**Universidade de Aveiro**
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# Avaliação ecotoxicológica de efluentes industriais tratados por ativação do persulfato usando nanoparticulas de CuO

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Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestre em Eco-toxicologia e Análise de Risco, realizada sob a orientação científica do Doutora Isabel Maria Cunha Antunes Lopes, investigadora principal do CESAM (Centro de Estudos do Ambiente e Mar) e do Departamento de Biologia da Universidade de Aveiro, Portugal, e do Doutor Mohammadreza Kamali do Departamento de Engenharia Química da Universidade Católica de Leuven, Bélgica.

To my family: **Rita and Alireza, and Peyman**

**o júri**

| | |
|---|---|
| presidente | Prof. Doutor Carlos Miguel Miguez Barroso<br>Professor Auxiliar, Universidade de Aveiro |
| Arguente | Doutora Cátia Alexandra Ribeiro Venâncio<br>Investigadora Principal, Universidade de Coimbra |
| Orientadora | Doutora Isabel Maria Cunha Antunes Lopes<br>Investigadora Principal em Regime Laboral, Universidade de Aveiro |

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**palavras-chave**

texto livro, arquitectura, história, construção, materiais de construção, saber tradicional.

**resumo**

As águas residuais oriundas das atividades industriais podem causar elevada toxicidade para o biota que habita os compartimentos ambientais recetoras dessas águas. Deste modo, são necessárias tecnologias de tratamento de águas residuais que sejam eficientes de modo a: a) removerem os contaminants e b) permitirem a sua a conversão em recursos hídricos de boa qualidade. Neste contexto, o objetivo principal da presente tese foi avaliar a eficiência de processos de oxidação avançada (POA) no tratamento de efluentes industriais. Para atingir este objetivo principal, primeiro foi realizado um estudo cienciométrico para identificar as principais lacunas de conhecimento no que respeita a aplicação de vários POA, nomeadamente no que se refere à: a) otimização dos POA para o tratamento de compostos orgânicos recalcitrantes, e b) necessidade da caracterização ecotoxicológica após o tratamento do efluente e garantir a boa qualidade dos efluentes tratados. Em segundo lugar, avaliou-se a eficiência de um POA, pela ativação de persulfato (PS) utilizando nanomateriais de CuO, no tratamento de um efluente artificial (com 50 mg/L de Rodamina B). Para tal, foram testados diferentes tipos de tratamentos num efluente artificial feito em água destilada. Os resultados obtidos identificaram o tratamento que consistiu na aplicação de 0,5 g/L de CuO e 5 mM de PS como o que apresentou maior eficácia na remoção da RhB (100%) após 120 minutos de reação. As condições de tratamento mencionadas foram então aplicadas ao efluente artificial realizado em meio ASTM (um meio artificial que simula água doce; [RhB] 0 = 50 mg/L). Foi observado um decréscimo na eficiência de remoção de RhB para 29% após 30 min e 57% após 60 min de reação, possivelmente devido à complexidade do meio. Assim, a integração da ativação catalítica e térmica foi adotada sob a mesma condição experimental, mas com uma temperatura elevada até 45 °C. Como resultado, a degradação completa de RhB foi observada dentro de 60 min de reação. A toxicidade letal do efluente artificial foi avaliada, antes e após o tratamento POA, para *Daphnia magna*. A toxicidade de CuO e PS também foi avaliada. Os resultados indicaram que o efluente tratado ainda era altamente tóxico para *D. magna* e que o PS foi provavelmente a principal causa dessa alta toxicidade. No seguimento destes resultados, foi realizado um conjunto complementar de experiências em que o efluente artificial foi tratado nas mesmas condições, exceto no que respeita À concentração de PS utilizada que foi de 1mM. Após 60 min do tempo de reação, foi observada degradação completa de RhB. A toxicidade letal do efluente, antes e após o tratamento POA, foi então avaliada para o rotífero *Brachionus calyciflorus*, expondo este organismo a diluições em série dos dois efluentes (6,25%, 12,5%, 25%, 50%, 100%). A concentração letal média do efluente antes do tratamento foi de 44,3%, enquanto para o efluente tratado foi de 8,24%, sugerindo uma toxicidade letal muito maior do efluente tratado. É colocada a hipótese de que esta toxicidade elevada é devida ao PS, uma vez que *D. magna* e *B. calyciflorus* expostos apenas a este composto apresentaram mortalidade de 100%. Mais ainda, a formação de compostos intermédios durante o tratamento POA, pode também ter contribuído para o aumento da toxicidade do efluente tratado. De forma geral, os resultados obtidos sugerem que outros compostos oxidantes devem ser considerados para serem utilizados em POA para tratamento de efluentes de águas residuais, bem como as concentrações de CuO devem ser ajustadas ou a remoção destas nanopartículas e iões metálicos deve ser melhorada de forma a permitir a obtenção um efluente tratado que não apresente ou apresente baixa toxicidade para o biota.

**keywords**

Wastewater treatment, Ecotoxicity, Advanced Oxidation Processes, Rhodamine B, Cladocera, Rotifers.

**abstract**

Wastewaters originated from industrial activities can cause severe toxic effects to the biota inhabiting the receiving environment. Hence, there is a need for efficient treatment technologies to a) removing the contaminants, and b) providing good quality water resources. In this context, the present thesis main goal is to assess the efficiency of advanced oxidation process (AOP) in the treatment of industrial effluents. To attain this main goal, first a scientometric study was performed to identify the main gaps in the application of various AOps, namely regarding a) optimization of AOPs for the treatment of recalcitrant organic compounds, and b) the need for ecotoxicity characterization after effluent treatment to ensure the good quality of the final treated effluents. Secondly, the efficiency of an AOP, by the activation of persulfate (PS) using CuO nanomaterials, in the treatment of an artificial effluent (with 50 mg/L Rhodamine B) was assessed. For this, different treatment designs were tested in the artificial effluent done in distilled water. The obtained results identified the treatment using 0.5 g/L of CuO, 5 mM of PS to exhibit the highest the effectiveness as it removed 100% of RhB after 120 minutes of reaction. The mentioned treatment conditions were then applied to the artificial effluent performed in ASTM medium (an artificial medium simulating freshwater; [RhB]0=50 mg/L). A drop was observed in RhB removal efficiency to 29% after 30 min, and 57% after 60 min due to the complexity of the medium. Hence, integration of catalytic and thermal activation was adopted under the same experimental condition but with an elevated temperature to 45 °C. As a result, complete degradation of RhB was observed within 60 min of reaction. The lethal toxicity of the artificial effluent to Daphnia magna was assessed before and after the AOP treatment. The toxicity of CuO and PS was also assessed. The results indicated that the treated effluent was still highly toxic to D. magna and that PS was probably the main cause for such high toxicity. Following these results, a complementary set of experiments was performed by treating the effluent with the same conditions except for the PS concentration used that was reduced to 1 mM. After 60 min of the reaction time, complete degradation of RhB was observed. The lethal toxicity of the effluent before and after the AOP treatment was then assessed for the rotifer Brachionus calyciflorus, by exposing these organisms to serial dilutions of the effluents (6.25%, 12.5%, 25%, 50%, 100%). The median lethal concentration of the effluent before treatment was 44.3% while that for the treated effluent was 8.24%, suggesting a much higher lethal toxicity of the treated effluent. It is hypothesised that such high toxicity is due to the PS, since both D. magna and B. calyciflorus exposed to this chemical alone showed 100% mortality. Adding to this, the formation of intermediate compounds during the AOP treatment, may have also contributed to the increased toxicity of the treated effluent. Overall, the obtained results suggested that other oxidant compounds should be considered to be used in AOPs to treat (waste)water effluents, as well the concentrations of CuO must be adjusted or the removal of these nanoparticles and metallic ions should be improved to allow obtaining a treated effluent with no to low environmental toxicity.

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## Table of Acronyms

| | |
|---|---|
| **AOXs** | Adsorbable Organic Halides |
| **AOPs** | Advanced Oxidation Processes |
| **ASTM** | American Society of Testing and Materials |
| **AT** | After Treatment |
| **BET** | Brunauer, Emmett, Teller |
| **BT** | Before Treatment |
| **CECs** | Contaminants of Emerging Concern |
| **COD** | Chemical Oxygen Demand |
| **CPS** | Concentrating Solar Power |
| **ENMs** | Engineered Nanomaterials |
| **EC** | Effective Concentration |
| **$H_2O_2$** | Hydrogen Peroxide |
| **JCPDS** | Joint Committee on Powder Diffraction Standards |
| **LC** | Lethanl Concentration |
| **nZVI** | Nano Zero Valent Iron |
| **PMS** | Proximonsulfate |
| **PS** | Persulfate |
| **RhB** | Rhodamine B |
| **ROS** | Reactive Oxygen Species |
| **SEM** | Scanning Electron Microscope |
| **TOC** | Total Organic Carbon |

| | |
|---|---|
| **UI** | Ultrasonic Irradiation |
| **UV** | Ultraviolet |
| **WoS** | Web of Science |

# Chapter 1. General Introduction

Contamination of the water resources (i.e., surface and underground) is currently among the most challenging environmental issues in many countries all over the world which has resulted in the scarcity of clean water resources. In addition, wastewaters contaminated with various organic and inorganic compounds can bring severe toxic effects to the living organisms in the receiving environments [1,2].

Water contamination can be originated from natural and anthropogenic sources. Industrial activities, as the main source of the anthropogenic contaminants, are responsible for the release of chemical compounds of various types (i.e., organic and inorganic) and hence generating highly contaminated effluents [3,4]. Dyes are among the complex organic contaminants appearing in the content of various industries, especially textile and pulp and paper production processes [5,6]. They can cause lethal and sublethal toxicity for the living organisms at quite low and environmentally relevant concentrations (e.g., de Jesus Azevedo et al., (2021), and Skjolding et al., (2021). Also, they create intense colours in the water bodies, which can limit the light penetration into the water bodies. As a consequence, the primary production can be limited resulting in oligotrophic conditions [9–11].

Treatment of the contaminated waters by removing the organic and inorganic chemical compounds can be considered as an effective way to recover the water resources and to reduce its toxicity to the environment. In this regards, various biological and physico-chemical treatment technologies have been developed and implemented to deal with the generated effluents from various origins. Biological methods mainly activated sludge is the mostly used in various industries [12]. Anaerobic digestion is also another method for the treatment of industrial effluents which result in the production of biogas (mainly methane) from the decomposition of organic compounds. Several studies have indicated the treated effluents have

high qualities to recover and reuse in applications such as agriculture [13]. However, most of the biological treatment technologies are not able to degrade the complex and recalcitrant organic compounds present in the discharged industrial effluents.

Physical treatments (e.g., adsorption) has been already considered a way to remove chemicals from the contaminated waters. There have been various types of adsorbents such as activated carbon and clay-based materials have been used to this end [14]. There have been recent trends in the literature for the application of low-cost and sustainable materials such as waste-derived carbonaceous adsorbents (e.g., biochar) for the adsorption of various types of contaminants [15]. However, the main issue in the application of adsorption techniques is that the contaminants are only transferred from the liquid phase into the solid phase, which requires further treatments. In addition, physical barriers such as membrane technologies are yet suffering from the technical issues (such as fouling) and costs associated with the need for periodic cleaning and replacing the membrane.

To address this issue, chemical-based methods have been rapidly developed in recent decades to degrade the (mainly organic) contaminants [16,17].

However, most of the conventional treatment technologies such as coagulation and flocculation and ozonation are still expensive and not efficient enough to deal with the complicated organic molecules present in the composition of several industrial effluents. Hence, the development of more efficient and cost-effective methods has become a trend among the scientific community.

Advanced oxidation processes (AOPs) are among the most popular chemical treatment techniques for the treatment of industrial and non-industrial effluents. The basis of these methods is on the generation of powerful oxidative agents (such as radicals) with an extremely short lifetime to attack and decompose the organic contaminants. One of the most advantageous features of oxidation agents is that they are generally not selective and hence they can degrade a wide range of organic contaminants efficiently.

Various conventional types of AOP-based technologies such as ozone-based technologies have been studied so far widely. More recently, photocatalytic degradation of contaminants has been also received attention for the treatment of

contaminated (waste)waters. Figure 1.1 shows a typical mechanism of the photocatalytic degradation of contaminants, which is based on the excitation of the electrons from the valence band of the semiconductors as a result of being irradiated. Such electrons are responsible for the generation of powerful oxidation agents.

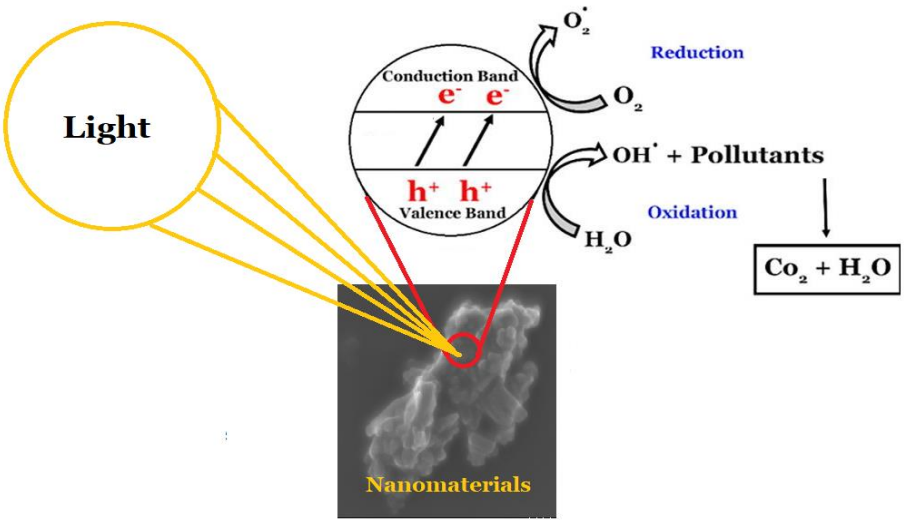


**Fig.1.1.** A schematic of the photocatalytic degradation of organic contaminants using nanomaterial semiconductors, adopted from [18].

In terms of sustainability considerations, there are difficulties in providing UV light or solar irradiation especially since the intensity of UV light in solar irradiation is very limited. Hence, there has been a trend in the literature to develop nanomaterials that can absorb visible light such as by creating oxygen vacancies to the structure of nanomaterials. This can be for instance done by doing some elements such as C or N to the crystalline structure of $TiO_2$ or ZnO which can ultimately aid to adsorb more visible light. However, by manipulation of the synthesis method to adsorb visible light, the costs of the synthesis increases which can adversely affect the commercialization rate of these materials [19–21].

To address the existing issues, the application of various oxidants such as hydrogen peroxide, persulfate (PS), proximonsulfate (PMS), chlorine, and iodine has been considered. However, in many cases, especially for the highly contaminated effluents laden with complex organic compounds, oxidants alone are

not able to provide efficient and fast degradation kinetics. For instance, the textile industry, as one of the essential industries, uses high quantities of dyes and auxiliaries. Azo dyes (as the largest class (60–70%) of dyes can cause severe environmental and toxicological issues [22]. Also, the effluents containing dyes have typically a high level of chemical oxygen demand (COD) which can limit the dissolved oxygen in the medium. Also, they can hinder the penetration of light into the aquatic medium and can reduce the primary production of the aquatic ecosystems [23,24].

Hence, some methods have been proposed for the activation of the oxidants to produce powerful oxidation agents such as radicals and singlet oxygen. In this regards, various methods such as thermal and application of catalysts have been adopted for the activation of oxidants to enhance the rate of the radical generation [25–27]. Such AOPs have indicated acceptable performance to deal with a wide range of organic contaminants such as organic dyes [28,29].

However, there are still sustainability concerns for the application of such technologies for real-scale applications, mainly including efficiency, cost-effectiveness as well as the toxic nature of the final treated effluents. Hence, the current trend in the literature is to identify cost-effective activation methods for oxidation agents.

According to a very recent study, the number of studies on the effects of state-of-the-art treatment technologies on the toxicity removal from the treated effluents is still very rare in the literature [30]. The ecotoxicity removal efficiency of these treatments may be addressed through a panoply of ecotoxicological assays, involving species from different trophic and functional levels. Some of the freshwater model species that are commonly used in these ecotoxicity assays include the planktonic primary consumers *Daphnia magna* and *Brachionus calyciflorus* (Fig. 1.2) [8,20,21]. These are standardized species that exhibit high sensitivity to chemical contamination. Furthermore, the standard short-duration assays available for these species allow a fast and cost-effective assessment of the ecotoxicity of efluents and chemicals.

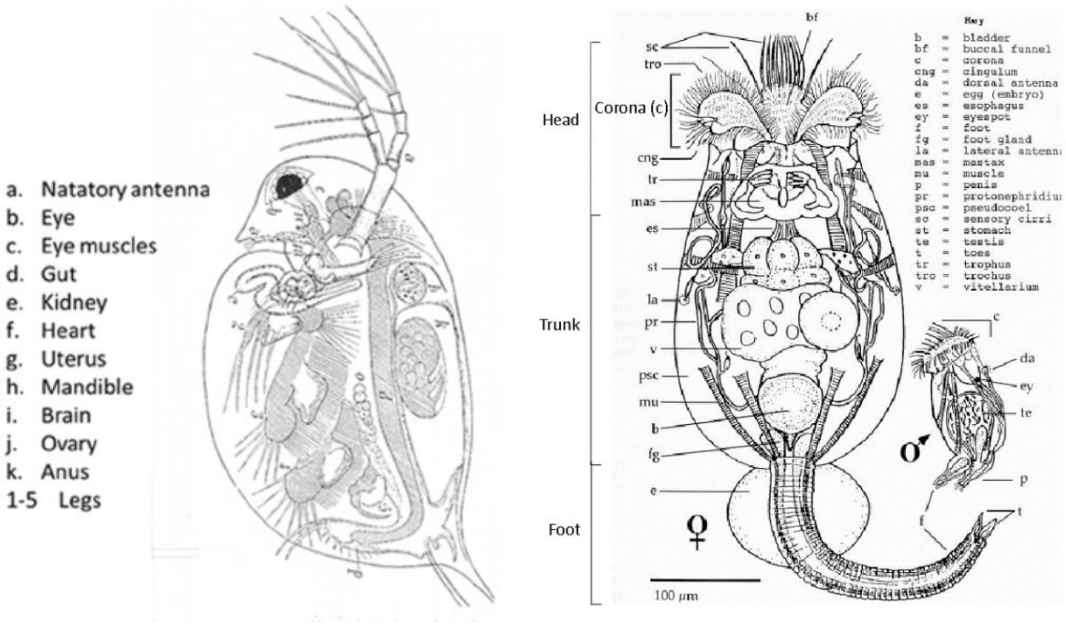


**Fig. 1. 2.** *D. magna* (left) [31], rotifer (right) [32].

To address the mentioned research gaps, the present study has aimed to answer the following research questions (SQs):

- What is the state-of-the-art situation of the knowledge in the treatment of industrial effluents, and what are the existing scientific gaps?

- Can engineered nanomaterials (ENMs) with a homogeneous shape and high specific surface area be prepared using facile and green methods such as ultrasonic irradiation?

- Can advanced oxidation processes using the engineered nanomaterials (CuO) and oxidation agents (persulfate) be efficiently used for the treatment of industrial effluents?

- To what extent the applied advanced oxidation processes can decrease the toxicity of the industrial effluents?

To answer the mentioned SQs, a scientometric assessment has been performed (please see chapter 2) on the technologies that have been used so far for the treatment of (waste)waters to identify the progress that has been made in this field, to identify the position of the toxicity studies, and to propose the future studies to fill the existing gaps.

The scientometric assessment has been followed by an experimental study involving the synthesis of homogeneously dispersed CuO nanomaterials using an ultrasonic-assisted synthesis method for the activation of PS towards the degradation of Rhodamine B from the synthetic effluents(please see chapter 3). In addition, thermal activation of PS, as well as CuO catalytic-thermal combined activation of PS was explored and compared to the sole activation methods applied. Finally, the acute toxicity of the effluents before and after treatment with the applied technologies was studied using *D. magna* and rotifers the indicator microorganisms.

# Chapter 2. Engineered Nanomaterials for (Waste)Water Treatment - A Scientometric Assessment and Sustainability Aspects

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## Abstract

Application of nanomaterials for the treatment of effluents originated from various industrial and non-industrial sources, has been rapidly developed in recent decades. In this situation, there is a need for conclusive studies to identify the current status of the knowledge in this field and to promote the commercialization of such technologies by providing recommendations for future studies. In the present manuscript, a scientometric assessment on the progress made in this field has been performed and the results have been organized and discussed in terms of science statistics, research hotspots and trends, as well as the relevant sustainability aspects. Based on a set of keywords, identified through a pre-literature analysis, a total of 6539 documents were retrieved from the Web of Science (WoS) database and analyzed to achieve the main goals of this study. The results demonstrate that the studies in this field have been initiated since the beginning of the 2000s but were mainly performed in lab and pilot scales. Also, China and Iran were identified as the most contributing countries in this scientific area in terms of the number of publications. Among various types of engineered nanomaterials (ENMs), there has been especial attention for the application of iron-based nanomaterials as well as carbonaceous structures (such as graphene oxide and biochar). Besides, there are not still strong collaborations formed among researchers in this area worldwide. Regarding the research hotspots, the synthesis of green and sustainable nanomaterials (e.g., biosynthesis approaches) has received attention in recent years. The results can also demonstrate that the most widely studied pathway for the removal of pollutants from (waste)waters

involves the adsorption of the pollutants using ENMs. Treatment of contaminants of emerging concern (CECs) as well as exploring the mechanisms involved in the treatment of contaminated (waste)waters using ENMs and the possible by-products are considered the current trends in the literature. Regarding the sustainability aspects of ENMs for (waste)water treatment, the results achieved in this study calls for in-depth sustainability studies, which consider parameters such as economic, environmental, and social aspects of nanomaterials utilization for (waste)water treatment purposes, besides the technical parameters, to push transferring such technologies from lab and pilot scales to large and real-scale applications.

## 2.1. Introduction

Currently, there are a number of industries all over the world such as textile [33,34], pulp and paper [35–37], oil and gas [38], and pharmaceutical [39,40] which generally consume huge amounts of water and consequently produce highly contaminated effluents [41]. Such effluents are normally laden with relatively high concentrations of organic and inorganic contaminants, which, if the effluent is not efficiently treated, are released into the aquatic environment where can pose adverse effects to the biota [1,42,43]. Hence, various studies have been carried out so far to find out the applicable alternatives to deal with such contaminated effluents [17,44]. The technologies which have been developed so far in this regard can be simply divided into biological and physico-chemical treatment technologies [45]. Biological methods such as activated sludge [46–48], anaerobic digestion [49–52], fungal treatment [53,54], lagoons [55], constructed wetlands [56], among others, can be considered as the conventional technologies for the water recovery and to overcome the secrecy of the clean water resources. Despite the rapid development of biological treatment technologies, they normally fail to degrade recalcitrant and organic compounds of emerging concerns such as adsorbable organic halides (AOXs) which can be found in the content of various industrial effluents [57]. This is mainly due to the toxic effects that such compounds cause to the microbial communities which are responsible for the

degradation of organic compounds [58]. To address this issue, various physical and chemical technologies have been developed rapidly in recent years to deal with such compounds. In this regard, physical methods such as ultrasonic irradiation (UI) [59,60], ultraviolet (UV) irradiation [61], membrane-based technologies [62–64] have been developed and adopted mainly in lab and pilot scales. However, the degradation kinetics when UI or UV are applied is relatively low, which can limit their popularity for real applications. Also, physical barriers such as membranes can produce secondary wastes besides the relatively high treatment costs due to the need for periodic replacement of the membrane as a result of membrane fouling [65,66]. In such conditions, AOPs [67,68] such as Fenton-based processes [36,69], catalytic oxidation or adsorption with nanomaterials [27], electrochemical degradations [70,71], and ozone-based treatments [72,73] have been developed significantly in recent years. In this regard, the application of nanomaterials can create opportunities for the efficient treatment of highly contaminated effluents [74]. Kamali et al. [17] studied the sustainability criteria of industrial wastewater treatment technologies using ENMs. They concluded that ENMs can offer high treatment efficiencies although there are some concerns about the probable subsequent environmental and toxic effects when they are released into the environment [75–77]. They also stated that there is a need to identify the most appropriate types of ENMs and the respective operating conditions to be able to use those ENMs for real-scale applications. To this end, the present study has aimed to perform a conclusive study on the efforts that have been performed so far for the application of ENMs for (waste)water treatment and to recommend further studies to accelerate the development of sustainable technologies for full-scale applications.

## 2.2. Methodology

The present scientometric study on the application of ENMs for (waste)water treatment was initiated by retrieving the related documents from the Web of Science (WoS) Core Collection database. To this end, a primary literature review was carried out in order to identify the most important keywords and to design the

most appropriate combination of keywords used in the relevant studies published in the literature [78–81]. As indicated in Table 2.1, the keywords related to the treatment of (waste)waters (# 1 and # 2) and those to ensure the relevancy of the results to the application of ENMs (# 3) were the subjects of an advanced search in the WoS database. Various morphologies of ENMs were included in the study by considering the relevant keywords identified based on the valid classifications already presented in the literature [82–85]. It was tried to consider all the relevant publications and hence no specific period was considered for the publications in this field. Then, the results were combined using AND operator (# 4) to identify the published documents in this field. The retrieved documents were also screened to ensure the relevancy and reliability of the documents retrieved for the subsequent analysis. The screened data were added to the marked list in WoS and then exported with the required formats to be entered to the utilized tools, i.e., Scientopy and CiteSpace. In addition to the mentioned tools, some data such as publication year was directly extracted from WoS without any further processing.

**Table 2. 1.** Combination of the keywords used to retrieve the documents published in WoS on the applications of engineered nanomaterials for (waste)water treatment.

| Set | Keywords | Results |
|---|---|---|
| # 1 | TI=(treat* or removal or degrad* or adsor* or absor* or elimin* or puri* or desali n* or *decontamin*) | 2,685,793 |
| # 2 | TI=(*water* or Aqu* or synthetic or effluent* or solution) | 1,985,160 |
| # 3 | TI=(*nanoparticl* or *nanomaterial* or *nanostructure* or nanotechnolog* or quantum dot* or heterogeneous particle array* or hollow spher* or nanolens* or nanowire* or nanoribbon* or nanorod* or nanobelt* or nanosheet* or nanoleav* or nanoflower* or nanotube* or *nano particl* or *nano material* or *nano structure* or nano technolog* or nano lens* or nano wire* or nano ribbon* or nano rod* or nano belt* or nano sheet* or nano leav* or nano flower* nano tube* or *nano-particl* or *nano-material* or *nano-structure* or nano-technolog* or nano-lens* or nano-wire* or nano-ribbon* or nano-rod* or nano-belt* or nano-sheet* or nano-leav* or nano-flower* or nano-tube*) | 684,580 |
| # 4 | #1 AND #2 AND #3 | 6,539 |

The created marked list was exported with “csv” format for further analysis using the ScientoPy tool. Various scientometric parameters were analyzed using this tool including documents, contributions, trends, and sources. Citespace (5.7.R1) was also utilized for further analysis of the data exported from the created

marked list (with “txt” format) regarding the citations received by authors and journals. Variables such as betweenness centrality (see [80]) were used to obtain the scientometric results in the present study.

## 2.3. Results and discussion

Towards a systematic analysis of the publications on the application of ENMs for (waste)water treatment, scientometric parameters were organized in two main categories including a) science history, and b) Research hotspots and trends.

### 2.3.1. Research Statistics

#### 2.3.1.1. Publications

A total of 6539 documents published on the application of ENMs for the treatment of (waste)waters (initiated since 1995) were screened and analyzed in the present study. According to Fig. 2.1, a rapid increase in the relevant publications in the literate can be observed after the 2000s where the number of published documents has considerably increased from 3 documents published in 2000 to more than 900 in 2019. Although at the time of preparation of the present manuscript (September 2020), it was not possible to include all the publications of 2020, it also can be expected to reach a higher number of publications in this year compared to 2019. Such a high number of published documents in the literature, especially research papers (87% of all the documents published, see the supplementary information, Fig. A-1), can clearly demonstrate the huge and increasing attention and investments on this subject among the scientific community [86].

An advanced search was also performed in WoS to identify the studies carried out so far in the literature on the large-scale treatment of contaminated (waste)waters using ENMs. The results indicate that although there are some reports on the large-scale production of ENMs such as Ag-ZnO [87], indium-based infinite coordination polymer hierarchical nanostructures [88], and Sn−$SnO_2$ nanoparticles [89] for (waste)water treatment, the studies on the real-scale

treatment of (waste)waters using the large-scale produced ENMs are rare in the literature. Hence, it can be stated that the current efforts in this field are focused on the a) identification of the most sustainable ENMs for (waste)water treatment [90], b) large-scale production of the most effective ENMs to be used for (waste)water treatment, and c) addressing the existing challenges and knowledge gap to promote the commercialization of ENMs for (waste)water treatment applications [91–93].

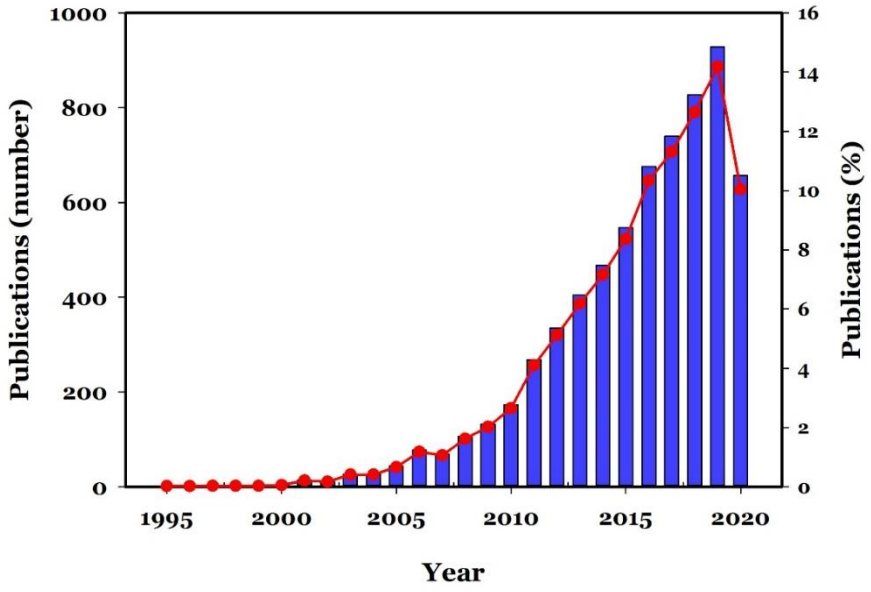


**Fig. 2. 1.** Published documents on the application of ENMs for (waste)water treatment; including the number (blue) and percentage (red) of the publications in each individual year to all the papers published on this subject. It has to be mentioned that the data presented in this figure includes the publications until the 10th of September 2020. WoS was utilized to retrieve the achieved data.

### 2.3.1.2. Contributors

This sub-section has aimed to discuss the contribution of the countries, authors, sources, and organizations in the publications related to the application of ENMs for (waste)water treatment. According to figure 2.2, China, Iran, and India have already published the highest number of scientific documents in this regard.

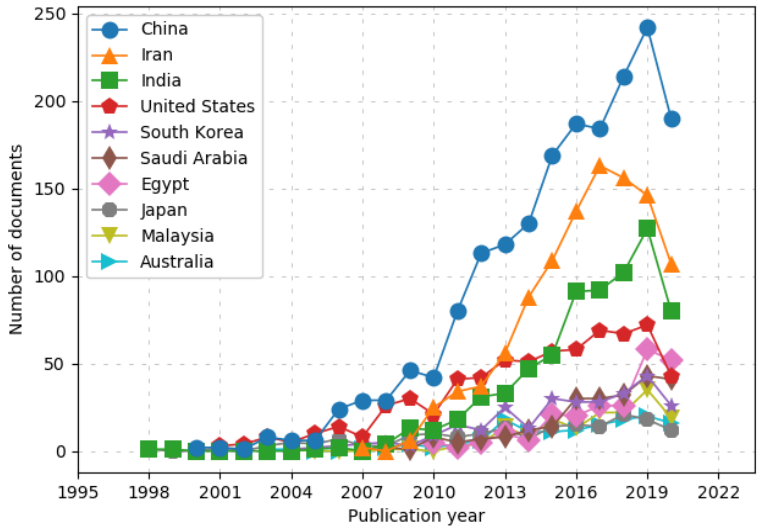


**Fig. 2. 2.** Contribution of various countries for the publication of scientific documents on the application of ENMs for (waste)water treatment. Scientopy was utilized to analyze the data achieved from WoS. The contribution of various organizations of these countries has been presented in supplementary information (Fig. A.1).

Among the authors, Liu, Y. [94], Li, Y. [95], and Wang, Y. [96] share the highest contributions with 47, 41, and 36 documents published in this field, respectively. In addition, Li, Y. [97] is considered as the most active author within the last five years among all the authors in this field (see Fig. A.2, and Table A.1, supplementary information). Figure 2.3 represents the output of the CiteSpace regarding the citations received by the most influencing authors in this field. According to the results achieved, Ho Y.S. [98], and Gupta V.K. [99] are placed at the first ranks of the most cited authors. It is worth mentioning that the 3 top-cited authors are not among the most contributing authors. This can highlight the fact that the number of documents published cannot be considered as a sole parameter for the impact of an author within the scientific community.


**Fig. 2. 3.** A schematic illustration of the most cited authors on the application of ENMs for (waste)water treatment. The figure is with minimized overlap. Citespace toll was utilized to analyze the data. In this figure, the number of citations received by the authors is differentiated by the font size.

Besides, the author's co-occurrence network analysis can demonstrate the extent of the collaborations among the authors. The results of this analysis have been presented in Fig. 2.4. According to this figure, the authors' cooperation network figure has 932 nodes and 994 connections and represents a very low density (0.0023) demonstrating low global cooperation and communication in this field. This can be interpreted as one of the main reasons for the slow commercialization rate of ENMs for (waste)water treatment.

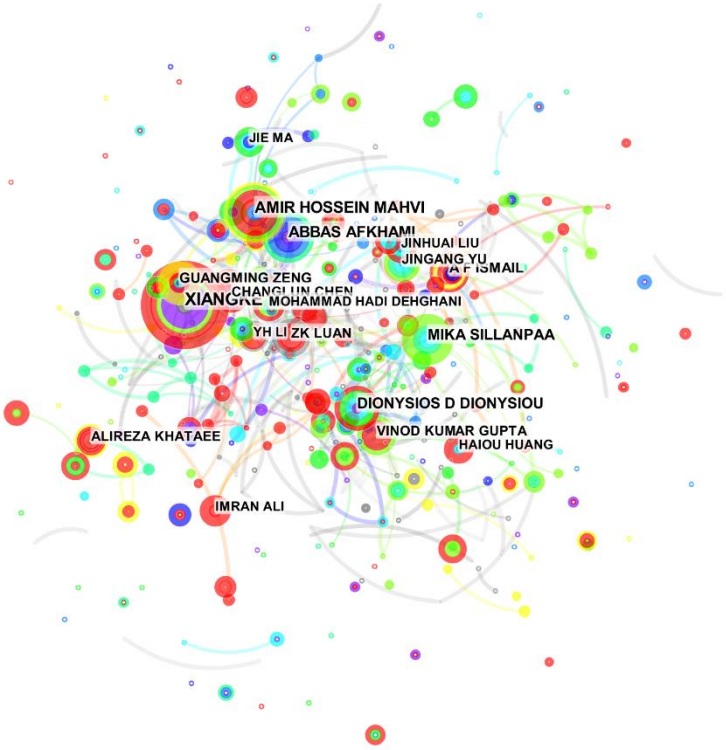


**Fig. 2. 4.** The author's co-occurrence network map. Citespace toll was utilized to analyze the data.

Regarding the sources for the relevant publications, two variables including the frequency and the citation analysis were used to identify the share and the impact of the sources for the publishing of the related documents. According to the results achieved (Fig. 2.5), "desalination and water treatment", "chemical engineering journal" and "RSC advances" have been the most active journals for the publication of scientific documents in this field in terms of frequency of the published documents.

Finally, figure 2.6 represents the analysis of the citations received by the sources for the publications on the application of ENMs for the treatment of contaminated (waste)water. In this regard, the Journal of Hazardous Materials (3894 citations), Chemical Engineering Journals (3251 citations), and Water Resources (3076 citations) have occupied the first positions. Also, Desalination and Water Treatment has been the most active journal in the last 5 years.

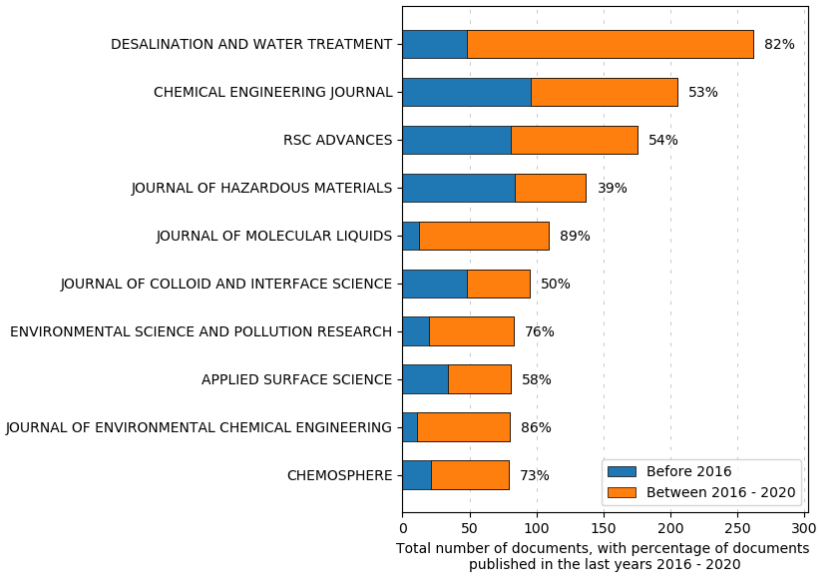


**Fig. 2. 5.** The results of the source analysis regarding the frequency of the published documents, performed using Scientopy tool.


**Fig. 2. 6.** Output of the CiteSpace analysis of the citations received by the sources for the publication of the scientific documents on the application of ENMs for (waste)water treatment. The figure is with minimized overlap.

## 2.3.2. Research hotspots and trends

The keyword analysis is considered an essential tool to identify the trends in a specific scientific field [100–102]. The trends in the keywords' evolution were

mapped using CiteSpace using the databank prepared for this study. The results have been demonstrated in Fig. 2.7. As can be seen in this figure, the research activities in this area have been initiated since the beginning of the current century, mainly for the “adsorption” of the contaminants from the aqueous media. Materials such as “activated carbon” and “carbon nanotubes” have been the most widely studied adsorbents for the removal of various contaminants. The keywords related to the “photocatalytic degradation” of the contaminants have also appeared since the beginning of the current century but with less frequency compared to adsorption. Since 2007, the keywords associated with the mechanisms involved in the removal of environmental contaminants using ENMs have appeared in the literature. Figure 2.7 can also confirm the trend in the application of iron-based nanomaterials (such as zero-valent iron) as well as membrane hybrid technologies since 2007. Novel ENMs such as graphene oxide have also been widely studied after 2010. Biochar is another carbonaceous material that has been introduced for the treatment of (waste)waters in recent years for the treatment of nutrients [103,104], metals [105], and organic compounds (mainly through the activation of oxidation agents (such as persulfate) [106,107] to produce powerful radicals to attack and decompose the organic compounds). This keyword has appeared since 2018 (Fig. 2.7) and there is a need for more studies to transfer this technology for real applications. Keywords related to the treatment of the (waste)water polluted with CECs such as pharmaceuticals (e.g., tetracycline after 2016) have been appearing in the literature demonstrating the current trends in the literature to deal with such contaminants using various types of ENMs.

Figure 2.7 can also reveal that the green synthesis of ENMs has appeared among the most widely used keywords since 2013. The application of environmentally friendly and non-toxic precursors is one of the most important features of green synthesis approaches [78,79]. In this regard, the biosynthesis of ENMs, which implies the application of microorganisms or plant extracts for the synthesis of ENMs, has received attention since 2015.

The cumulative number of keywords in the relevant scientific documents has been also plotted in Fig. 2.8 using the Scientopy tool. As can be observed, “adsorption” is the most widely used keyword, which represents the main studied

mechanism for the application of ENMs for (waste)water treatment, followed by nanoparticles, carbon nanotubes, water treatment and photocatalysis. However, keywords related to the cost analysis of the nanotechnology for (waste)water treatment applications have not yet been appeared in the main 100 keywords. This can demonstrate the lack of information in this regard in the related literature. Also, keywords related to the toxicological effects of the ENMs used for such applications are appearing among the related keywords after 2010 (Fig. 2.7), but only in very recent years. Scientopy analysis can demonstrate that among the relevant keywords, “toxicity” has been appeared in only 26 papers, which can indicate the need for further studies to identify the probable environmental and health impacts of the ENMs when released to the environment after being used for the treatment of contaminated (waste)waters.

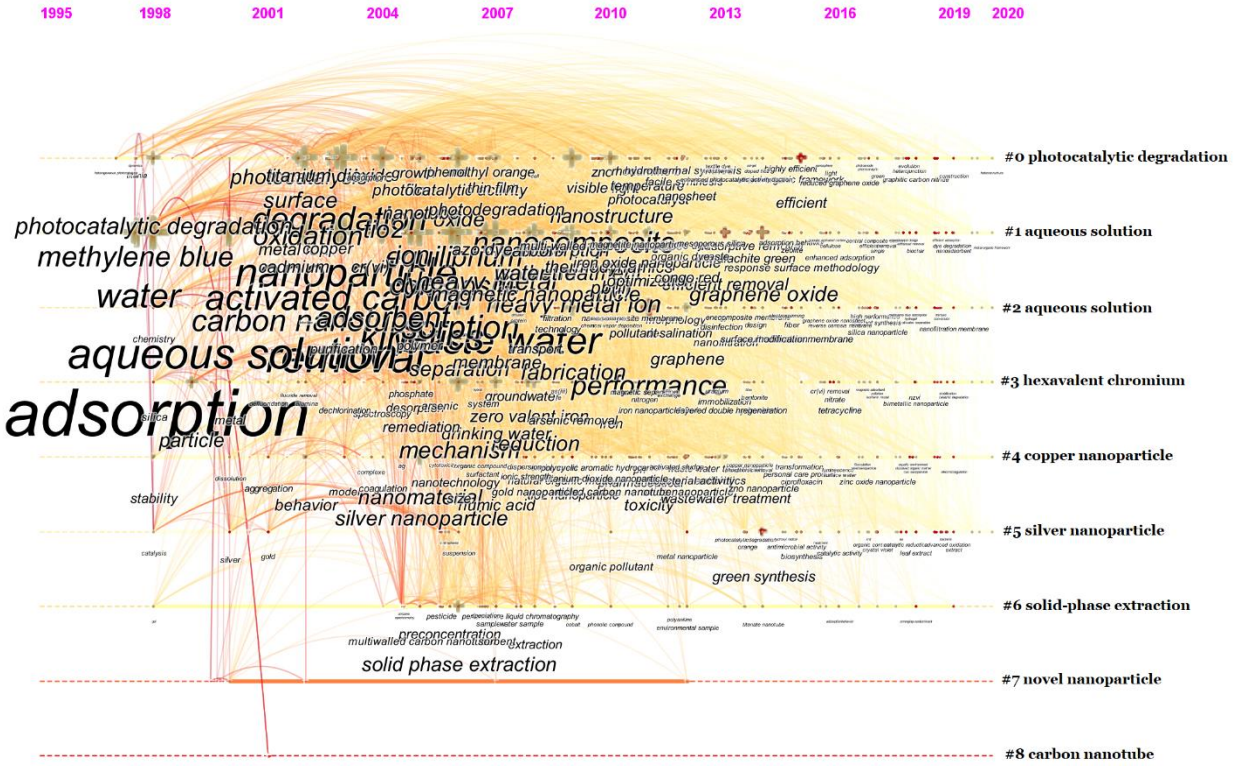


**Fig. 2. 7.** Evolution trend of keywords in the scientific documents published on the application of engineered nanomaterials for (waste)water treatment. The size of nods represents the frequency of keywords occurrence.

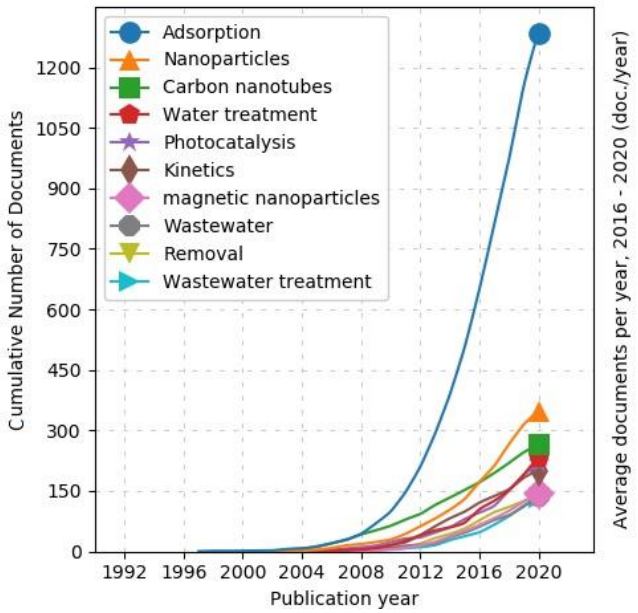


**Fig. 2. 8.** Appearance of the keywords in the publications on the application of ENMs for (waste)water treatment, analyzed using the Scientopy tool.

Figure 2.9 represents the results of the “subject” analysis. As indicated in this figure, “engineering”, “chemistry”, “materials science” and “environmental sciences and ecology” are the main subjects according to the published documents in this area. It can demonstrate the interdisciplinary nature of the studies in this field, where the preparation and characterization of ENMs are linked with the treatment of the contaminated effluents to prevent subsequent environmental and ecological adverse effects.

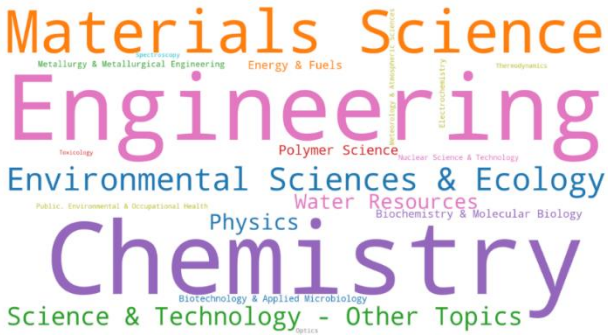


**Fig. 2. 9.** Word cloud analysis of the main subjects of the publications on the application of ENMs for (waste)water treatment. Scientopy tool was utilized to analyze the data.

### 2.3.3. Sustainability aspects

This section aims at discussing the sustainability aspects of the application of ENMs based on the results achieved from the scientometric analysis performed in this study.

#### 2.3.3.1 Technical aspects

Studies on the application of ENMs for the treatment of (waste)waters originated from various sources have been initiated since 25 years ago with an increasing rate in the number of publications after the 2000s, as indicated in Fig. 2.1. In this regard, from the number of published documents, especially in the recent 5 years, it can be concluded that a huge amount of human and financial resources have been invested so far to develop the science in this field. It can be due to this fact that most of the conventional treatment technologies (mainly biological methods) are not so efficient to deal with the recalcitrant organic compounds and contaminants of emerging concerns. However, a detailed search in WoS can support this idea that there is still a very limited number of reports on the application of this technology for real and full-scale (waste)water treatment purposes. As discussed before, there is still a very poor connection between the researchers in this field and the respective network has not been shaped considerably (Fig. 2.4). This can be considered as one of the reasons for the slow progress of commercialization of these technologies.

$TiO_2$, ZnO, and magnetic nanomaterials (especially zero-valent iron) are among the most widely used nanomaterials for the treatment of contaminated (waste)water. The presence of these nanomaterials among the most important keywords (Fig. 2.7) can also indicate the huge amount of effort paid to explore the efficiency of these nanomaterials for (waste)water treatment applications. According to our best knowledge, nano zero-valent iron (nZVI) is the only nanomaterial that has been used for the treatment of industrial effluents [110], which can promote the Fenton and Fenton-like reactions which are efficient processes to deal with organic pollutants in the content of industrial effluents [111–

114]. Perhaps there are some main reasons for a tendency to use nZVI for such purposes including the magnetic nature of these materials which can create the possibility of their recovery and reuse after being used for the treatment of polluted effluents [115]. Also, recent studies have revealed the low toxicity of nZVI towards aquatic organisms [114,116,117].

As demonstrated in Table A.2 (supplementary information), most cited documents in the literature have mainly focused on the application of iron-based nanomaterials (mainly α-$Fe_2O_3$), as well as the combination of membrane technologies and iron-based nanomaterials. It can be interpreted as the potential of the iron-based nanomaterials to address some sustainability aspects such as providing the possibility of recovery and reuse of those nanomaterials using a magnetic field which may reduce the treatment costs as well as the total release of the ENMs after being used into the water bodies [118–121]. Membrane technologies have also been considered as the leading physical treatment technologies to deal with the contaminated waters developed since the previous century [44]. However, the literature has stated that membrane fouling is the main existing drawback for the wider application of such technologies [122–125]. Decoration of membranes with appropriate types of ENMs can be considered as one of the possible strategies to deal with this issue [126–128]. Besides, the application of carbonaceous materials, such as carbon nanotubes, especially from natural carbon resources has been studied widely in recent years proved which can contribute to carbon sequestration while treating the contaminated (waste)water [129]. Very recent trends in this field include the production of low-cost carbonaceous materials from natural feedstock materials such as biomass wastes as the sole adsorbents or as the support for other types of nanomaterials (such as catalytic semiconductors) in order to enhance the degradation of various types of pollutants from the polluted (waste)waters. For instance, carbonaceous materials have been widely used recently for the efficient removal of dyes from real and synthetic effluents [130]. There is also a trend in the scientific community for the application of such carbon-rich materials as outstanding adsorption agents for metals [131]. Carbon nanotubes, activated carbon, and very recently biochar materials have been used successfully for such purposes. especially, biochars as

the products of the pyrolysis of the biomass wastes can bring a number of advantages such as immobilization of carbon and preventing the release of greenhouse gas into the atmosphere causing global warming and climate change [101,132]. Incorporation of magnetic nanomaterials into carboneous materials is another trend in this field in order to enhance the adsorption capacity for various environmental contaminants [133,134].

According to Fig. 2.7, “carbon nanotubes” is the third most widely used keyword in the relevant literature with 1199 publications. Also, magnetic biochars as cheap and reusable adsorbents have received huge attention recently for the adsorption of metals [135]. Fig. 2.8 can also reveal the fact that the ENMs have been widely used so far for the adsorption of the contaminants from the content of effluents. However, adsorption can bring such sustainability aspects by transferring the pollutants from the liquid phase into the solid phase. Hence, the degradation of the organic compounds through (for instance) photocatalytic processes has attracted attention. In this regard, nanomaterials such as titanium dioxide [136] and zinc oxide [137] have been widely used for the photocatalytic degradation of pollutants. A suggestion for future studies is to prepare carbonaceous-based composites with the mentioned nanomaterials. The addition of a magnetic compartment to such composites can grant the magnetic properties facilitating the recovery and reuse of the mentioned catalytic materials.

To enhance the feasibility of the ENMs application for the treatment of industrial effluents, which is currently among the main sustainability barriers which limit transferring the technology from the lab to real scales, other suggestions can also be provided. As well-described in the literature, photocatalytic degradation [138,139] using ENMs such as ZnO [140,141] and $TiO_2$ [142,143] (especially magnetic versions such as $TiO_2/Fe_3O_4$ [144]) is considered an efficient way for the decomposition of recalcitrant organic pollutants. In this regard, ENMs-UV systems [44] have already attracted attention but such methods require a source of electricity to generate UV irradiations. Also, the system needs periodical maintenance and replacing the UV lamps. This can potentially increase the attributed treatment costs and makes the technology difficult to scale up. To overcome this issue, solar irradiation [145,146] can be used as a source of energy

to activate ENMs. However, the intensity of UV irradiation in sunlight is normally below 10% [17]. Hence, visible light active generations of photocatalysts (such as nitrogen-doped titanium dioxide [147] with adequate oxygen vacancies [20,148,149]) have come into the picture of the possibilities for the next generation (waste)water treatment technologies. Another attractive solution to overcome this issue would be concentrating solar energy [150–152] which can theoretically enhance the performance of photocatalysts to deal with environmental pollutants. To this end, an applicable suggestion for future studies can be the combination of solar concentrating systems such as parabolic throughs (Fig. 2.10).

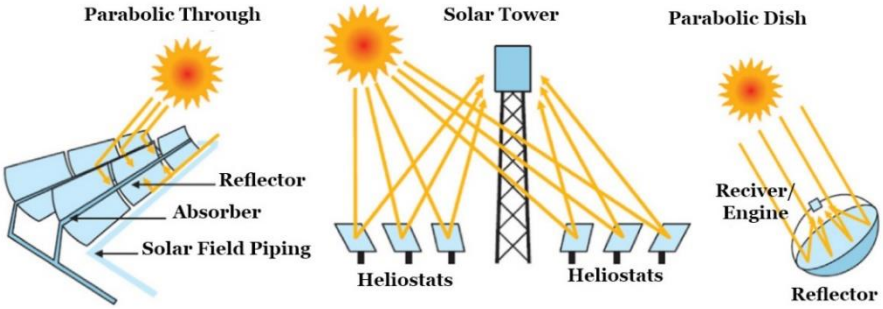


**Fig. 2. 10.** Main concentrating solar power (CPS) systems, adopted from Zhang et al., (2013) [153]. CSP systems are novel concepts that have been developed to harvest solar energy and transform it into other useful forms such as electrical energies.

Application of such combinations can provide opportunities for photocatalytic processes for the treatment of highly polluted effluents to be adopted especially in developing countries in which the treatment of the generated effluents is among the most important priorities.

Among the most contributing countries and organizations, China and Iran have published the highest number of scientific documents on the application of various types of ENMs for (waste)water treatment applications. In this regard, implementation of developing programs in China (such as “special economic zones of the People's Republic of China” [154] and “economic and technological development zones” [155] and national innovation system in Iran [156]) have considerably assisted to promote the scientific research in this field. However, it

can be recommended for the organizations which are active in this field to invest more in the transferring of the technologies which have been already developed in lab and pilot scales to real scale applications.

### 2.3.3.2 Fate and ecotoxicology

Besides the technical aspects of the application of ENMs for (waste)water treatment, subsequent impacts of such technologies to the receiving environments are of high importance regarding the sustainability considerations. To identify the extent of the studies performed in this regard, the data bank retrieved from the WoS was explored using a set of relevant keywords such as toxicity, ecotoxicity, and environmental fate. The results demonstrated that only limited information is available in the literature for the fate and the ecotoxicological effects of the nanomaterials used for the (waste)water treatment. As illustrated in Fig. 2.7, “toxicity” has appeared among the keywords after 2010. However, there is a need for more in-depth studies on the effects of the treatment with nanomaterials under different mechanisms (i.e., adsorption and degradation) on the reduction of toxicity from the contaminated (waste)water.

There are also some main aspects to be considered for a wider application of ENMs for (waste)water treatment including the validation of the efficiency of the treatment with ENMs on the reduction of the toxicity of the effluents [157–164], as well as the probable toxic effects of the nanomaterials after being released into the receiving environment. However, there are a limited number of studies on the toxic nature of the treated effluents with ENMs. Chai et al., (2011) demonstrated that a 4-h photoelectrocatalytic degradation of p-nitrophenol solution using the sieve-Like $SnO_2/TiO_2$ nanotubes resulted in eliminating the toxicity of the effluents on the luminescent marine bacterium *Vibrio fisheri* (formerly known as *Photobacterium phosphoreum*). Also, another study showed that photocatalytic treatment of synthetic methylene blue containing effluents using ZnO nanomaterials resulted in the decrease of the cytotoxicity to L929 mouse fibroblast cells compared to the untreated solution [166]. It has to be stated here that there are several parameters that can affect the toxic nature of the effluents after being treated with ENMs. In addition to the effectiveness of the treatment method applied for the

decomposition of the recalcitrant organic compounds, the mechanisms involved in the treatment process and the mineralization potential of the system, the dissolution rate of the nanomaterials and the effects of the released ions on the toxicity of the treated effluents can determine the toxic behaviour of the treated effluents with ENMs. In a recent study [167], ciprofloxacin containing synthetic effluent was treated using a UV-$TiO_2$ system and also the toxicity studies were performed on *Vibrio fischerii*. The results demonstrated that the formation of the toxic by-products from the decomposition of the main contaminant resulted in high toxicity to the bacterium.

Life-cycle assessments of the application of ENMs used for the treatment of contaminated waters can also aid to have a better understanding of the environmental performance of such treatment technologies. In this regard, adopting the green chemistry principles can potentially contribute to producing ENMs with low subsequent environmental effects [168].

Some studies published in the literature indicate that ENMs may cause adverse effects to biota; the intensity of the toxicity depends on many properties of the ENMs, like for example, its shape, length, surface area, among others [169–173]. More studies are required to investigate the influence of such characteristics on ENM toxicity, to allow establishing the amount of ENMs that can be potentially released from nano-based (waste)water treatment plants into the environment. Furthermore, such knowledge may enable tailoring some of the ENMs properties in a way to obtain compounds with high efficiency in the remediation of contaminated (waste)water while having no or reduced toxicity to the biota.

#### 2.3.3.3 Socio-economic aspects

Social aspects are among the main sustainability criteria which can determine the approach of the communities to the new technologies. Since the treatment of contaminated (waste)water and providing clean sources are of high importance for the ecosystem and human health, societies may be very sensitive to the technologies which are implemented for the treatment of the polluted (waste)water. An advanced search in the data bank extracted from the WoS using

the relevant keywords indicated that despite the importance of the water quality for the societies [174,175] very limited number of studies have been performed and published on the social acceptance of the ENMs-based (waste)water treatment technologies. The research in Guatemalan (community of San Mateo Ixtatán) demonstrated that the application of ceramic filters impregnated with Ag nanomaterials is a socially acceptable technology especially when the local materials and labour are and can attract high degrees of social acceptance with the ability to provide high-quality household water quality [176].

However, economic considerations can determine the potential of the technology to compete with other technologies for real-scale applications. A precise screening of the dataset created in this study indicated that the keywords related to the economic aspects can be found only in 139 relevant documents. In addition, most of the mentioned documents have claimed that the methods developed for the synthesis of nanomaterials and their applications for (waste)water treatment are economic but without providing any detailed economic analysis to be able to compare the ENMs-based technologies with other conventional or cutting-edge technologies [177–179].

It has to be also mentioned that the keywords related to the cost analysis of the ENMs applicability for wastewater treatment cannot be observed in the main keywords that appeared in the publications. It can be considered as one of the main barriers to the rapid transferring of such technologies from the lab to pilot and real scales because there is still a lack of information for the cost-effectiveness of such technologies, especially compared to other oxidation-based technologies such as Fenton and ozone-based treatments.

Also, there is currently an increasing interest in the literature for the recovery of materials using ENMs resulting in the purification of polluted (waste)waters. For instance, recovery of metals such as Cr [180], Cu [181], Pb [182], etc has been investigated as an effective way to reduce the toxicity of the effluents and also to recycle chromium in the context of the circular economy. This is evident that the main mechanism involved in the recovery of various materials from the effluents is adsorption which has been already appeared as the main trends in the application of ENMs for (waste)water treatment (Fig. 2.8). However, the economic analysis of

the recovery of various elements using ENMs has not been considered in the majority of the related studies which can be recommended for future studies to promote the application of ENMs for real applications. Although there are several review papers (239 reviews) published in the literature on the application of ENMs for (waste)water treatment (e.g., [183–185]), there is an urgent need for comprehensive reviews which provide recommendations on how to overcome the existing technical, economic and social barriers to make such technologies commercial.

## 2.4. Conclusion

The present manuscript has aimed to perform a scientometric analysis on the application of ENMs for (waste)water treatment. Using a certain set of keywords, 6539 documents were identified and retrieved for further analysis. Although various types of ENMs have been applied to this end, specific types such as iron-based nanomaterials, carbonaceous nanomaterials such as carbon nanotubes, and nano-membrane technologies have received higher degrees of attention. However, most of the studies in this regard have been performed in lab and pilot scales. According to the results of the present study, there is also a need for further studies on the economic aspects of nano-based technologies and also on the ecotoxicity of the ENMs and the effluents before and after being treated with nanomaterials to push the commercialization of these technologies.

# Chapter 3. Persulfate Activation with CuO Nanomaterials for the Treatment of Rhodamine B Aqueous Solution - Mechanisms and Acute Toxicity to the cladocera *Daphnia magna* and the rotifer *Brachionus calyciflorus*

## 3.1. Introduction

Pollution of water resources is currently among the most important issues worldwide [1]. Water contaminants can be divided into various groups including inorganic compounds such as metals and nutrients, as well as organic compounds are released into the wastewaters from various sources including households, agricultural activities, and industrial activities [186]. Hence, the wastewaters can be classified based on the origin as sewage wastewater, and industrial effluents.

Several industries all over the world produce large amounts of wastewaters and release them into the receiving environments [187]. Especially, in developing countries, this issue can be highlighted because there is a lack of efficient facilities in many industrial sectors for the treatment of the generated effluents [188]. The stringent environmental regulation for the discharge of industrial effluents has also made it inevitable to considerably reduce the contamination load before discharging the effluents [45].

Various industries such as the pulp and paper industry [189], textile industry [190], and food industry produce [191] highly contaminated effluents with relatively high loads of recalcitrant and non-biodegradable organic compounds.

However, in most industrial effluents, there are complex organic compounds that cannot be decomposed by the means of microorganisms when biological methods are used for the treatment of the generated wastewaters. In addition, there are organic compounds such as organic dyes which are toxic to the microbial communities. The presence of such compounds may lead the biological treatment method to fail [44].

Application of AOPs has been considered in recent years to deal with toxic and non-biodegradable organic compounds. The basis of these methods is the generation of powerful and non-selective oxidative agents (such as radicals and singlet oxygen) in the medium to attack and decompose the organic compounds. Among various radicals, hydroxyl radicals, sulfide radicals, iodine radicals, and chlorine radicals generated from the respective oxidants have been widely applied very recently [27,192].

On the other hand, the application of efficient catalysts such as engineered nanomaterials (ENMs) has been receiving huge attention in recent years to be used as catalysts for the activation of oxidants towards the production of various types of oxidation agents. The main advantage of the application of ENMs is that they can provide high specific surface areas and active sites for the oxidation to occur [174]. There are various mechanisms involved in the generation of radicals using ENMs. Among all, photocatalytic generation of radicals (mainly hydroxyl radicals) has been studied widely using nanomaterials such as titanium dioxide and zinc oxide as the most famous semiconductors in this regard [193,194].

To address these needs, advanced oxidation processes based on the activation of oxidants have been developed and implemented in several wastewater treatment activities. Oxidants cover a range of materials such as conventional ones for instancehydrogen peroxide ($H_2O_2$), and novel oxidation agents such as PS, PMS, iodine, and chlorine. According to the literature, various methods have been developed for the activation of such oxidation agents thermal, ultrasonic, microwave, and the application of catalysts [195–198]. In this regard, identifying the most sustainable methods for the activation of the oxidants is considered a state-of-the-art trend among the scientific community.

Despite the importance of the quality of the treated effluents especially in terms of their subsequent effects on the receiving environments, there is a limited number of toxicological studies on the effluents treated using advanced oxidation processes (see chapter 2). As some examples, Yeber et al., (1999) reported a 50% reduction in the acute toxicity of a cellulose bleaching effluent treated through photocatalysis using $TiO_2$ and ZnO. Nemr, et al., (2018) used AOP to detoxify an acid Red 17 dye solution and assessed its efficiency in toxicity removal by

exposing the rotifer *Brachionus plicatilis* (a marine species) to the untreated and treated solutions, observing 20 and 5% or mortality, respectively, at the end of the assay. Such toxicity characterization of the treated effluents is of much relevance since during the AOP the formation of more toxic transformation products or intermediates may occur [201].

The present work intended to assess the chemical and ecotoxicological efficiency of an AOP using copper oxide nanoparticles and persulfate (as an oxidation agent) on the removal of organic contaminants (Rhodamine B) from a synthetic effluent. For this, CuO nanomaterials were prepared using an ultrasonic-assisted method and characterized using various techniques and then used for the activation of persulfate for the degradation of RhB in the content of the synthetic effluents prepared using deionized water and ASTM. In addition, a combination of thermal and catalytic activation of persulfate on the degradation of RhB was used. In the next step, the treated effluents were subjected to toxicity studies using ecotoxicological indicators including cladocera *D. magna* and with the rotifer *B. calyciflorus.*

## 3.2. Materials and methods

### 3.2.1. Chemicals

Reagents including copper (II) sulfate (CuSO4, >98%), purchased from Fisher Chemicals and sodium hydroxide (NaOH, ≥98.0%) obtained from Acros Organics were used for the synthesis of CuO nanomaterials. Rhodamine B (RhB, $C_{28}H_{31}ClN_2O_3$, >99%) was purchased from Fisher Scientific and used for the preparation of the synthetic effluents (50 mg/L of distilled water or ASTM medium) to run the treatment tests and also ecotoxicity assays with *D. magna* and the rotifer *B. calyciflorus*. Potassium persulfate (PS, $K_2S_2O_8$, >99%) was obtained from Fisher Scientific to provide the different concentration oxidant solution (1, 2.5 and5 mM) in the treatment medium. All the reagents were used as received without any further purification.

### 3.2.2. Synthesis of CuO nanomaterials

For the synthesis of CuO nanomaterials, first, 2.5 g of $CuSO_4$ was dissolved in 100 mL deionized water and stirred well for 10 min under continuous magnetic stirring. In parallel, a solution containing 2.5 g NaOH in 100 mL of deionized water was prepared and stirred for 10 min at ambient temperature. The latter solution was added to the former solution drop wisely at 60 °C under ultrasonic irradiation using an ultrasound cleaning bath (Hielscher, UP200s W, 24 kHz). The resulting mixture was stirred for another 30 min and the brown precipitates were filtered using Whatman filter papers and washed several times with deionized water and dried at 60 °C overnight and finally collected for characterization.

### 3.2.3. Characterization of CuO nanomaterials

Various characterization techniques were employed to explore the properties of the prepared powders. The X-ray diffraction analysis was performed to determine the crystalline structure of the prepared materials. For this, continuous scanning from 20° to 80° 2θ was conducted at a scan rate of 2° 2θ/min. In addition, the morphology of the materials was analysed using a scanning electron microscope (SEM). To this end, a slurry containing the prepared powder in ethanol was placed under ultrasound for 10 min for better separation of the particles. Then, a drop of the slurry was placed on a grid for the characterization with SEM. In addition, Brunauer, Emmett, Teller (BET) surface area and analysis were performed using nitrogen gas adsorption-desorption using a Micromeritics Gemini 2380 equipment (USA).

### 3.2.4. Treatment of the synthetic effluent

Activation of PS using the prepared CuO nanomaterials towards the degradation of RhB in the synthetic effluent prepared in distilled water was first optimized using a Taguchi experimental design. In practice, CuO nanomaterials were suspended in a 100 mL aqueous solution containing RhB (50 mg/L) under

continuous magnetic stirring at 350 rpm. The absorbance behaviour of the RhB solution was monitored in all the tests using a UV-Vis spectrometer in wavelengths ranging from 300 to 700 nm. The intensity of the visible light adsorption was measured at 554 nm [202] to trace the concentration of the dye in the aqueous medium. The experiments were repeated 3 times. An L-9 Taguchi statistical design (Table 3.1) was established using Minitab-17. Eq. 1 was used to identify the relative importance of the studied parameters and their levels based on the calculated S/N ratios.

$$\frac{S}{N}[\mathrm{db}] = -10log\frac{1}{N}(\sum_{i=1}^{n}(Y_i)^2) \qquad \text{Eq. 1}$$

In this equation, $Y_i$ represents the response data of the Taguchi statistical design, and n is the number of experiments designed.

**Table 3. 1.** L-9 Taguchi experimental condition design for identification of the relative importance of the parameters for the activation of PS using CuO nanomaterials for the degradation of RhB.

| Run | Treatment method | CuO Dosage (g/L) | $[PS]_0$ (mM) | pH |
|---|---|---|---|---|
| 1 | Self-degradation | 0 | 0 | 4 |
| 2 | PS alone | 0 | 2.5 | 7 |
| 3 | PS alone | 0 | 5 | 10 |
| 4 | CuO NMs alone | 0.25 | 0 | 7 |
| 5 | Activation of PS with NMs | 0.25 | 2.5 | 10 |
| 6 | Activation of PS with NMs | 0.25 | 5 | 4 |
| 7 | CuO NMs alone | 0.5 | 0 | 10 |
| 8 | Activation of PS with NMs | 0.5 | 2.5 | 4 |
| 9 | Activation of PS with NMs | 0.5 | 5 | 7 |

The experiments were performed for 30 minutes and the intensity of the respective peak of RhB was immediately measured and reported. After identifying the optimum conditions, complementary experiments were performed at a prolonged reaction time (2 h) with the sampling intervals of 10, 20, 30, 60, 120 minutes. Controls including CuO alone and PS alone were also considered in the experiments. The identified optimum conditions (selected for the toxicity studies) was used to treat the synthetic effluents prepared with ASTM (American society of

testing and materials) (please see Table 3.2 for information on the optimal conditions used to treat the effluent prepared in ASTM for toxicity assays with *D. magna*). This is because the subsequent toxicity tests need to be performed using this culture medium. The composition of ASTM is presented in Table 3.2. The optimum condition was also coupled with elevating the reaction temperature to 45 °C to reach the complete degradation of RhB in the ASTM medium. The treated effluents were used for the 48 h-Acute Immobilization assay with *D. magna* (section 2.5.1).

Following the ecotoxicity data obtained with the acute assays with *D. magna*, which revealed no removal of toxicity in the treated effluent a new effluent was prepared in ASTM (with the same concentration of RhB-50mg/L), though some modifications were done to the treatment process. Namely, PS concentration was reduced to 1 mM under a prolonged (60 min) thermal-assisted degradation of RhB using 0.5 g/L of CuO nanomaterials as the catalyst. The efficiency of this treatment in toxicity removal was checked by performing the 24 h-mortality assay with *B. calyciflorus* (please see Table 3.4 in section 3.2.5.2).

**Table 3. 2.** Additives used for the preparation of ASTM.

| **Chemical name** | **Chemical Formula** | **Concentration in Milli-Q water (mg/L)** | **Amount added in 20L of Milli-Q water (mL)** |
|---|---|---|---|
| Potassium chloride | KCl | 8 | 200 |
| Magnesium sulfate heptahydrate | $MgSO_4.7H_2O$ | 246 | 200 |
| Sodium bicarbonate | $NaHCO_3$ | 192 | 200 |
| Calcium sulphate dihydrate | $CaSO_4.2H_2O$ | 120 | 1500 |

The RhB concentration in the non-treated and treated effluents was analysed using a UV-vis spectrophotometer (Thermo Scientific), at an absorption intensity of 554 nm as the indicator of the RhB concentration. A total organic carbon (TOC) analyser (Thermo Scientific$^{TM}$) was used in order to determine the efficiency of the treatment systems for the remocal of TOC.

### 3.2.5. Ecotoxicity assays

To further assess the efficiency of the treatment methods applied, the lethal toxicity of the synthetic effluent assessed before and after the application of the treatment methods. For this, toxicity assays with two freshwater species of primary consumers were carried out, with the cladocera *D. magna* and with the rotifer *B. calyciflorus*. These two species are commonly used as model species in ecotoxicity assays due to their high sensitivity to chemical contamination, easiness to maintain cultures in the laboratory, representativeness of primary consumer in natural populations of zooplankton, and because, by being primary consumers, play an important role in the food chain.

#### 3.2.5.1. 48 h-Acute Immobilization assay with *Daphnia magna*

The ecotoxicity of the synthetic effluent prepared in ASTM was assessed by running the Acute Immobilization test with *D. magna* according to the guideline OECD 202 (2004) [203]. For this, less than 24 h-old neonates of *D. magna*, from the 3$^{rd}$ brood, were exposed to the treatments described in table 3.3. Neonates of *D. magna* were obtained from laboratory cultures maintained at the Applied Ecology and Ecotoxicology Laboratory, of the Department of Biology, University of Aveiro. Culturing the new generations of *D. magna* normally takes around two weeks. After approximately 10 days of culturing, the organisms release their first neonates (n1). Within two or three days, the adults release a new generation (n). For the toxicity tests, only 3rd, 4th and 5th generations (i.e., n3, n4 and n5) series of neonates were used.

The ASTM medium served as the negative control (ASTM, 2002) [204], as it is the medium used to culture these organisms. Four replicates were run for each treatment, each consisting of a test vessel filled with 20 mL of the test solution, where five neonates of *D. magna* were introduced. Exposure occurred for a period of 48 hours at controlled room temperature (20 ± 2 °C) and photoperiod 16:8 h light:dark. The test solutions were not changed during the assay and no food was added to the organisms. Immobilization was checked after 24 and 48 hours of

exposure. An organism was considered immobile/dead if exhibited no movements for 15 seconds after being gently stimulated with the tip of a pipet.

**Table 3. 3.** Conditions of the Acute Immobilization assay with *D. magna* before, and after treatment with CuO/PS system.( BT-Before treatment, AT-After treatments).

| Run | Toxicity test conditions | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **Medium** | **$[RhB]_{Initial}$ (mg/L)** | **CuO dosage (g/L)** | **$[PS]_{Initial}$ (mM)** | **Time (min)** | **pH** | **Volume (mL)** | ***D. magna* (number per replicate)** | **Replicates (number)** |
| BT-RhB | ASTM | 50 | 0 | 0 | - | 7.5 | 20 | 5 | 4 |
| ASTM | ASTM | 0 | 0 | 0 | - | 7.5 | 20 | 5 | 4 |
| AT-RhB (no precipitation) | ASTM | 50 | 0.5 | 5 | 120 | 5.87* | 20 | 5 | 4 |
| AT-RhBP (with precipitation) | ASTM | 50 | 0.5 | 5 | 120 | 5.87 | 20 | 5 | 4 |
| AT-RhB (no precipitation) | ASTM | 50 | 0.5 | 5 | 120 | 7.5 | 20 | 5 | 4 |
| AT-RhBP (with precipitation) | ASTM | 50 | 0.5 | 5 | 120 | 7.5 | 20 | 5 | 4 |
| CuO (CuO alone) | ASTM | 0 | 0.5 | 0 | 120 | 5.87 | 20 | 5 | 4 |
| CuO (CuO alone) | ASTM | 0 | 0.5 | 0 | 120 | 7.5 | 20 | 5 | 4 |
| CuOP (CuO with precipitation) | ASTM | 0 | 0.5 | 0 | 120 | 5.87 | 20 | 5 | 4 |
| CuOP (CuO with precipitation | ASTM | 0 | 0.5 | 0 | 120 | 7.5 | 20 | 5 | 4 |
| PS (alone) | ASTM | 0 | 0 | 5 | 120 | 5.87 | 20 | 5 | 4 |
| PS (alone) | ASTM | 0 | 0 | 5 | 120 | 7.5 | 20 | 5 | 4 |
| ASTM | ASTM | 0 | 0 | 0 | - | 5.87 | 20 | 5 | 4 |
| ASTM | ASTM | 0 | 0 | 0 | - | 7.5 | 20 | 5 | 4 |

* Final pH of the treatment.

### 3.2.5.2. 24 h-mortality assay with *Brachionus calyciflorus*

The characterization of the ecotoxicity of the synthetic effluent prepared in the third set-up with ASTM medium was done by running the 24 h-mortality assay with the rotifer species *B. calyciflorus*. This assay followed the methodology of the RotoxKit F® protocol (MicroBioTests, Ghent, Belgium). The test organisms were obtained from *B. calyciflorus* cysts, bought from Microbiotests Inc., that were incubated for 15-16 hours in the synthetic freshwater at continuous light illumination of 1000-4000 lx and at a controlled temperature of 25 °C. After hatching, *B. calyciflorus* (less than 2 h-old) were exposed to five dilutions (6.25%, 12.5%, 25%, 50%, and 100%) of the treatments described in table 3.4. ASTM medium was used as the negative control. The assays were run in 24-well plates, each well was considered a replicate. For each dilution/treatment, five replicates were performed. In each replicate, 1 mL of the test solution and 5 neonates of *B. calyciflorus* were introduced. Exposure occurred for a period of 24 hours in an incubator set to 25 ± 1 °C and in the dark. The number of live and dead animals was recorded after 24 h. Rotifers were considered dead if no movement was observed within 5 seconds. To further study the effects of the Cu ions, additional experiments were also designed to study the effects of Cu ions released from CuO nanomaterials by removing the Cu ions through a precipitation method. For this, the pH of the treated effluents was increased to 9. After the filtration to remove the precipitates, the pH was again adjusted to 5.87, and 7.5 for the toxicity studies.

**Table 3. 4.** Conditions of the mortality assay with rotifers before, and after treatment with CuO/PS system. (BT-Before treatment, AT-After treatments)

| Run | Medium | Volume (mL) | [RhB] (mg/L) | CuO (g/L) | $[PS]_0$ (mM) | pH | Replicates | Rotifers (no. per replicate) | Tested dilutions (%) |
|---|---|---|---|---|---|---|---|---|---|
| BT-RhB | ASTM | 1 | 50 | 0 | 0 | 7.5 | 5 | 5 | 6.25, 12.5, 25, 50, 100 |
| ASTM | ASTM | 1 | 0 | 0 | 0 | 7.5 | 5 | 5 | 100 |
| ASTM (after treatment) | ASTM | 1 | 0 | 0 | 0 | 7.5 | 5 | 5 | 100 |
| AT-RhB | ASTM | 1 | 50 | 0.5 | 1 | 7.5 | 5 | 5 | 6.25, 12.5, 25, 50, 100 |
| CuO (alone) | ASTM | 1 | 0 | 0.5 | 0 | 7.5 | 5 | 5 | 6.25, 12.5, |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| CuO with Precipitation | ASTM | 1 | 0 | 0.5 | 0 | 7.5 | 5 | 5 | 25, 50, 100 6.25, 12.5, 25, 50, 100 |
| PS (alone) | ASTM | 1 | 0 | 0 | 1 | 7.5 | 5 | 5 | 6.25, 12.5, 25, 50, 100 |

### *3.2.5.3.* Data *analysis*

Microsoft Excel and SigmaPlot were used to analyse the results achieved. The mortality data were compared between treatments and the control by performing a one-way analysis of variance (one way-ANOVA) followed by the multicomparison Dunnett's. The assumptions of ANOVA were checked for normality with the Kolmogorov-Smirnov test and variance homoscedasticity with the Levene´s test. The estimation of the dilutions causing 20% and 50% of mortality ($LC_{20}$ and $LC_{50}$, respectively) and the corresponding 95% confidence limits was performed by using the software Priprobit (Sakuma, 1998).

## 3.3. Results

### 3.3.1 Characterization of the materials

Fig. 3.1 represents the X-ray diffraction pattern of the prepared dark brown powders. The reflection peaks of the materials were indexed using the Joint Committee on Powder Diffraction Standards (JCPDS). Sharp and intense peaks are evident between 30 and 40° 2θ. In addition, several peaks with less intensities were recorded in the XRD pattern which can all be attributed to the CuO (JCPDS: 00-41-0254) [205]. Purity of the materials for specific applications is also of high importance. From the XRD results achieved, no secondary peaks for impurities could be detected which can confirm the formation of pure CuO nanomaterials.

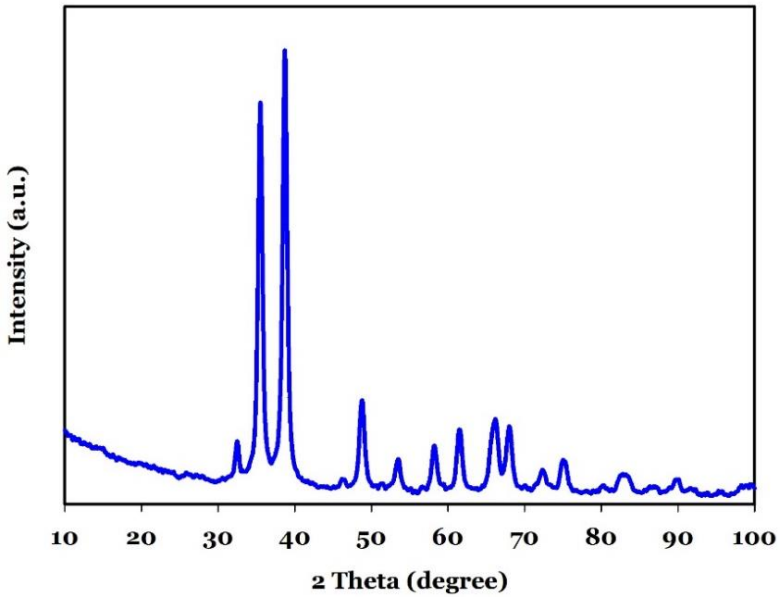


**Fig. 3. 1.** X-ray diffraction pattern of the prepared powders indicating the formation of pure CuO, JCPDS: 00-041-0254.

Figure 3.2 presents the scanning electron microscopy (a), and transmission electron microscopy (b) of the CuO materials prepared. According to this figure, the prepared powder consists of agglomerates of sheet-like structures. Formation of such a sheet-like structure can be attributed to ultrasonic irradiation as discussed in the literature [206]. Such 2-dimensional structures normally represent a relatively high specific surface area which is a critical property for the nanomaterials which are desired to be used in AOPs because they provide large active sites for the oxidative reactions to occur. Such a hypothesis was validated by performing specific surface area and porosity analysis.

The BET specific surface area and porosity analysis of the prepared sheet-like CuO structures confirmed the relatively specific surface area of 36 $m^2/g$. In addition, Fig. 3.3 shows the adsorption/desorption isotherms of the prepared powders.

According to this figure, a typical hysteric behaviour of mesoporous materials can be distinguished with an average pore size of 88 Å. The shape of the adsorption/desorption curves allows the hysteresis loop to be classified as IV as per the IUPAC classification [207]. This type of loop is often associated with mesoporous materials.

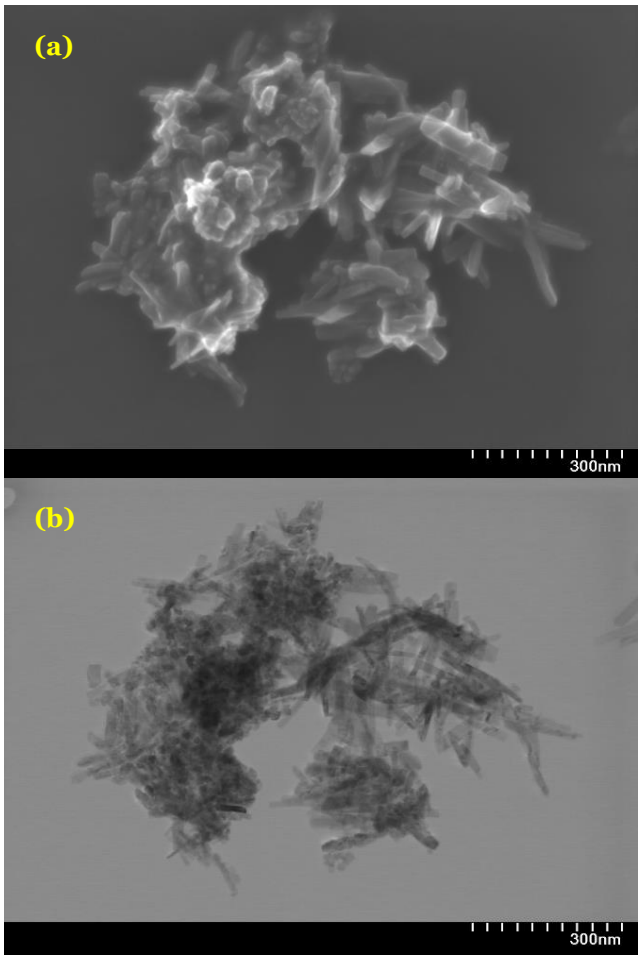


**Fig. 3. 2.** SEM (a) and TEM (b) images of the prepared CuO nanomaterials.

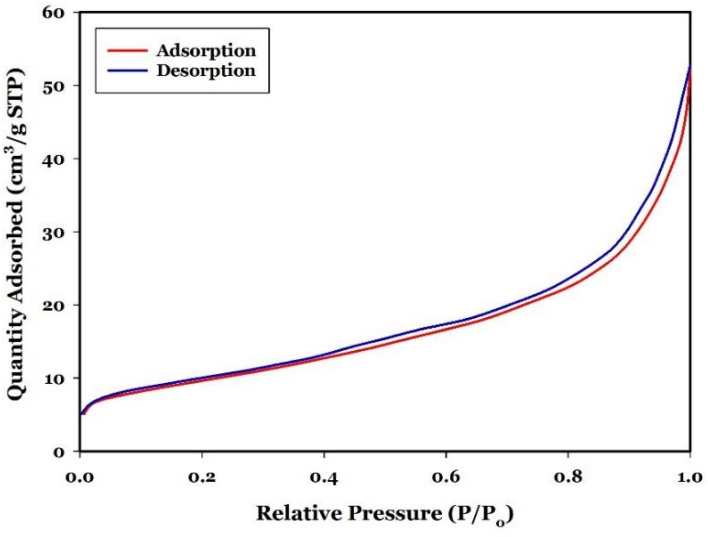

**Fig. 3. 3.** Adsorption and desorption isotherms of the prepared CuO nanomaterials.

### 3.3.2. Treatment of RhB

#### 3.3.2.1. Treatment of synthetic effluents with distilled water

In the present study, an advanced oxidation process based on the application of the prepared CuO nanomaterials (as the catalyst), and PS (as the oxidation agent) was developed and used for the treatment of the synthetic effluent of RhB (50 mg/L) in different media (i.e., deionized water and ASTM). This section presents the results achieved.

As mentioned before in the materials and methods section (3.2) an optimization method was employed based on the Taguchi experimental design which allows achieving the optimum operating conditions using a low number of experiments [208–210]. Figure 3.4 represents the results of the removal of the RhB using the designed L-9 Taguchi experimental design. The experiments were performed in a pre-defined reaction time of 30 min and UV-vis spectra of the medium were used to identify the concentration of RhB. The intensity of the peak at 554 nm decreased in all the experimental runs indicating the removal of RhB. The maximum removal of RhB among the designed Taguchi experimental conditions was achieved under the $[PS]_0$=5 mM, a CuO dosage of 0.5 g/L and pH=7 with deionized water and 68% removal of the dye was obtained after 30min of reaction. Figure 3.5 illustrates the outcome of the L-9 Taguchi experimental design. According to this figure, the optimum conditions for the removal of RhB was identified as $[PS]_0$=5 mM, CuO=0.5 g/L and pH=4. Furthermore, Fig. 3.5 shows the optimum parameters/levels achieved by analysing the results of the L-9 Taguchi experimental design using removal (%) as the response parameter. This figure can indicate that PS and CuO play a determinant role in the removal of RhB. Without PS and CuO, only a low degree of removal was achieved while their combination resulted in the optimum removal efficiency. Also, this graph demonstrates that the PS (especially when increased from 0 to 2.5 mM) is the most important parameter, followed by the presence of CuO nanomaterials in the

medium. In addition, pH had the least impact compared to the PS and CuO nanomaterials.

However, due to the fact that the toxicity tests would be performed using ASTM medium (pH=7), the maximum degradation under pH=7 was selected and subjected for optimization through performing the experiments by extending the reaction time based on the hypothesis that more radicals can be generated under elevated reaction times. The results of repeating the optimum conditions under an elevated reaction time of 120 min have been indicated in Fig. 3.6.

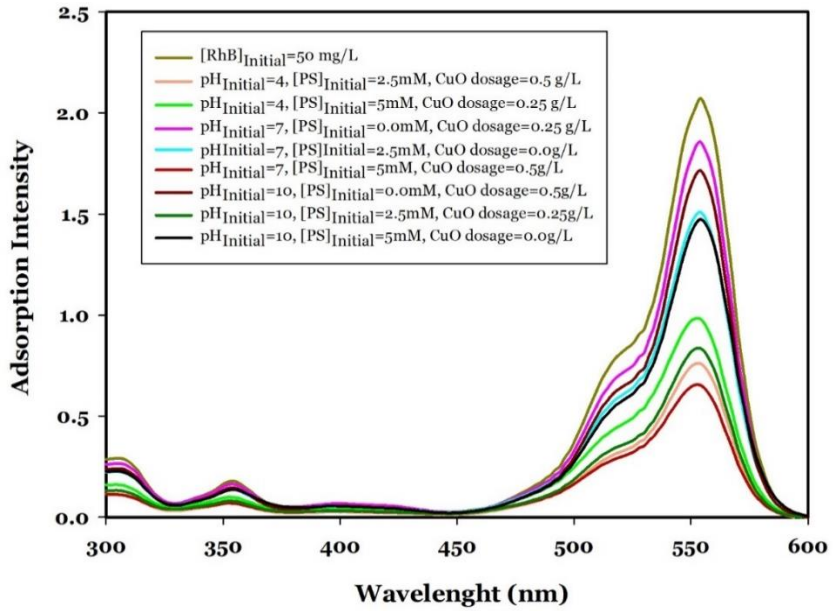


**Fig. 3. 4.** Taguchi experimental conditions for the degradation of RhB.

According to Fig. 3.6, after 30 min of reaction, 68% of RhB was removed while when the reaction time increased to 60 min, 94% of this organic dye was removed. A TOC removal equal to 71% was achieved after the treatment. It can be due to this fact that PS can be further activated after 30 min by copper oxide nanomaterials for the degradation of RhB. This trend was also observed after 60 min and 100% degradation of RhB was reached after 120 min.

Activation of PS can be also performed using a thermal treatment. Fig. 3.7 demonstrates the experiments for the removal of RhB using under an elevated temperature to 45 °C for the activation of PS (5 mM) without the nanomaterials.

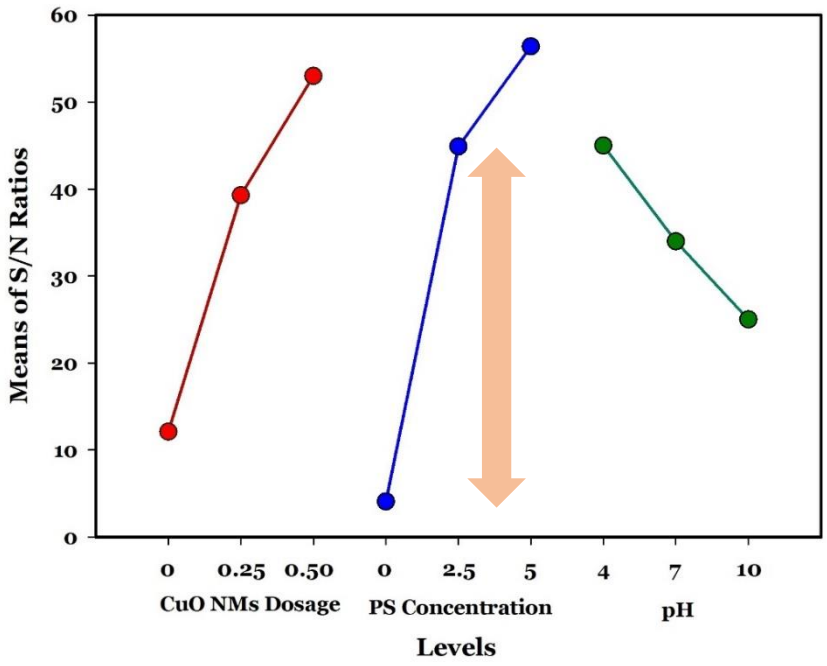


**Fig. 3. 5.** The results of the Taguchi Experimental design.

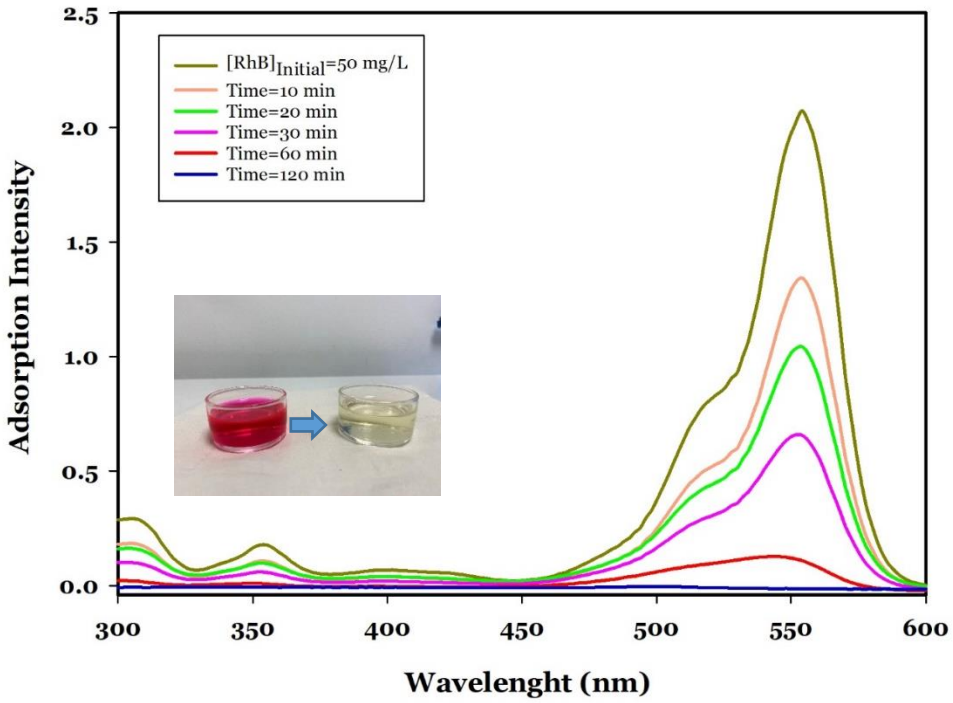


**Fig. 3. 6.** Effect of operating conditions of $[PS]_0$=5 mM, CuO=0.5 g/L and pH=7, Time=120 min on the degradation of RhB with deionized water, TOC removal=71%.

As can be seen in figure 3.7, degradation of RhB using the thermal activation of PS is less efficient compared to the CuO nanomaterials assisted activation of PS for the decomposition of RhB. After 30 min, 48% of RhB was removed using this system and reached 67% after 60 min (TOC removal=51%). By prolonging the experiments to 120 min, 96% of the RhB was removed from the medium. However, no significant changes in colour were observed.

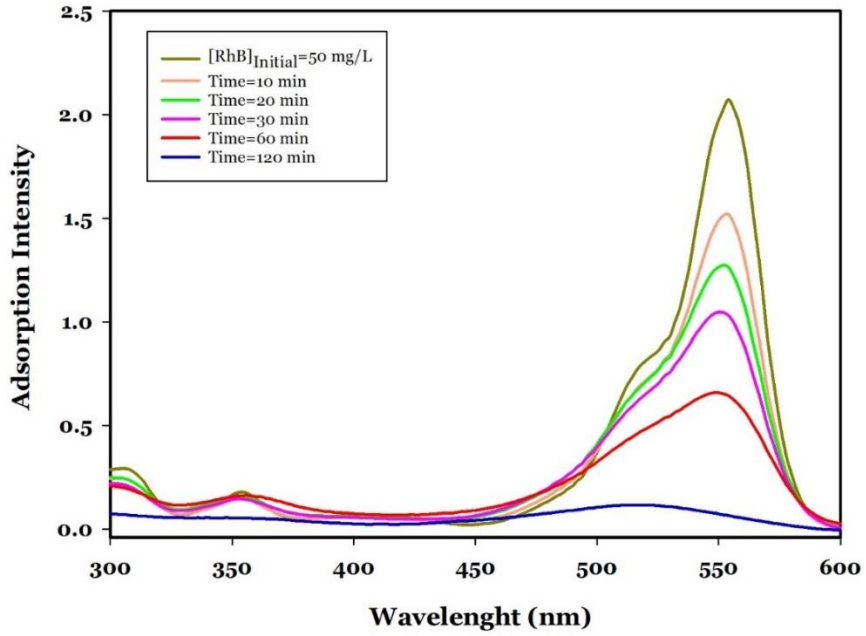


**Fig. 3. 7.** Effects of the operating condition of $[PS]_0$=5 mM, CuO=0.0 g/L, pH=7 and temperature=45 °C on the degradation of RhB with deionized water, TOC removal=51%.

### 3.3.2.2. Treatment of synthetic effluents with ASTM

Considering that the toxicity studies need to be performed in the ASTM medium, the conditions that resulted in the complete degradation of RhB were applied for the treatment of the synthetic effluents prepared using the ASTM medium. For this, RhB (50 mg/L) was added to the ASTM medium prepared with the composition mentioned in Table 3.2.

Figure 3.8 demonstrates the results of the treatment of RhB (50 mg/L) in ASTM medium under the operating conditions of $[PS]_0$=5 mM, CuO=0.5 g/L and pH=7. As it can be observed, the degradation efficiency dropped considerably to 29% after 30 min of reaction compared to the experiments with distilled water (68%, Fig. 3.6). A TOC removal of 49% was acieved under this operating conditions. In addition, while 94% of RhB (50 mg/L) was removed after 60 min with distilled water, this value was 57% using ASTM as the reaction medium. The maximum degradation of 78% was finally achieved after 120 min of the treatment process. Such a decrease in the efficiency of the system can be attributed to the presence of ions in the reaction medium which can stimulate the conditions of the wastewaters with high ionic strenghts [211].

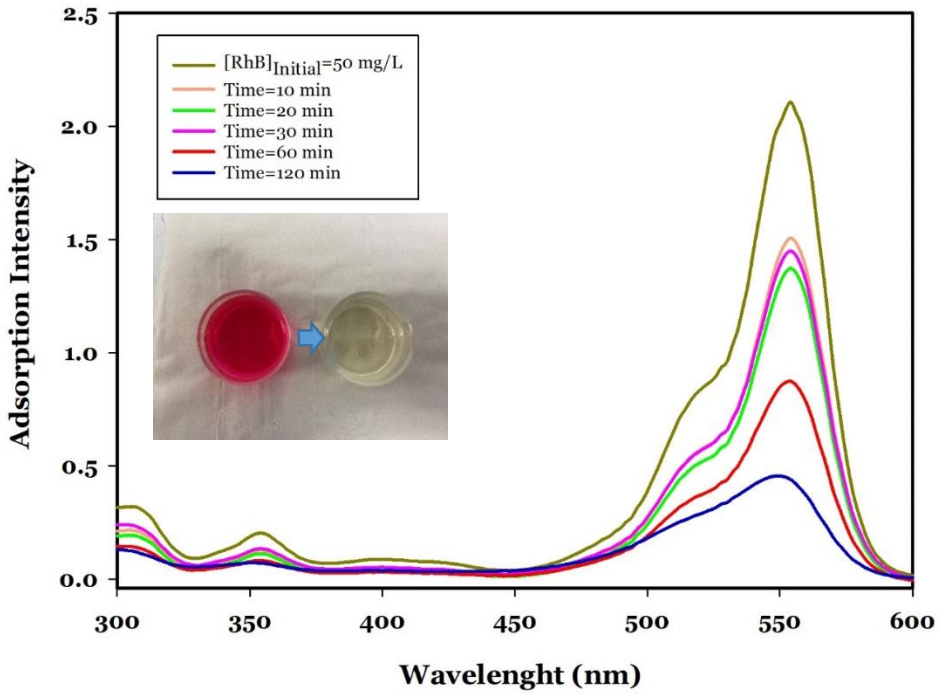


**Fig. 3. 8.** Effects of operating conditions including $[PS]_0$= 5 mM, CuO=0.5 g/L and pH=7 on the degradation of RhB with ASTM, TOC removal=49 %.

Figure 3.9 indicates the results of the combination of catalytic and thermal activation of PS for the treatment of RhB in the ASTM medium. AS can be observed, with the operating conditions of $[PS]_0$=5 mM, CuO=0.5 g/L and pH=7 with the ASTM medium, and under an elevated temperature of 45 °C, complete removal of RhB was achieved after 20 min of reaction. In addition a high TOC removal of 94% was achieved under these operating conditions. While only 25% of the RhB was removed at the same time interval without elevating the temperature from room temperature (Fig. 3.8) to 45 °C.

The results can indicate that increasing the temperature is an applicable way to reach the complete removal of effluents containing relatively high concentrations of organic compounds. This can be a practical option especially because most of the industrial effluents have high temperatures resulted from the industrial production processes [212]. The effluents resulted from this experimental run were used for the toxicity tests with *D. magna* (section 3.3.3.1).

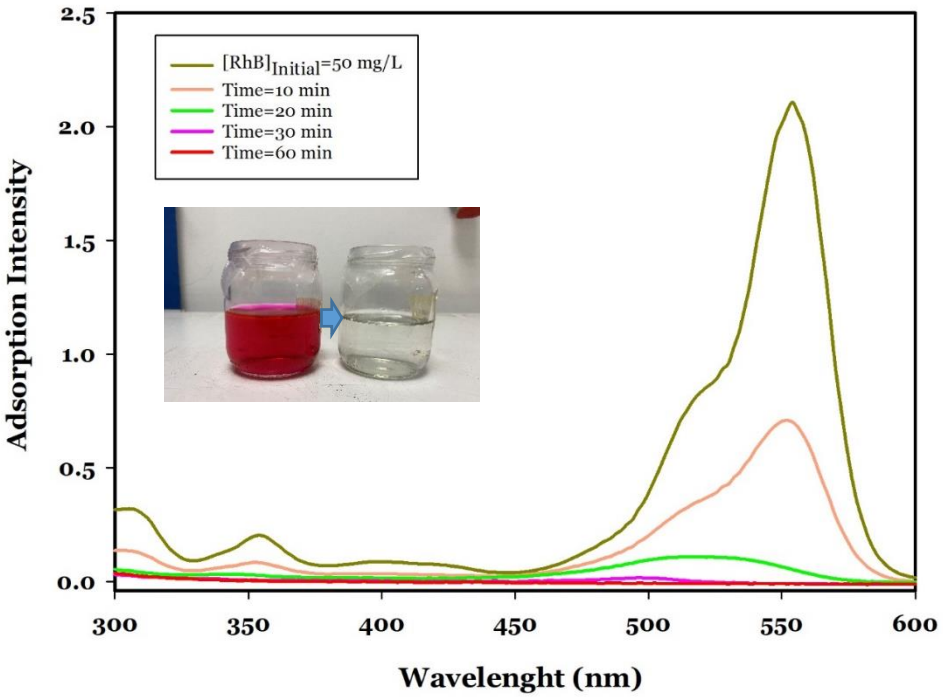


**Fig. 3. 9.** Effect of operating conditions of $[PS]_0$=5 mM, CuO=0.5 g/L and pH=7 and temperature=45 °C and on the degradation of RhB with ASTM, TOC removal=94%.

It was also assumed that by prolonging the reaction time, more oxidation agents can be produced in the medium which can diminish the need for higher PS concentrations. Hence, a complementary experiment was also performed using the following experimental conditions: $[PS]_0$=1 mM, CuO=0.5 g/L and pH=7 under 45 °C for the removal of RhB (50 mg/L) with the ASTM medium. The results have been presented in Figure 3.10. As can be observed in this figure, 92% of the RhB degradation was achieved after 30 min of the reaction and after 60 min of reaction, 100% of the RhB removal was achieved. A TOC removal of 69% was also achieved for this treatment run.

Evolution of a secondary peak can be also observed by promoting the reaction at 500 nm. This peak is representative of the by-products such as de-ethylation of the aromatic rings of RhB which has resulted in a blue shift to 500 nm.

The results can indicate that a catalytic-thermal activation of even low PS concentration (1 mM) can be considered an efficient method to deal with the real

wastewaters containing high concentrations of organic compounds. A higher PS concentration will considerably increase the treatment costs which can be considered as a sustainability barrier for the development of these technologies.

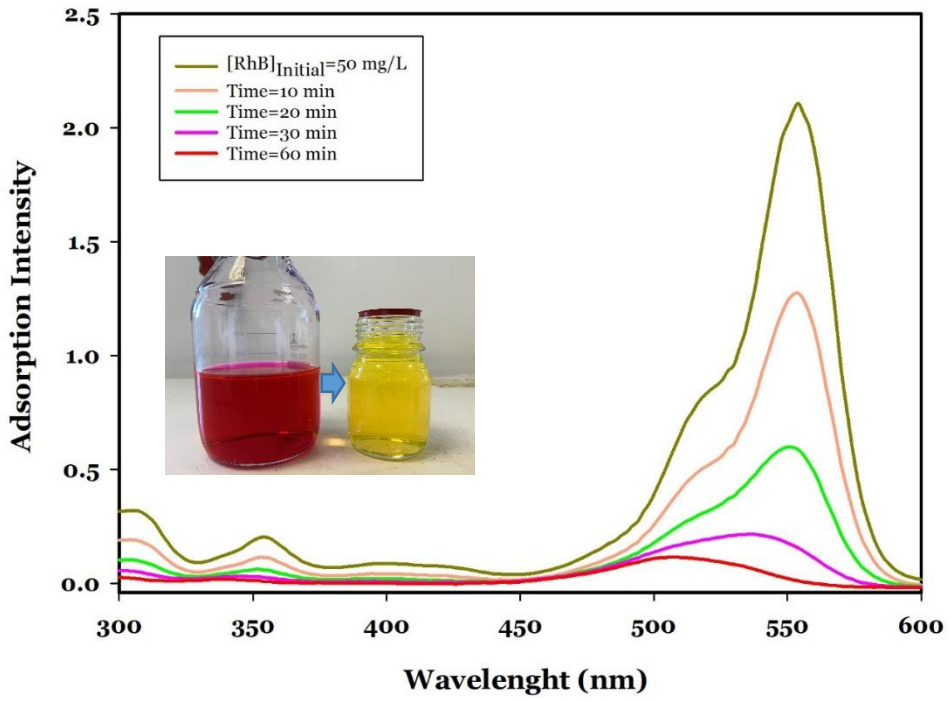


**Fig. 3. 10.** Effects of the operating conditions of $[PS]_0$=1 mM, CuO=0.5 g/L and pH=7 and temperature=45 °C and on the degradation of RhB with ASTM, TOC removal= 69.3%.

### 3.3.3. Toxicity of the effluents (before and after treatment)

In this section, the toxicity results of the synthetic effluents before and after treatment with the studied AOPs will be presented and discussed. To this end, the effluents resulted from the operating conditions including $[PS]_0$=5 mM, CuO=0.5 g/L and pH=7 and temperature=45 °C and on the degradation of RhB with ASTM were used for the acute toxicity tests (48 h) using cladocera *D. magna* and $[PS]_0$=1 mM, CuO=0.5 g/L and pH=7 and temperature=45 °C were used for the acute toxicity tests (24 h) using rotifer *B. calyciflorus*.

### 3.3.3.1. 48 h-Acute Immobilization assay with *Daphnia magna*

In figure 3.11 are presented the cumulative mortality results obtained in the acute immobilization assay performed with *D. magna* neonates. The synthetic effluent before being treated with AOP caused significant mortality (100%) in daphnids just after a 24 h period of exposure (Fig. 3.11; $p<0.05$). After applying the AOP treatment to the effluent (AT-RhB), with or without Cu precipitation, the same percentage of mortality was observed within the 24 h period of exposure, both for the treated effluent with no pH adjustment (pH=5.87) and with pH adjustment to 7.5 (Fig. 3.11, A,B). Furthermore, significant mortality (100%) was observed for daphnids exposed to 5 mM PS solely (at pH 5.87 and 7.5) and to ASTM with pH adjusted to 5.87 ($p<0.05$). These results suggest that though RhB was removed from the effluent the PS and the existing ions are causing high mortality in the *daphnids*. Adding to this, the formation of some new compounds such as N-de-ethylated intermediates and/or metabolites during the AOP processes may as well contribute to such high mortality of test organisms. As for the results obtained by exposing *D. magna* to CuO without and with precipitation of copper, they also suggest that the nanoparticles or the copper ions released by them during the experiment are compromising the survival of the organisms (Fig. 3.11, A,B).

The results of the Cu ions precipitation demonstrated that the precipitation after treatment with different initial pHs of the medium (i.e., 5.87, and 7.5) had no significant effect on the reduction of the toxicity to *D. magna* and all the microorganisms died after 24 h of the toxicity tests. However, more tests were included in the toxicity tests to find the pure effects of the ions released from the CuO nanomaterials by addition of CuO (0.5 g/L) to the ASTM medium ($[RhB]_0$=0 mg/L, $[PS]_0$=0 mM). After filtration, the medium was used for the toxicity tests with *D.magna*. In this case, the mortality was reduced (with 7 alive microorganisms out of 20 *D.magna)* under the initial pH=7.5 after 24 h of the toxicity test while all the microorganisms died after 48 h of the tests. While, when the initial pH was 5.87, all the microorganisms were dies within the initial 24 h of the toxicity test.

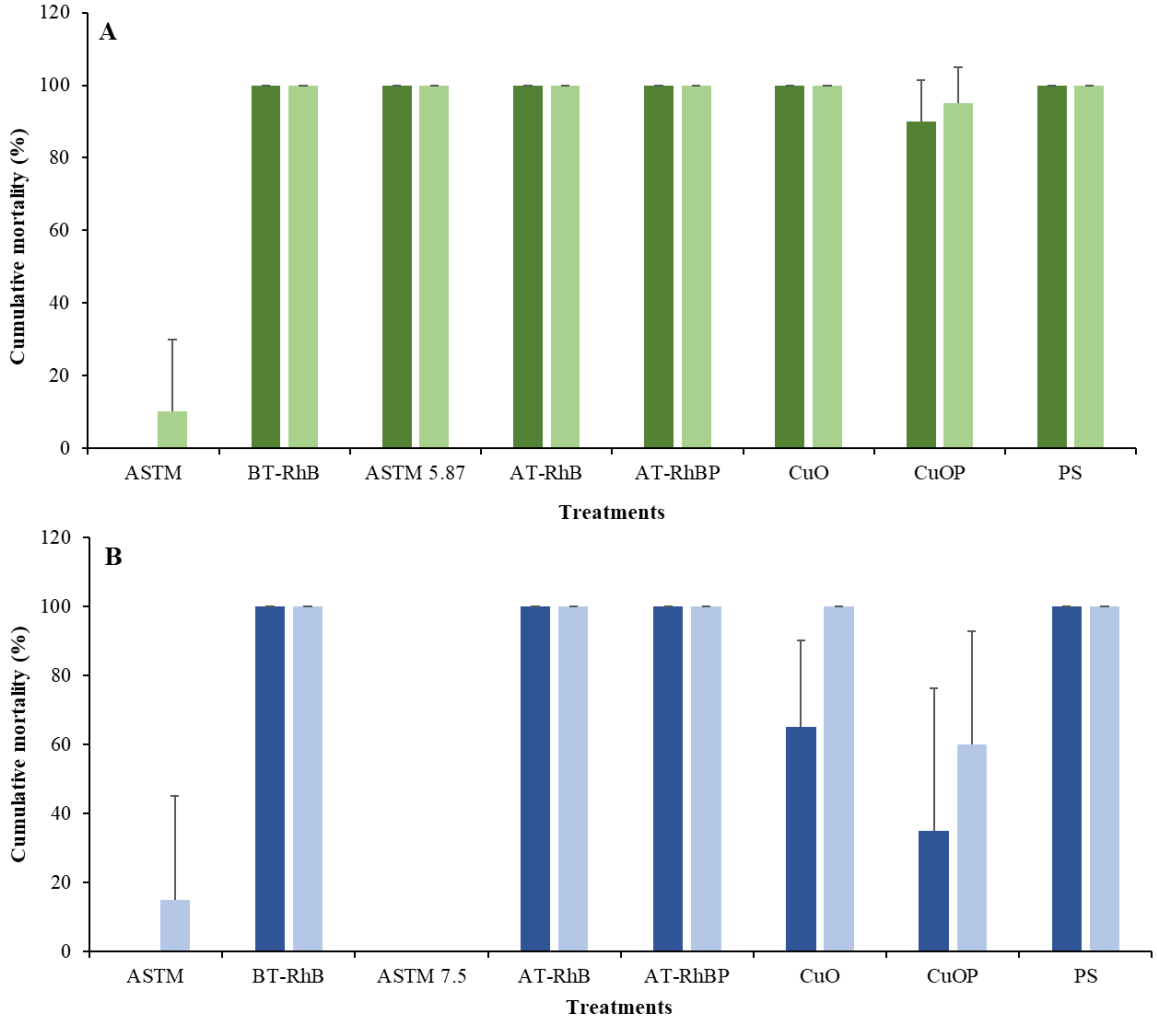


**Fig. 3. 11.** Average cumulative mortality (%) of neonates of *D. magna* after being exposed, for 24 h (dark blue or green) and 48 h (light blue or green), to: ASTM-initial control; BT-RhB-synthetic effluent before being treated; ASTM 5.87 and ASTM 7.5–control medium with pH adjusted to 5.87 and 7.5; AT-RhB-synthetic effluent after being treated; AT-RhBP-synthetic effluent after being treated and after precipitating copper; CuO-copper oxide nanoparticles; CuOP-copper oxide nanoparticles with precipitation; PS. A-treatments at pH 5.87 (pH of the effluent after being treated); B-treatments with pH adjusted to 7.5 (close to the pH of ASTM medium).

Precipitation tests were also performed with the same experimental conditions (i.e., CuO=0.5 g/L, ASTM medium, $[RhB]_0$=0 mg/L, and $[PS]_0$=0 mM) with different initial pHs (i.e., 5.78 and 7.5) The results have been also indicated in Fig. 3.11. It

was observed that the precipitation procedure decreased the mortality, especially under the initial pH=7.5. In fact, after 24 and 48 h of the tests, 13, and 8 microorganisms (out of 20) were alive. Also, precipitation in the case of initial pH=5.87, 2 and 1 microorganisms were alive after 24 and 48 h of the test, respectively.

### 3.3.3.2. 24 h-mortality assay with *Brachionus calyciflorus*

The toxicity studies with rotifers were performed using the effluents treated under a combination of CuO/PS and thermal treatment ($[RhB]_0$=50 mg/L, $[PS]_0$=1 mM, CuO=0.5 g/L and pH=7.5 and temperature=45 °C) with various dilutions including 0% (control, ASTM), 6.25%, 12.5%, 25%, 50%, and 100%. The results of the Acute (mortality) toxicity tests with rotifers before and after treatment are presented in Fig. 3.12. As can be observed in this figure, effluents before treatment represent no toxic effects to the studied organisms at the dilution of 6.25% ($[RhB]_0$=3.125 mg/L), and low degree of toxicity at the dilutions of 12.5% (24 alive rotifers out of 25), and 25% (24 alive rotifers out of 25). The number of alive rotifers in all the replicates dropped to 8 (out of 25), and 2 (out of 25) in the dilutions of 50%, and 100%, respectively. There was a significant difference between the control and before treatment effluents with dilutions of 50%, and 100%. The $LC_{20}$ and $LC_{50}$, and respective (95% confidence limits), were calculated for the BT-RhB and were as follows: 27.0% (20.8-32.9) and 44.3 (36.6-54.1)%, respectively. However, after treatment of the synthetic effluents with the studied advanced oxidation processes resulted in the toxicity to the treated effluents even under the dilution of 6.25%. Under this dilution, 6 rotifers (out of 25) died, and the number of dead rotifers increased to 15 rotifers (out of 25 in all replicates) in the dilution of 12.5%. No alive rotifers were observed in the dilutions of 25%, 50%, and 100% (effluents after treatment, no dilution). The Dunnett´s test on the results achieved indicated that there is a significant difference between control and all the dilutions after treatment of the synthetic effluents with the advanced oxidation processes ($p<0.05$). The $LC_{20}$ and $LC_{50}$ were calculated for the AT-RhB and were as follows: 5.01 (3.61-6.34)% and 8.24 (6.54-10.1)%, respectively. To identify the

reasons for the toxic nature of the treated effluents to the rotifers, a set of experiments were planned and executed. Fig. 3.12 presents the effects on the addition of CuO alone in the ASTM medium, with and without precipitation. The Dunnet test indicated that there is no significant difference between the control and ASTM with CuO, with and without precipitation.

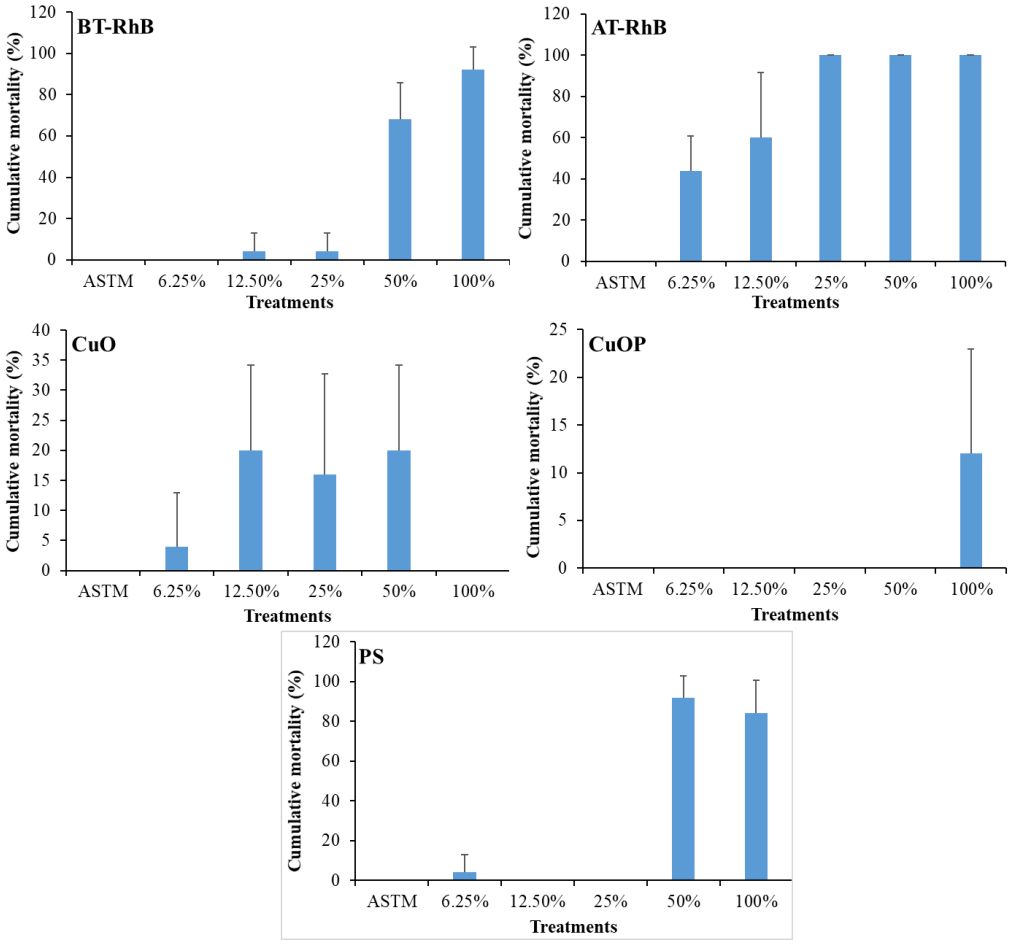


**Fig. 3. 12.** Average cumulative mortality (%) of neonates of *B. calyciflorus* after being exposed, for 24 h, to ASTM-initial control and serial to dilutions of the following treatments: BT-RhB-synthetic effluent before being treated; AT-RhB-synthetic effluent after being treated; CuO-copper oxide nanoparticles; CuOP-copper oxide nanoparticles with precipitation; PS-potassium persulphate.

However, it was observed that precipitation reduced the mortality in rotifers which can be associated with low Cu ions in the medium. These results are per the results from other studies in the literature about the toxicity of the Cu ions to the microorganisms [213,214].

Finally, the effects of PS on the toxicity of rotifers was studied by the addition of persulfate (1 mM) into the ASTM medium. The results have been represented in Fig. 3.12.

According to the results achieved, PS did not show any toxic effects to rotifers in dilutions of 0%, 6.25%, 12.5%, and 25%. However, the Dunnet test confirmed the significant difference in the mortality of the rotifers in the dilutions of 50% and 100%. Only 2, and 4 rotifers in the mentioned dilutions, respectively.

It can be concluded that the toxicity to the rotifers results in the presence of PS in the reaction medium. More precisely, the reaction between PS and CuO has resulted in toxicity to the rotifers because in PS alone we have only toxicity at 50% and no dilution conditions but in the treated effluents we have toxicity in all the conditions.

# Chapter 4. Discussions, final remarks, and future outlook

Degradation of recalcitrant organic compounds from polluted effluents has attracted huge attention in recent years. Among the organic compounds, dyes are of high importance in terms of their possible toxic effects on the environment and living organisms [215].

There are some studies in the literature stating that dyes can bring severe toxic effects to aquatic life [216]. For instance, median effective concentration of RhB to *D. magna* ($EC_{50,48h}$) has been calculated to be 22.9 mg/L [10,217,218]. It has been observed that RhB can form reactive oxygen compounds [5]. Also, Agus et al., (2015) concluded that Rhodamine B induces dose-dependent lipid peroxidation and cervical epithelial cells proliferation [219]. In another relevant study, Castro et al., (2019) [220] concluded that the effluents from the textile industry are highly toxic to *Aliivibrio fischeri.* Hence, there is a need for efficient and cost-effective methods to remove the organic dyes from the industrial effluents. CuO-based ENMs have been used as heterogeneous catalysts for the activation of conventional oxidants such as hydrogen peroxide. However, due to the economic considerations for the purchase of hydrogen peroxide and also risks attributed to the handling and use of this oxidant, there has been a tendency for the *in situ* generation of powerful radicals for the decomposition of recalcitrant compounds.

There have been some reports in the literature for *in situ* generations of hydrogen peroxide using CuO/γ-$Al_2O_3$ nanomaterials for the electrochemical degradation of azo dye amaranth from aqueous solution [221]. The results of the mentioned study indicated the system was not so efficient in the absence of the catalyst (9% degradation of dynein 3 h). However, by addition of the catalyst 90% of dye removal was achieved within 3 h under optimum conditions of oxygen flow of 0.4 ml/min, electricity power of -0.4 V and pH 4.3. They also achieved 60% of

total organic carbon removal using the designed system. However, such systems need energy (in the form of electricity) for the *in-situ* generation of radicals.

In this study, the *insitu* generation of radicals from PS was investigated. CuO nanocatalysts were prepared using a cost-effective, facile and productive method based on a green ultrasonic-based route. The method used for the synthesis of nanomaterials resulted in the preparation of homogeneously dispersed nanoparticles (with an average size of about 60 nm) and a relatively high specific surface area of 36 $m^2$/g. As a hypothesis, the nanomaterials with the high specific surface area can provide large active sites for the chemical reactions which result in the generation of radicals to attack and decompose the recalcitrant organic compounds. The nanomaterials prepared were used for the activation of this oxidant and the results indicated the effectiveness of the prepared nanomaterials (0.5 g/L) for the activation of PS (5 mM) towards the decomposition of RhB (50 mg/L) in the synthetic effluents prepared using deionized water. According to Fig. 3.6, after 120 min, 100% of RhB was removed. The UV-Vis spectra also can represent the fact that another peak with very low intensity appears in the peak corresponding to the degradation peak of 120 min at 500 nm. From a mechanistic point of view, the radicals generated in the medium (Fig. 4.1) can attack the aromatic chromophore ring of RhB and decompose this organic dye to the final products ($CO_2$, and $H_2O$), or the intermediates of the RhB decomposition [222–224]. In an important study recently performed by Du et al., (2017), it was concluded that in addition to the oxidative radicals, activated persulfate is a dominant reactive oxygen species (ROS) that is produced under CuO/PS system as indicated in Fig. 4.1. The living organisms can not tolerate the accumulation of ROS and die [226]. According to this figure, oxidation agents such as hydroxyl radicals, sulfide radicals and singlet oxygen species are generated when PS is activated using an efficient activation method such as using a nano-catalyst. This results in the removal of RhB, and hence, a reduction in the intensity of the respective peak at 554 nm. However, under AOPs, some by-products are generally formed due to the incomplete degradation of organic compounds present in the medium. In case enough oxidation agents are available, the by-products can also further decompose to the final products of the reduction which are $CO_2$, and

$H_2O$ (as indicated in Fig. 4.1). The presence of by-products can be also distinguished by the peaks which are generated in the UV-Vis spectra of the effluents after treatment. De-ethylation of the aromatic rings of RhB may result in a blue shift of the peak to 500 nm, as can be observed in Fig. 3.6. In addition, the treated effluent represented a light green color. This color can indicate the formation a series of N-de-ethylated intermediates [227].

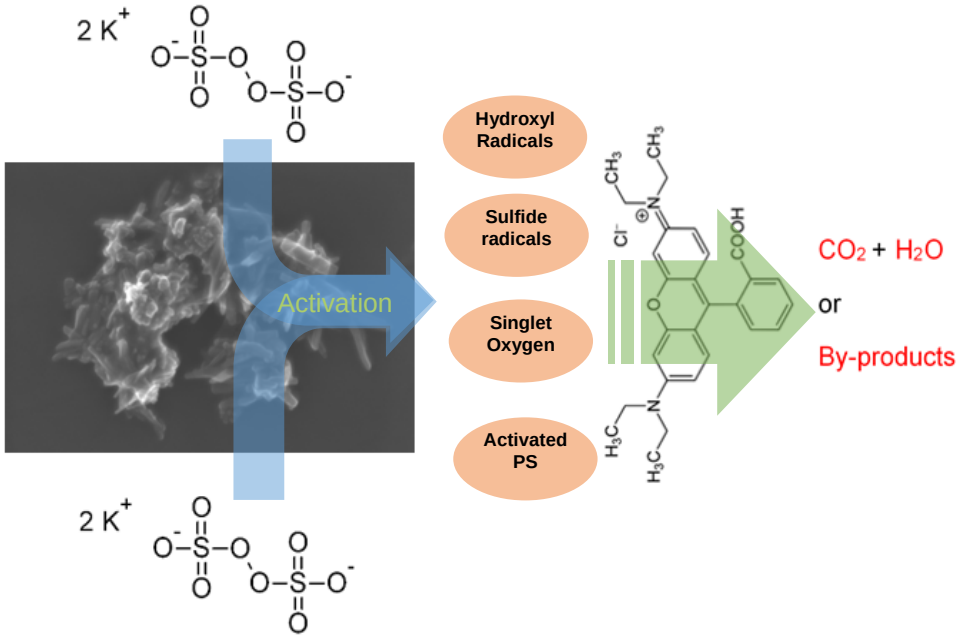


**Fig. 4. 1.** The main mechanisms involved in the degradation of RhB using CuO/PS treatment system. Activation of PS results in the formation of oxidation agents such as sulfate ($SO4^{\bullet-}$) radicals, hydroxyl radicals, and singlet oxygen which contribute to the degradation of RhB.

Degradation of RhB using the thermal activation of PS was less efficient compared to the CuO nanomaterials assisted activation of PS for the decomposition of RhB. After 30 min, 48% of RhB was removed using this system and reached 67% after 60 min. By prolonging the experiments to 120 min, 96% of the RhB was removed from the medium. However, no significant changes in the colour were observed as can be observed in Fig. 4.2. In this case, it is assumed that the thermal activation of PS is not efficient enough to produce oxidation agents for the efficient decomposition of RhB into the final products. The peak that appeared at 514 can also be considered as the main by-product of the RhB

transformation using this system. This peak can be associated with the formation of *N*-ethylrhodamine [228,229]. Figure 4.2 represents the possible transformation product of RhB using the thermal activation of PS (associated with the peak that appeared at 514 nm).

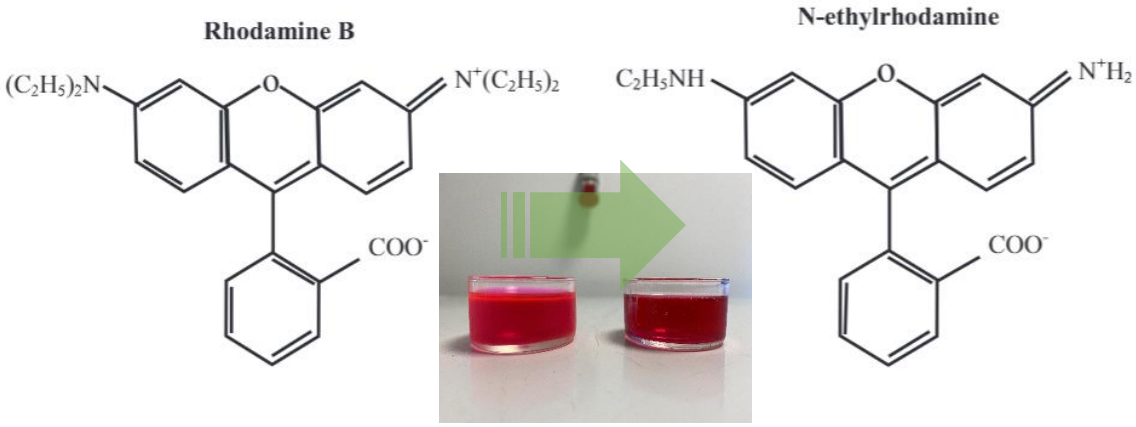


**Fig. 4. 2.** Possible transformation product of RhB when a thermal activation was used to generate the oxidation agents from PS under the operating condition of $[PS]_0$=5 mM, CuO=0.0 g/L, pH=7 and temperature=45 °C.

Considering that the toxicity studies were performed in the ASTM medium, the conditions that resulted in the complete degradation of RhB were applied for the treatment of the synthetic effluents prepared using the ASTM medium. This can better simulate the conditions of the real effluents.

There are several studies in the literature stating that the generation of oxidative radicals and their reaction with target pollutants can be negatively affected by the ionic strength of the effluents [230]. The results of the present study can also confirm these findings.

Various methods have been tested to deal with effluents with high ionic strength. However, it seems that a single chemical or biological method can not result in the effective treatment of the effluents with a high degree of ionic strength. Each of the treatment methods suffers from significant drawbacks. According to the existing literature, biological methods are facile and cost-effective to deal with a wide range of effluents including municipal wastewaters [231,232]. However, when dealing with effluents of high ionic strength or with toxic organic compounds, they normally fail to treat the effluents [233–235]. For instance, the growth of non-

halophiles can be highly inhibited with the presence of sodium chloride [236]. This can potentially lead to lower the efficiency of the biological treatment systems to treat such effluents. Hence, there has been a need to dilute the wastewaters of high salinity before treatment with biological treatments which can result in the consumption of a large amount of water, and increasing the volume of the effluents to be treated. This also can potentially lead to an increase in treatment costs.

Thus, in the present thesis, it was attempted to develop a combined advanced oxidation process to treat the effluents with high salinity. To this end, the activation of PS using a thermal treatment was adopted to generate the oxidative radicals (Fig. 4.3). In addition, thermal activation of PS was coupled with the catalytic activation of CuO nanomaterials to maximize the generation of oxidative radicals for the efficient degradation of RhB.

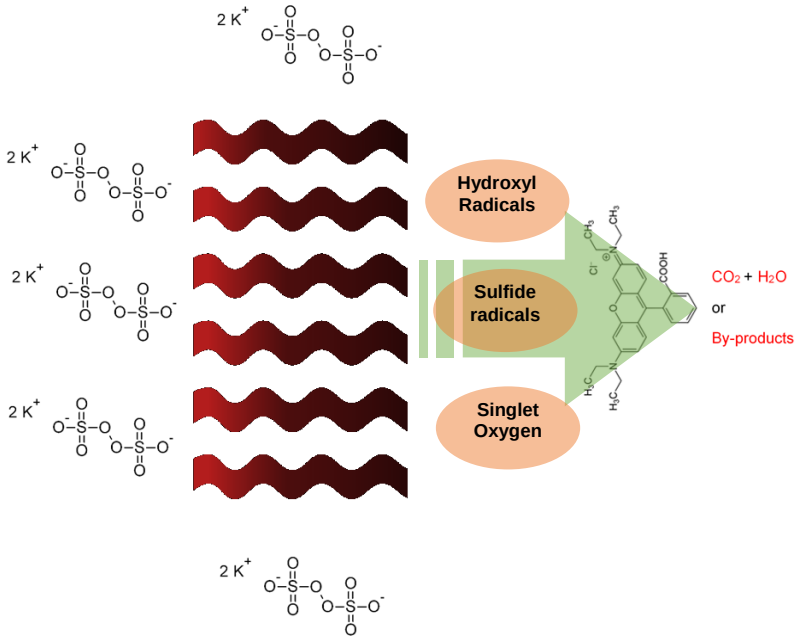


**Fig. 4. 3.** A schematic of the mechanisms involved in the thermal activation of PS for the degradation of RhB.

One of the main hypothesis of this thesis was to study the effectiveness of the developed AOPs on the toxicity removal of the treated effluents. The reusability of the effluents after being treated is considered as one of the most important sustainability pillars when selecting a treatment method among the existing alternatives. Based on the effectiveness of the treatment methods applied, various applications such as agricultural or cleaning purposes can be desired. However, to be reusable, the effluents should present no or a low ecotoxicity to ecological receptors. Although there are a number of physico-chemical methods that have been developed so far for the treatment of industrial effluents, there is only a very limited number of reports discussing their effects on the toxicity of the effluents. Table 4.1 shows some examples of studies performed on the toxicity of the effluents before and after treatment with various biological and physico-chemical methods. According to this table, it is suggested that in general the biological treatment methods are not efficient enough to deal with the pollutant laden with recalcitrant organic compounds and contaminants of emerging concern (CECs) such as pharmaceuticals [237]. Adsorption with activated carbon and application of ozone-based advanced oxidation processes have been also indicated efficient for the treatment of industrial effluents but with sublethal toxic effects to *D. magna* [220].

In the present study, the synthetic effluent (with 50 mg/L of RhB) caused an extremely high lethal toxicity to *D. magna* and *B. calyciflorus*, as all animals exposed to 100% of the effluent before treatment died within a 24 h period of exposure. This was an expected result, given that the $LC_{50}$ of RhB reported in the literature for several freshwater species of invertebrates are lower than the concentration used in the effluent [8]. Rowiński and Chrzanowski, (2011) reported an $LC_{50,24h}$ of RhB for *Thamnocephalus platyurus* of 8.09 mg/L while Skjolding et al. (2021) reported $LC_{50}$ of RhB between the range of 14 to 24 mg/L for three freshwater species (*Raphidocelis subcapitata*, *D. magna* and *Danio rerio*), being the $LC_{50,48h}$ for *D. magna* 24 mg/L.

A high lethal toxicity was also observed for the effluent after treatment with both 5 mM and 1mM of PS, for *D. magna* and *B. calyciflorus* assays, respectively. Actually, for the rotifer species, the toxicity of the treated effluent ($LC_{50}$ = 8.24%)

increased compared to the non-treated effluent ($LC_{50}$ = 44.3%). It is suggested that this observed mortality was not due to the presence of residual RhB, since it was shown that the CuO/PS treatments were very efficient in removing RhB (more than 90% of RhB was removed in the two scenarios), thus, if any residual RhB remained in the treated effluent it would be at concentrations much lower (< 5 mg/L) than the ones expected to cause mortality in *D. magna* and *B. calyciflorus*. Considering the high lethal toxicity caused by PS (at a concentration of 5 mM and 1 mM, for daphnia and rotifer, respectively) to the two species it is hypothesised that part of the mortality observed in the treated effluent was due to the presence of this compound. Results published in the scientific literature suggest PS be highly toxic to biota; Olmez-Hanci et al., (2014) found that 2.5 mM of potassium PS caused 85% of immobilization (surrogate endpoint of mortality) in *D. magna* after 48h of exposure. Adding to PS, it is also suggested that CuO nanoparticles may have induced some lethal toxicity, namely for *D. magna*. Neonates of this species exposed to 0.5 g/L of CuO died within 24 h, and though the precipitation of CuO decreased the observed mortality in *D. magna*, it was still high at the end of the assay. These results are in line with toxicity data of CuO nanoparticles reported in the literature for *D. magna* and other freshwater organisms; Blinova et al., (2010) computed an $LC_{50,48h}$ of 2.6 mg/L CuO for *D. magna*, a value more than one order of magnitude lower than the concentration used in the present study to treat the effluent. Rotini et al., (2018) also indicated that CuO nanoparticles can bring an $LC_{50,48h}$ of 16.94 ± 2.68 mg/L to rotifers (*Brachionus plicatilis*). This toxicity may be due both to the nanoparticles and also the Cu ions. It has been indicated in the literature that Cu ions can be released from CuO and some parameters such as pH and the properties of materials such as crystallinity are very important in the release of Cu ions [235]. This phenomenon can cause toxic effects to the livingorganisms. To eliminate the effects of the Cu ions, the treated effluents were the subject of elevating the pH to precipitate the Cu ions released from CuO nanomaterials. According to the literature, certain metallic elements can be precipitated in specific pHs [236]. For Cu, the best-compromised pH is 8.5-9.5 for copper. Hence the pH of the treated effluents was increased to 9 and after filtration

to remove the precipitates, the pH of the remaining effluents was adjusted to the desired pH for the toxicity tests (i.e., 5.87 and 7.5).

Adding to the direct toxicity of PS, CuO nanoparticles and the Cu ion released by them, it is also hypothesised that intermediate compounds could have been formed during the AOPs for the treatment of the effluent, which may as well be responsible for the observed toxicity in *D. magna* and *B. calyciflorus*. For example, Krawczyk et al., (2020) studied, among others, the use of peroxydisulfate (PDS) for the treatment of a textile effluent contaminated with dyes. He observed that the photocatalysis of PDS produced sulphate radicals, which in turn reacted with the dye present in the effluent leading to the formation of several by-products, mainly derivatives of hydroxylated anthraquinone (the used dye). These authors studied the toxicity of these by-products to *D. magna* and other freshwater biotas and demonstrated that they could significantly impair the survival of the organisms. Considering this study, it is acceptable to assume that similarly, some byproduct could have been formed by the reaction of PS with the sulfate ions (or other ions) present in the AOP treatment of the RhB synthetic effluent, being also responsible for the toxicity observed in the treated effluent. According to these results, it is suggested that the other oxidant compounds should be considered to be used in AOPs to treat (waste)water effluents, as well the concentrations of CuO must be adjusted or the removal of these nanoparticles and metallic ions should be improved to allow obtaining a treated effluent with no to low environmental toxicity.

This strategy is also feasible for real applications because most of the effluents discharged from the production activities are of high temperatures and there is no need to apply an external source of energy to elevate the temperature [238].

Following the obtained results in the present work, some research needs and directions can be proposed for future studies:

- Preparation of the CuO nanomaterials from the natural resources instead of the chemical reagents using the synthesis method employed in this study. This can potentially increase the sustainability of the CuO for the treatment of industrial effluents.

- To develop technologies for the immobilization of CuO when used for the treatment of industrial effluents to prevent their release into the environment.
- To develop efficient post-treatment technologies to remove/recover the chemical compounds which are responsible for the toxicity of the treated effluents using CuO/PS treatment systems.
- To apply the results achieved from this study for the treatment of real effluents and to study the toxic effects of the real industrial effluents before and after treatment with the mentioned advanced oxidation processes.
- To extend the ecotoxicological studied to long-term studies to have a better understanding of the probable toxic effects of the treated effluents using the advanced oxidation processes.
- Given that some of the compounds formed during the AOPs may be more toxic than the parent compounds, running an ecotoxicity assay at different stages of AOP may help to identify which are the compounds responsible for the ecotoxicity observed at the end of the treatment, thus, helping in the process of ameliorating the AOP.
- Ecotoxicity assays with species representative of different trophic and functional levels are important given their differential sensitivity to different types of chemicals
- Given main aim for treatment processes of effluents is to enable their safe release into the environment and reuse of the water, AOP must be very efficient in removing the chemicals and the toxicity, therefore, the characterization of the efficiency on ecotoxicity removal should be performed with chronic toxicity assay.

**Table 4. 1.** Example studies performed on the toxicity of the wastewaters treated with various biological and physico-chemical methods.

| Wastewater | | Treatment Technology | | Toxicity Assay | | | Ref. |
|---|---|---|---|---|---|---|---|
| **Origin** | **Pollution load** | **Type** | **Efficiency** | **Type** | **Microorganism** | **Observations** | |
| Meat by-products processing | COD*: 8308 ± 1823 mg/L | Aerobic Sequencing Batch Reactor | 98.7% | Inhibition of light emission | Marine bacteria of the species *Vibrio fischeri* | While the effluents represented high toxic effects (EC50* < 60%), treated effluents demonstrated low or no toxicity (EC50 > 82%). | [239] |
| Pharmaceutical effluents | - Acetaminophen: 550–38000 ng/L - - Caffeine: 13000–100000 ng/L - Ciprofloxacin: 420–2700 ng/L | Various treatment technologies including biological, physical, advanced chemical oxidation, and a combination of two or more of them. | - <50% for biological treatments. - >95% for activated carbon and ozonation. | Larval zebrafish behaviour | larval zebrafish | No significant behavioural alterations were observed in the organisms exposed to extracts of sewage effluent. | [237] |
| Various types of effluents | Different pollution loads | Ozonation and activated carbon | Over 80% | Various acute and chronic toxic effects | Various organisms | - Ozonation or activated carbon treatment methods are efficient for toxicity removal. - Ozonation generates toxic transformation products that can be removed by a post-treatment. | [240] |
| Twelve industrial park wastewater treatment plants | Different pollution loads | Sewage wastewater treatment | Not specified | a) Bioluminescence inhibition b) Acute toxicity c) Genotoxicity d) Cytotoxicity | a) *Photobacterium phosphoreum* T3 spp. b) *Euglena gracilis*, *Tetrahymena Thermophila and D. magna* straus c) *Vicia faba* *d) Human hepatoma cell line HepG2* | - Majority of the anaerobic-anoxic-oxic ($A_2$/O)-based processes demonstrated good removal efficiencies of wastewater toxicity. - Sequencing batch reactor (SBR)-based processes represented the lowest toxicity removal efficiency among the studied methods | [241] |

* COD: Chemical Oxidation Demand, EC: Effective Concentration.

**Table 4.1.** Continued.

| Wastewater | | Treatment Technology | | Toxicity Assay | | | Ref. |
|---|---|---|---|---|---|---|---|
| **Origin** | **Pollution load** | **Type** | **Efficiency** | **Type** | **Microorganism** | **Observations** | |
| Textile industry effluents | Not specified. | Sequential aerobic treatment | 20-30% | Lethal and sub-lethal (i.e., feeding inhibition and immobilization) tests. | *Aliivibrio fischeri, Raphidocelis subcapitata, D. magna and Lemna minor* | The ecotoxicological data confirmed that the raw textile effluent was very toxic, with *A. fischeri* being the most sensitive organism<br>While the toxicity of the effluent collected after the treatment performed by the textile company was clearly reduced, we still recorded sublethal toxicity to *D. magna*. | [220] |
| Two sewage wastewater treatment plants | Not specified | Biological treatments including: a) MLE (modified Ludzack-Ettinger), and b) aerobic-anaerobic-oxidation) | 19.6% and 74.44% reduction in suspended solids (SS) by MLE and aerobic-anaerobic-oxidation processes, respectively. | - Acute toxicity (immobility for mortality)<br>- Chronic toxicity (reproduction effect for estrogenicity) | *Daphnia magna* | - Acute $EC_{50}$ of influents for MLE and aerobic-anaerobic-oxidation processes were 54.13 ± 32.64% and 30.38 ± 24.96%, respectively.<br>- The $EC_{50}$ reduced to 96.49 ± 7.84% and 100% after treatment.<br>- Acute toxicity reduction was correlated with SS concentration.<br>- Lethal effect reduced after treatment. | [242] |

# Annex A

## A.1) Scientometric analysis

Figure A.1 presents various document types published in this field. According to the results achieved, research papers share around 87% of all the documents published in this field followed by the proceeding papers with 6% of the publications. Reviews also share about 4% of all the published documents in the literature.

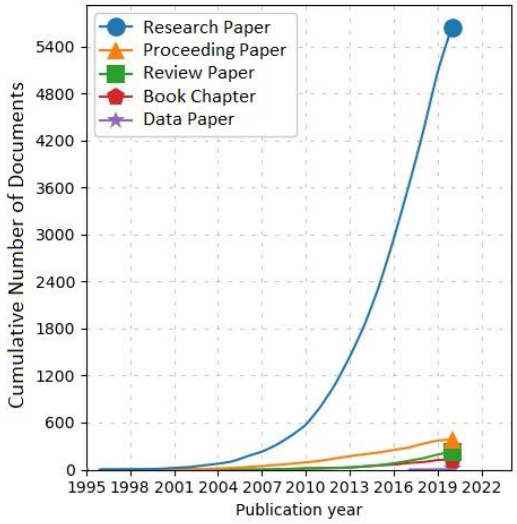


**Fig. A. 1.** The share of the various types of documents published in the literature on the application of ENMs for wastewater treatment. Scientopy tool was utilized to analyze the data.

Fig. A.2, and Table A.1 present the contribution of the authors for the production of the scientific documents on the application of engineered nanomaterials for water and wastewater treatment.

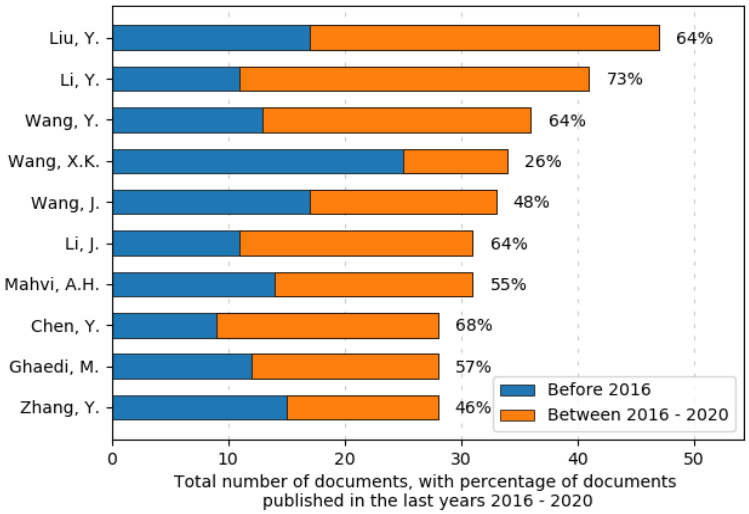


**Fig. A. 2.** Contributing authors in the publications on the application of ENMs for wastewater treatment. Scientopy tool was utilized to analyze the data achieved.

**Table A. 1.** Details regarding the contributing authors in the publication of scientific documents on the application of ENMs for wastewater treatment.

| Position | Author | Total | Sample document |
|---|---|---|---|
| 1 | Liu, Y. | 47 | [243] |
| 2 | Li, Y. | 41 | [97] |
| 3 | Wang, Y. | 36 | [244] |
| 4 | Wang, X.K. | 34 | [245] |
| 5 | Wang, J. | 33 | [246] |
| 6 | Li, J. | 31 | [247] |
| 7 | Mahvi, A.H. | 31 | [248] |
| 8 | Chen, Y. | 28 | [249] |
| 9 | Ghaedi, M. | 28 | [250] |
| 10 | Zhang, Y. | 28 | [128] |

In terms of the contribution of various organizations, Islamic Azad University (Iran), Chinese Academy of Science (China) and the University of Tehran (Iran) have occupied the first ranks (Fig. A.3) indicating the fact that they have already spent high degrees of investments probably to address the need for sustainable technologies to deal with the produced effluents, which are considered among the most important environmental issues in developing countries.

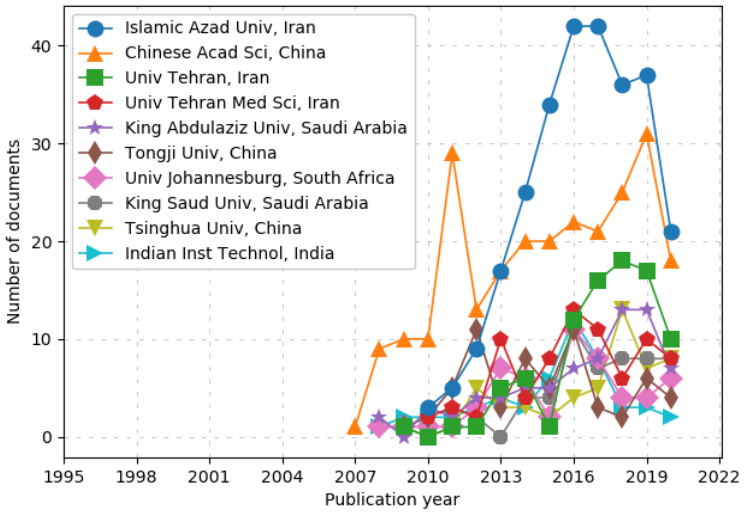


**Fig. A. 3.** Contribution of various organizations for the publication of scientific documents on the application of ENMs for wastewater treatment, extracted using Scientopy tool.

Table A-2 presents the most cited documents published in the literature on the application of ENMs for water treatment. Based on the information presented in this Table, it can be stated that all the highly cited papers are review papers and there are not any research papers among the highly cited papers. Although review papers are to conclude the previously studied paper and present a global picture of the progress in any scientific area, they usually do not present any rank for the most effective research papers in order to be able to identify the trends in the field.

**Table A. 2.** The most cited documents on the application of ENMs for the treatment of wastewaters.

| Title | Publication year | Citations (WoS) | Ref. |
|---|---|---|---|
| Self-assembled 3D flowerlike iron oxide nanostructures and their application in water treatment | 2006 | 1340 | [251] |
| Use of iron oxide nanomaterials in wastewater treatment: A review | 2012 | 1071 | [252] |
| Applications of nanotechnology in water and wastewater treatment | 2013 | 1001 | [253] |
| A review of water treatment membrane nanotechnologies | 2011 | 970 | [254] |
| Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: A review | 2013 | 766 | [255] |

## A.2) Toxicity tests

Figure A.4 represents the microscopic images of the *D. magna* before treatment, and after 24 h of the toxicity tests in the after treatment condition.

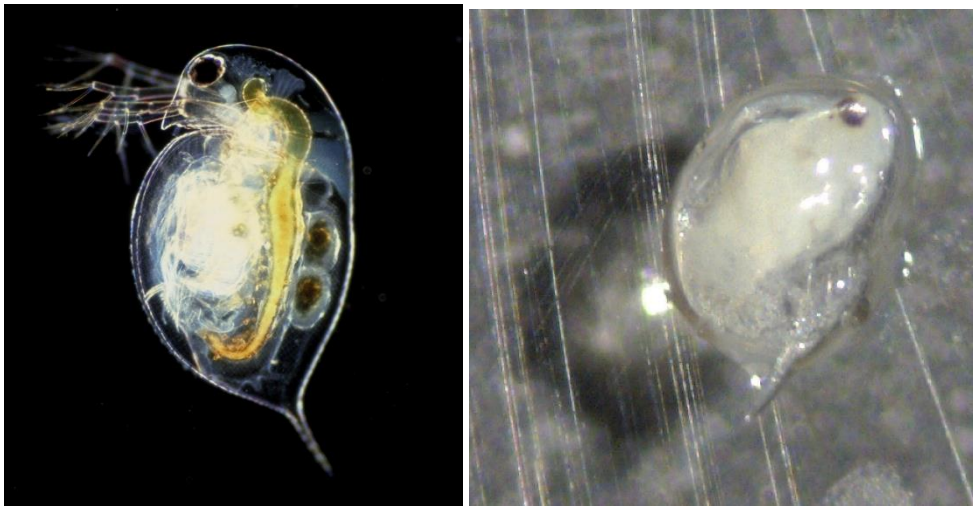

**Fig. A. 4.** *D. magna* (alive and healthy) (left), and the died *D. magna* after 24 h of the tests in the after treatment condition.

## References


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