L Fe <sub>2</sub> O <sub>3</sub> + 10 mg/L H <sub>2</sub> O <sub>2</sub>	$10 \text{ min}$	$\overline{\phantom{a}}$	$1.91E + 03$
$O_3/H_2O_2/MnO_2$	13 mg/L O <sub>3</sub> + 50 mg/L MnO <sub>2</sub> + 10 mg/L H <sub>2</sub> O <sub>2</sub>	$10 \text{ min}$		$8.13E + 04$

*GAC;* Granular activated carbon, *PMS;* Peroxymonosulphate, *PS;* Persulfate.

 $H_2O_2$  for 10 min, which significantly reduced total coliforms by 8.13E+04 MPN/mL. Notably, O<sub>3</sub>/peroxymonosulfate (PMS) signif-icantly reduced 1.00E+05 MPN/mL of total coliforms using a lower ozone dosage of 13 mg/L O<sub>3</sub> and 3 mg/L PMS over 60 min [[16\]](#page-10-0). Catalytic ozonation approaches, such as  $O_3/Fe^{2+}$ ,  $O_3/Fe_2O_3$ ,  $O_3/MnO_2$ , under different ozone dosages with varying retention times, also displayed varying degrees of efficacy in reducing microbial contaminants (Table 3).

Ozone  $(O_3)$  alone and  $O_3$  with catalysts exhibit differing potentials in reducing microbial contaminants.  $O_3$  alone, at a dosage of 13 mg/L over 40 min, significantly reduced microbial counts, with *E. coli* and total coliforms by 1.95E+05 MPN/mL and 6.17E+04 MPN/ mL, respectively [[16\]](#page-10-0). However, when ozone is combined with catalysts such as  $Fe^{2+}$ ,  $Fe_2O_3$ , or MnO<sub>2</sub>, varying degrees of improvement in microbial reduction are observed (Table 3). For instance,  $O_3/Fe^{2+}$  at a dosage of 13 mg/L  $O_3$  and 2.5 mg/L  $Fe^{2+}$  over 60 min reduced *E. coli* by 7.76E+03 MPN/mL, indicating a notable enhancement compared to O<sub>3</sub> alone [\[16](#page-10-0)]. Similarly, O<sub>3</sub>/Fe<sub>2</sub>O<sub>3</sub> at 13 mg/L O3 and 25 mg/L Fe2O3 over 30 min reduced *E. coli* by 1.17E+04 MPN/mL, showcasing a moderate improvement [\[16](#page-10-0)]. Additionally, O3/MnO2 at 13 mg/L O3 and 50 mg/L MnO2 dosage over 15 min exhibited the highest enhancement, reducing *E. coli* by 4.17E+04 MPN/mL, surpassing the efficacy of  $O_3$  alone [\[16](#page-10-0)].

Significant drawbacks have been noted, such as the potential formation of organic and inorganic by-products when certain catalysts are employed. Organic and inorganic by-products like aldehydes [[70\]](#page-12-0) and nitrates (NO<sub>3</sub><sup>-</sup>) [[71\]](#page-12-0), respectively, have been reported to be harmful to humans. In ozone combined with Fenton processes (O<sub>3</sub>/Fe<sup>2+</sup> or O<sub>3</sub>/Fe<sub>2</sub>O<sub>3</sub>), the presence of iron ions (Fe<sup>2+</sup>/Fe<sup>3+</sup>) or iron oxide as catalysts can lead to the formation of iron-based precipitates, necessitating additional filtration steps and potentially increasing operational complexities and costs [[72,73\]](#page-12-0). Additionally, the stability and longevity of catalysts such as  $Fe<sub>2</sub>O<sub>3</sub>$  and MnO<sub>2</sub> under continuous use need careful consideration, as degradation over time can impact the overall efficiency and performance of the AOP [[74,75\]](#page-12-0).

# *3.3.2. Photo-based AOPs*

Photolytic and photocatalytic AOPs are crucial in pathogen elimination within wastewater treatment contexts. Photolysis involves the breakdown of compounds induced by light, particularly ultraviolet (UV) radiation [[76\]](#page-12-0), whereas photocatalysis involves the use of catalysts alongside UV [\[77](#page-12-0)]. When applied in AOPs, photolysis can lead to the generation of reactive oxygen species (ROS), primarily hydroxyl radicals (•OH), which are highly effective in disinfecting water by damaging microbial structures and disrupting cellular functions [\[77,78](#page-12-0)].

[Table 4](#page-7-0) shows the evaluated photolytic and photocatalytic-based AOPs and their potential to reduce bacterial load in wastewater. Among the tested AOPs, solar/H<sub>2</sub>O<sub>2</sub> treatment at a dosage of 20 mg/L with a retention time of 20 min resulted in a reduction of *E. coli*  <span id="page-7-0"></span>by 5.01E+01 MPN/mL and total coliforms by 3.98E+01 MPN/mL. Conversely, a similar solar/H<sub>2</sub>O<sub>2</sub> treatment at 20 mg/L of H<sub>2</sub>O<sub>2</sub> with an extended retention time of 90 min reduced total coliforms by 1.00E+06 MPN/mL. Further experiments using solar-photo-Fenton processes demonstrated varying potentials. At 20 mg/L H<sub>2</sub>O<sub>2</sub> and 10 mg/L Fe<sup>2+</sup> within 10 min, reduced *E. coli* by 1.00E+01 MPN/mL and total coliforms by 3.98E+01 MPN/mL. Conversely, 20 mg/L H<sub>2</sub>O<sub>2</sub> and 1 mg/L Fe<sup>2+</sup> with a 60 min retention time significantly reduced total coliforms by 1.00E+06 MPN/mL.

Comparing the efficiency of various catalysts in photocatalytic-based AOPs in reducing bacterial contaminants revealed distinct performance variations. UV-C/H<sub>2</sub>O<sub>2</sub> and UV/Fe<sup>2+</sup> were the most efficient, significantly reducing *E.coli* and total coliforms within relatively short treatment periods (Table 4). UV-C/H<sub>2</sub>O<sub>2</sub>, notably, achieved reductions of approximately 7.24E+07 MPN/mL for total coliforms in just 20 min, showcasing a high potential in bacterial deactivation. In contrast, Solar/Fe<sup>2+</sup> with 1 mg/L Fe<sup>2+</sup> and UV/PS with 3 mmol/L PS exhibited comparatively lower potential, achieving moderate reductions within longer treatment durations.

The efficacy of photolytic and photocatalytic-based AOPs in pathogen elimination depends on several factors, such as the intensity and wavelength of the light source, the presence of catalysts, the duration of exposure, and pathogen type [[76,79](#page-12-0)]. UV light with wavelengths in the germicidal range (around 254 nm) showed the potential to inactivate pathogens by damaging their nucleic acids and proteins [[80\]](#page-12-0). Additionally, introducing photocatalysts can enhance ROS generation and extend the range of targetable pathogens [\[81](#page-12-0)], making photolytic and photocatalytic-based AOPs diverse tools for wastewater disinfection in various settings.

# *3.3.3. Combined AOPs (hybrid)*

Combined AOPs, also known as hybrid AOPs, offer a promising approach for pathogen elimination in water and wastewater treatment [[82,83](#page-12-0)]. These hybrid systems integrate multiple AOPs with other treatment methods to enhance the removal efficiency of pathogens [\[84](#page-12-0)]. Among the tested methods, UV-A/Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> treatment with 1 g/L Fe<sup>2+</sup> and 20 mg/L H<sub>2</sub>O<sub>2</sub> for 80 min reduced total coliforms by 6.61E+04 MPN/mL ([Table 5](#page-8-0)). These results highlight the potential of these hybrid AOPs in microbial disinfection, with varying capabilities based on the specific treatment parameters.

In contrast, some combinations showed limited potential against microbial contaminants. For instance, UV coupled to graphitic carbon nitride (GCN) and silver chromate (UV/GCN/Ag<sub>2</sub>CrO<sub>4</sub>) treatment with 1 mg Ag<sub>2</sub>CrO<sub>4</sub>/ml effluent for 60 min yielded negligible reductions in *E. coli* and total coliforms. Similarly, UV/MnO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> treatment at 50 mg/L MnO<sub>2</sub> and 10 mg/L H<sub>2</sub>O<sub>2</sub> for 10 min did not demonstrate significant microbial reduction [\(Table 5\)](#page-8-0).

The hybrid AOPs exhibited notable strengths and limitations. On the positive side, these methods demonstrate high efficacy in reducing bacterial contaminants like *E. coli* and total coliforms, with some processes achieving substantial reductions within relatively short treatment times [[16,](#page-10-0)[31,32](#page-11-0)[,85,86](#page-12-0)]. The diversity of AOP combinations allows for tailored approaches, providing versatility in addressing various water treatment challenges [\[16](#page-10-0),[84\]](#page-12-0). However, challenges such as cost implications due to expensive reagents or catalysts [[87\]](#page-12-0), complexity in implementation requiring specialized equipment and expertise [\[88](#page-12-0)], and potential formation of harmful by-products or residuals necessitate careful consideration when selecting and designing AOP-based treatment strategies.

# *3.4. Potential challenges in preventing regrowth in AOP-treated effluents*

Despite AOPs being powerful oxidants with strong antimicrobial properties in a wide range of pathogens, they face challenges in preventing pathogen regrowth in treated wastewater [[83,89\]](#page-12-0). Pathogens with adaptive mechanisms, such as those capable of

# **Table 4**





*PMS;* Peroxymonosulphate, *PS;* Persulfate.

#### <span id="page-8-0"></span>**Table 5**

Summary of the studied hybrid AOPs on log reduction of pathogens (MPN/mL).



*IDS;* Iminodisuccinic acid, *CAS;* Alumino-copper silicate, *GCN;* Graphitic carbon nitride.

upregulating stress response proteins like *E. coli* [[90\]](#page-12-0) and *Salmonella* spp [[91\]](#page-12-0), demonstrated increased resilience to photolytic and photocatalytic-based AOPs [\(Table 4](#page-7-0)) subsequently reducing the overall effectiveness of these processes [[92\]](#page-12-0). Spore-forming pathogens like *Listeria monocytogenes* showed resistance to ROS [\[93](#page-12-0)]. These pathogens can survive and proliferate in post-treated effluents due to their resistant structures and protective mechanisms [94–[96](#page-12-0)].

Moreover, AOPs can disrupt pathogen biofilms due to their oxidative effects [[97,98\]](#page-12-0). However, incomplete removal of disrupted biofilms can still occur, like in the case of photolytic and photocatalytic AOPs, contributing to regrowth risks [\[99](#page-12-0)]. During AOPs, such as peroxyfenton, peroxidation, and iron-activated persulfate, organic pollutants in wastewater are mineralized. As a result, some residual organic matter (ROM) was noted to remain after treatment, providing nutrients to surviving pathogens and leading to regrowth challenges [\[83,100,101\]](#page-12-0). Furthermore, the production of disinfection by-products (DBPs) by ozone-based AOPs, such as aldehydes [\[102\]](#page-12-0) and organic acids [\[103\]](#page-12-0) were noted. These DBPs are reported to have variable antimicrobial activity, potentially influencing microbial interactions and regrowth dynamics within treated effluents [\[26](#page-11-0)[,104\]](#page-12-0). Factors like temperature and pH influenced respective AOPs' efficacy in pathogen control and regrowth prevention [\[105,106](#page-12-0)].

## *3.5. Challenges associated with the reuse of AOP-treated effluents*

Recent AOP studies have focused extensively on optimizing catalysts to enhance treatment efficiency [[19](#page-10-0)[,31](#page-11-0)[,107\]](#page-12-0). However, the presence of persisting catalysts in AOP-treated effluents influences these treatment methods' efficacy, environmental impact, and reuse purposes [[108](#page-12-0)]. Catalysts like TiO<sub>2</sub> [[109](#page-12-0)], iron-based catalysts [\[96](#page-12-0)], metal-organic frameworks (MOFs) [[110](#page-12-0)], and carbon-based materials play a significant role in AOPs by promoting ROS generation and facilitating contaminant degradation [\[111\]](#page-12-0). Even after treatment, these catalysts can persist in the effluent, contributing to their continued reactivity upon reuse or discharge into the environment [[112](#page-12-0)].

TiO2 catalysts in photocatalytic AOPs persisted in the effluent and continued to exhibit photocatalytic activity, enabling the degradation of contaminants upon exposure to sunlight or UV radiation in natural water bodies [[113](#page-13-0)]. Similarly, iron-based catalysts used in Fenton reactions were reported to persist in the effluent, retaining their ability to generate hydroxyl radicals (•OH) under suitable conditions [\[114,115](#page-13-0)]. MOFs and carbon-based materials enhanced the persisting catalytic activity in treated effluents, offering sustained pollutant removal capabilities beyond the treatment facility [[116](#page-13-0),[117](#page-13-0)]. While these catalysts contribute to effective pollutant removal during treatment, their post-treatment presence highlights the importance of understanding their fate and potential impacts on receiving water bodies or upon reuse.

## *3.5.1. Concerns of AOP catalysts and by-products on crop production*

Recent research findings highlight the diverse effects of residual AOP catalysts on soil biota and nutrient cycling processes. However, their long-term effects on crop productivity have not been quantified [\[118\]](#page-13-0). Metal nanoparticles from photocatalysis-based AOPs, such as Zn and Fe, are reported to accumulate in the soil over time potentially impacting soil biota and nutrient cycling processes [\[119,120\]](#page-13-0). While some photocatalysts, like Zn, Fe, and Mn, contribute to nutrient accumulation and growth stimulation in plants, others, like Ag, facilitate the uptake of toxic elements or lead to residue accumulation in soil and plant tissues [[121](#page-13-0)]. Furthermore, the accumulation of Zn, Fe, and Mn in soils alters plant metabolism, influencing biochemical pathways and potentially causing oxidative stress [\[122](#page-13-0),[123](#page-13-0)].

The Advanced Oxidation Process (AOP) generates by-products like ROS and residual chemicals that can significantly impact crops when effluents treated with AOP are used for irrigation [\[124,125](#page-13-0)]. Reactive oxygen species such as superoxide radicals (O<sub>2</sub>), hydroxyl radicals ( $\bullet$ OH), and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) can cause phytotoxicity, affecting plant cell membranes and photosynthesis while also altering soil microbial populations crucial for nutrient cycling [126–[128\]](#page-13-0). Additionally, ROS generated during AOPs is linked to soil redox conditions, affecting the availability of nutrients like nitrogen and phosphorus for plant uptake [[129](#page-13-0)]. Persistent ozone-based AOP by-products, such as aldehydes and organic acids, may accumulate in soil or crop tissues, potentially affecting soil health and crop quality [[130](#page-13-0)]. Changes in soil pH due to AOP by-products are reported to influence nutrient availability and plant growth. Low-pH contents could lead to increased nitrifying bacteria's aluminium toxicity [[131](#page-13-0)], resulting in low nitrate-N release [\[132\]](#page-13-0). Additionally, research indicates that nitrogen and phosphorus levels tend to be lower when the pH is 5.5 or below [\[132,133\]](#page-13-0). Moreover, residual chemicals like chlorinated compounds pose risks of chemical contamination [[134,135\]](#page-13-0).

## *3.5.2. Potential human health concerns associated with AOP catalysts*

The current study reports the use of photocatalysts such as TiO<sub>2</sub>, iron (Fe<sup>2+</sup> and Fe<sup>3+</sup>), MnO<sub>2</sub>, and Ag in wastewater treatment [\(Table 3,](#page-6-0) [Tables 4, and Table 5\)](#page-7-0). While effective in treating contaminants in water, these photocatalysts can also introduce human health risks if not properly managed, especially in crop irrigation scenarios. Studies suggest that TiO<sub>2</sub> nanoparticles may cause adverse effects on human health upon inhalation or ingesting of significant quantities [[136](#page-13-0),[137](#page-13-0)]. Similarly, iron (Fe<sup>2+</sup> and Fe<sup>3+</sup>) and silver (Ag) ions can pose health risks if present in irrigation water in elevated concentrations. Iron ions, for instance, are essential micronutrients for plants and humans, but excessive intake can lead to micronutrient toxicity and gastrointestinal issues, respectively [\[138,139\]](#page-13-0). Silver ions, known for their antimicrobial properties, can cause argyria in humans if consumed in excessive quantities [\[140,141\]](#page-13-0). Therefore, supplying these photocatalysts in crop irrigation scenarios requires careful consideration to minimize potential human health effects [[142](#page-13-0)].

# **4. Future research directions**

While this state-of-the-art review assessed the extent and understanding of AOPs in reducing pathogens and potential regrowth, it also pinpoints potential gaps that need further investigation. Forming an assumption that a similar study with the same trends exists in all other languages apart from English, this study relied on peer-reviewed journals published in English. Subsequently, this may have excluded valuable insights from other sources, such as the grey literature (project reports, academic theses, and conference proceedings) and articles published in other languages. Even though peer-reviewed articles are regarded as an assurance of quality [[143](#page-13-0), [144](#page-13-0)], future studies could consider and incorporate relevant information from a broader range of sources and databases, including wider selection criteria besides peer-reviewed journals in English only.

In the current study, only 3 out of 67 datasets have information on understanding the crucial aspect of pathogen regrowth dynamics [\(Fig. 4\)](#page-6-0). Future studies focused on the simultaneous reduction of organics alongside pathogens are needed to optimize the efficacy of AOPs. This could be achieved by adjusting AOP parameters or integrating them into complementary treatment processes like the decentralized wastewater treatment systems (DEWATS) with reduced organic levels as a post-treatment procedure [[69\]](#page-11-0). Experimental studies focusing on these aspects can yield valuable insights into optimizing AOP performance, especially in scenarios with varying organic loads commonly found in wastewater effluents.

The present study has revealed the resistivity of *E.coli* in a wide range of the AOPs studied. In some studies, *E.coli* was reduced, although with incomplete elimination [[19,](#page-10-0)[69,](#page-11-0)[91\]](#page-12-0). In future studies, *E.coli,* which is hard to remove, should be prioritized to achieve the required limits for agricultural reuse.

While the present study shows the varied potential reduction of pathogens by these AOPs, a clear trend pointing to the best AOP offering complete pathogen degradation and regrowth elimination is lacking. Therefore, a study is needed to simultaneously compare the efficacy of ozone-based AOPs, photolysis, photocatalytic-based AOPs, and hybrid AOPs in complete pathogen oxidation and eliminating the pathogen regrowth potential in the treated effluents.

Since there is a pressing need for well-treated effluents in agriculture [\[42](#page-11-0)], a notable research gap exists regarding the potential bioaccumulation effects of catalysts used in AOP-treated effluents for crop production [[8](#page-10-0)]. A comprehensive assessment of the impacts of AOP-treated effluents on agricultural systems is essential to determine potential risks such as bioaccumulation of catalysts in edible plant tissues, changes in soil biota composition, and alterations in nutrient mineralization processes. Moreover, a model study is required to quantify the long-term effects of the metal nanoparticles used in photocatalytic AOPs on soil health. Investigating these aspects will address the immediate concerns of human health risks associated with bioaccumulation and provide a more holistic understanding of the implications of AOPs in wastewater treatment and their integration into sustainable agricultural practices.

## **5. Conclusions**

Pathogen reduction and eliminating regrowth in wastewater are crucial for meeting stringent agricultural reuse standards. Only a few studies highlighted pathogen regrowth in AOP-treated effluents, underscoring the need for further investigation. High organic content hindered complete pathogen reduction and promoted regrowth by providing nutrients to surviving pathogens. By-products from AOP treatment, such as catalysts, reactive oxygen species (ROS), and aldehydes, have raised concerns about environmental and human health risks in wastewater reuse. These by-products can impact soil organisms, nutrient cycling, and plant metabolism in <span id="page-10-0"></span>agriculture. Upon accumulation in crop produce, these by-products, such as catalysts, could pose risks to human health when ingested as food. Addressing these gaps (pathogen regrowth, by-product formation, and their impacts on crop, soil, and human health risks) can make AOP-treated effluents valuable for crop production. In a circular economy framework, recovering water and nutrients from wastewater for agricultural use is crucial for sustainable resource management.

# **CRediT authorship contribution statement**

**Barnabas Oluoch:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Takudzwa Mandizvo:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Methodology, Formal analysis, Data curation. **William Musazura:** Writing – review & editing, Visualization, Validation, Supervision, Data curation, Conceptualization. **Taruvinga Badza:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Methodology, Formal analysis, Data curation. **Benton Otieno:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Stephen Ojwach:** Writing – review & editing, Visualization, Validation, Supervision, Software, Resources, Project administration, Funding acquisition, Data curation, Conceptualization. **Alfred Odindo:** Writing – review & editing, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization.

# **Data availability statement**

Data will be made available on request.

# **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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