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A review of research trends on the usage of photocatalysis for wastewater treatment: bibliometric analysis

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Abstract

Photocatalysis is seen as a viable alternative to treating water pollution, due to its flexibility, low cost, and ability to use visible light which is a plentiful and free energy source. Hence, determining the topics of interest and widening collaboration networks will go a long way in improving research in this field. In this study, we aimed to analyze the global research trends on the usage of photocatalysis for wastewater treatment using bibliometric analysis, centered on the outputs of publications, co-authorships, countries of affiliation, and author's keyword co-occurrences. Bibliometric analysis is a review method that is well-known and more conversant to Social Science. Employing it in Physical Science, which is rarely seen, will provide an avenue and yet another method of determining common research topics as well as the potential opportunities and future research in the field. A potential hybrid review paper of great importance to future research in the area will be produced. A total of 1373 articles published within 27 years between 1993 and 2020 were extracted from the Scopus database. In the beginning, less attention was given to the said topic, because after the oldest article was published in 1993, there was no record of other publications until after 5 years (1998). However, from 2002 there was a growing interest in research in that field, with a cumulative increase every year to date, except for a few years with fewer publications. Meanwhile, the number of publications has risen significantly from 2017 to 2020, with an increase of more than 70 publications every year; this is expected to increase rapidly in the coming years. Recently researchers are focusing on developing efficient photocatalysts for contaminants of emerging concern, like pharmaceutical and refinery wastewater, however, the usage of conducting polymers to produce nanocomposite which was found to be very effective is still lagged in wastewater treatment, as such it will be a good area of future research on effective photocatalysts for wastewater treatment.

Keywords Bibliometric analysis · Conducting polymers · Photocatalysis · VOSviewer · Wastewater

Introduction

The industrial revolution brought about a wide range of problems including water pollution, leading to a significant impact on the environment and living things. Direct

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discharge of industrial effluents into waterways makes them unfit for consumption, as the water may receive nonbiodegradable and undesirable chemicals from the effluents which proved to be hazardous, and death by pollutionrelated diseases is increasing day by day (Pawar and Lee

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2015; Chowdhary et al. 2020; Bruce and Limin 2021). Large effluents discharged by various industries into waterways are extremely poisonous. This leads to the contamination of surface and groundwater as it contains a high concentration of heavy metals and other harmful organic compounds, these compounds are believed to be carcinogenic, mutagenic, and in some cases teratogenic to living things (Hussain and Wahab 2018; Hitam and Jalil 2020). Coagulation, flocculation, sedimentation, filtration, and disinfection are ancient water remediation methods, but they are slow and ineffective. Apart from being unsustainable with the environment, some of these traditional approaches often necessitate a large amount of space, resulting in chemical waste and, in some cases, failing to eliminate a sufficient amount of hazardous contaminants, resulting in the production of secondary harmful products (Mani and Bharagava 2016; Hitam and Jalil 2020).

Advanced oxidation processes (AOPs) are among the new facile water treatment methods developed, they have gained prominence as a result of their effectiveness and ability to degrade pollutants in water via a redox reaction (Hodges et al. 2018; Khan et al. 2020; Santos et al. 2022). AOPs are effective for a broad spectrum of pollutants because of their robust nonselective oxidability; and the generation of nonhazardous byproducts like CO₂, H₂O, and other small inorganic ions (Yang et al. 2020). The AOPs are based on the generation and use of hydroxyl radicals (•OH), due to their high reduction potential (2.80 V vs. Normal hydrogen electrode), they can degrade a wide range of organic pollutants, including the most stable ones (Asghar et al. 2015; Li et al. 2021). Ultraviolet (UV) photolysis, hydrogen peroxide photo-Fenton, photo-ozonation, and heterogeneous photocatalysis are the main classes of AOPs. However, the benefit of using sunlight, which is a free source of energy, has increased the popularity of heterogeneous photocatalysis (Ghernaout and Elboughdiri 2020; Zhang et al. 2020; Mishra et al. 2022).

Photocatalysis as one of the techniques of AOPs has emerged as an effective way to speed up the degradation and removal of a wide variety of organic pollutants in contaminated water (Chi et al. 2020; Ma et al. 2022). Apart from its utilization of sunlight which is free and abundant in nature, photocatalysis is considered a low or nonwaste generation method, using highly reactive chemical species with high oxidation capacity to break complicated structures (Tomar et al. 2020; Choudhury 2021). Fujishima and Honda pioneered photocatalysis research in 1972 when they used TiO₂ electrodes in water splitting (Fujishima, A., and Honda 1972). Because photocatalysis can fully mineralize contaminants at low temperatures and pressures, it has gained tremendous popularity in the treatment of polluted gaseous and liquid wastes (Hitam and Jalil 2020; Sharma et al. 2020; Akiyama et al. 2022).

Bibliometric analysis is used to analyze and determine past and present research trends in a particular field of knowledge centered on academic repositories' research outcomes (Md Khudzari et al. 2018; Macías-Quiroga et al. 2020; Anuar et al. 2021; Tan et al. 2021). Scopus is considered the most extensive collection of peer-reviewed articles on a wide range of topics, as such, it is mostly used in bibliometric analysis to cover more topics that may not be available in other databases (Md Khudzari et al. 2018; Garrido-Cardenas et al. 2020; Cascajares et al. 2021). Despite the increasing interest in the field of wastewater treatment using photocatalysis, there are limited studies on the analysis of scientific publications done on the said subject matter. Both Garrido-Cardenas et al. 2020 and Macías-Quiroga et al. 2020 reported the research trends on the use of advanced oxidation processes for wastewater treatment in which photocatalysis was part of the discussion, however, the former presented the trend between the period of 1980 to 2018 while the latter reported between 1990 to 2018 with emphasis on the Ibero-American region.

Meanwhile, Singh and Borthakur 2018 reported a bibliometric and comparative analysis between the biodegradation and photocatalytic degradation of organic pollutants during the period between 1997 and 2017 (20 years), they stress the importance and capability of photocatalysis as one of the most promising techniques for the degradation of a variety of organic liquid and gaseous contaminants. In this review, the bibliometric analysis was performed to determine the emerging trends of scientific publications regarding photocatalytic wastewater treatment globally; this study provides insight into the current research on photocatalysis and common research topics as well as the potential opportunities and future research in the field.

Materials and methods

Description of the study area

Unlike review papers which usually evaluate a topic's most recent trends, problems, and future research directions, the study of bibliometric analysis is a deterministic approach for evaluating global research directions in particular fields based on the literature found in academic databases (Arsad et al. 2022). Bibliometric analysis is a review method that is well-known and more conversant to Social Science. Employing it in Photocatalysis will provide an avenue and yet another method of determining common research topics as well as the future direction in the field. The Scopus database was used to retrieve the data on January 27, 2021. The study's central theme was research papers that included photocatalysis* "OR photocatalyst*" wastewater treatment in the title and abstract. The first publication was in 1993, and the latest was in 2020. For the quest, the question text was: TITLE-ABS ("photocatalysis*" OR photocatalyst* "wastewater treatment") AND (EXCLUDE (PUBYEAR, 2021)) AND (LIMIT-TO (LANGUAGE, "English")) AND (LIMIT-TO (SRCTYPE, "j")), it gives 1493 documents. Additional phrases were added to the question string to exclude the review articles from our study, resulting in a total of 208 possible review articles being screened. After screening them we found 120 articles that are actual review articles, to exclude those review papers from the next search results, Scopus paper identifiers (EIDs) of the articles were taken and added to the next search query.

The central query theme's search results were analyzed using the following criteria: year, source, author, affiliation, country/region, subject area, and document type. The ranking was based on the bibliometric metrics such as total publications, total citations, CiteScore, and h-index. In addition, subthemes were also added to explore the output of various photocatalytic materials used in wastewater treatment. The major photocatalytic materials included are heterojunction, semiconductors, polymer, composite, and conducting polymer. The search text for each material was searched independently, using a search text containing precise terms depending on the intended material. For example: (TITLE-ABS ("photocatalysis*" OR "photocatalyst*" "wastewater treatment" AND heterojunction). The search results for the subthemes were examined based on the number of publications published per year. The process of data mining is presented in Fig. 1. Likewise, the table containing the search text used in the data extraction from the database can be seen in Table S1 of supplementary materials.

Central theme (Photocatalysis) 1778 records identifies by "photocatalysis*" OR photocatalyst* "wastewater treatment" in the Title and Abstract

Limit to 2020, English and Journals 1503 records identifies by limiting the search to Journal articles written in English from 1990-2020

Limit to science-related subject 1493 records identifies by limiting the search to Journal articles based on science-related subjects

Excluding review articles 1373 records remains after removing 120 review articles, identified by the Title, Abstract and full text

Sub-theme (Photocatalysis + major topics) The search was refined by adding specific terms to the central theme, to find potential gaps in the area of photocatalysis

Bibliometric maps

The downloaded data of 1373 articles were exported to VOSviewer software which is used in creating and visualizing bibliometric maps. The software used was version 1.6.7 originating from the Centre for Science and Technology Studies, Leiden University, Netherlands. Maps created using the software include countries and author keywords. A link is a connection or relationship that exists between any two objects; each link has an integer that reflects its power, the higher the integer the stronger the link. In the analysis of co-authorship, the number of publications co-authored by those countries is expressed in the strength of the links between them, whereas the total link strength indicates the total strength of a country's co-authorship links with other countries. Likewise, in co-occurrence analysis, the number of publications in which two keywords appear together is indicated by the link strength between author keywords.

Analysis of co-authorship

We included 61 countries in the analysis of co-authorship. The affiliated countries were clustered into 6 continents: Africa, Asia, Australia, Europe, North America, and South America.

Analysis of co-occurrence

Analyses of the co-occurrence of author keywords involve 1000 keywords from 1373 articles. Single synonyms and relatable wordings were skimmed, counted, and re-labeled before importing the keywords into the software. The lowest occurrences of a keyword to be assessed were set to 1 in the software. The average publication, year, number of occurrences, and link strength of the keywords were all viewed in the software.

Photocatalysis applications (subthemes of photocatalysis)

The frequency of research outputs between keyword co-occurrences and total publication of the subthemes were analyzed. The subthemes used are heterojunction, semiconductors, polymer, composites, and conducting polymers. The number of publications on these subthemes was analysed, respectively, to find the potential gap in the usage of photocatalysis in wastewater treatment.

Results and discussion

Development in research interest and publication output

Industries produce a large amount of wastewater into waterways, leading to environmental contamination (Sharma et al. 2022). Regular and conventional water treatment methods are not fast, efficient, and cost-effective (Pincheira et al. 2021). Among the new and easy water treatment methods, photocatalysis is seen as an alternative, due to its effectiveness, the capability to degrade contaminants through a redox reaction, and most importantly, the usage of sunlight which is an abundant and free source of energy (Wang et al. 2022). That is why growing research interest and publications on the treatment of wastewater were focused on photocatalysis. From Fig. 2, it can be seen that within 27 years, a total of 1373 research articles have been published on the usage of photocatalysis in wastewater treatment. In the beginning, less attention was given to the said topic, because after the oldest article was published in 1993, there was no record of other publications until after 5 years (1998). However, from 2002, there was a growing interest in research in that field, with a cumulative increase every year to date, except for a few years with fewer publications like 2004, 2005, 2007, 2009, and 2011. It is important to know that there is a massive increase in the number of publications from 2017 to 2020, with an increase of more than 70 publications every year. As a result, the annual publication is forecasted to grow, as researchers are now focusing on visible-lightdriven photocatalysis because of the abundance of sunlight in nature. The first known photocatalysts were wide bandgap semiconductors (Bitaraf and Amoozadeh 2021). Despite their popularity and effectiveness, they have significant drawbacks of absorption only at UV region, hence limiting

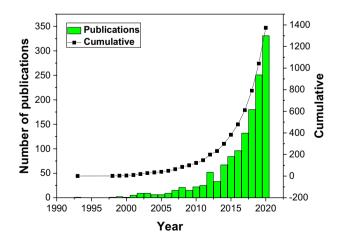


Fig. 2 Annual and cumulative numbers of research articles on photo

their photocatalytic activity (Yang et al. 2022). Besides, it is already known that solar energy comprises only 3-5%UV, whereas 43% of solar energy comprises visible light, therefore a significant amount of solar radiation is lost (Yang et al. 2022). Owing to that factor growing interest and publications were also focused on the visible-light-driven narrow bandgap semiconductors that absorb at visible region.

Interestingly, in 2020, despite the effect of the covid-19 pandemic that cripples research activities almost everywhere in the world, 331 research articles were published, and this is another indicator that there is a growing interest in the research in this area. A quick analysis of most of the research papers published within these years revealed that most of the articles are closed access, meaning that an intended research outputs. Out of all the research articles published as of 2020, only 17% were published as open access, as such, it is advisable to publish more in open access journals to increase the number of citations, attracts more readerships, and wide visibility of the research ideas in the field of wastewater treatment using photocatalysis.

Productive journals

Table 1 showed the results of the top 20 most productive journals, most of the productive journals are published by Elsevier. Chemical Engineering Journal comes first in the list with 63 total publications and the highest total citations of 2616. It has a relatively high CiteScore (15.2), as such, it is not surprising when it has the highest total publications, because usually, CiteScore influenced the decision of researchers in finding journals that suit their new findings in research (Md Khudzari et al. 2018). However, the only journal published by the Royal Society of Chemistry (RSC Advances) is second among the list with 37 total publications and total citations of 727. Journal of Hazardous Materials published by Elsevier is third in the list of most productive journals and also third in the list of journals with the highest total citations (1943), it has a CiteScore of 13.1 and 35 total publications respectively.

Interestingly, Applied Catalysis B: Environmental also published by Elsevier comes forth in the list of most productive journals with 34 total publications, however, it has the highest CiteScore (25.3) among all the 20 journals and falls second in the list of journals with the highest total citation (2100). This revealed that a journal may have a large number of total publications, but not a large number of total citations because of the issue of accessibility. This can be seen in Water Research Journal published by Elsevier, the journal has only 21 total publications and falls at 15th among the most productive journals, but surprisingly it received 1386 total citations making it 4th among the journal with the highest citations.

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Journal of Environmental Chemical Engineering 26 278 6.7 "Magnetically recoverable graphitic carbon nitride and 75 Journal of Photochemistry and Photobiology A: Chem. 26 6.31 5.2 "Magnetically recoverable graphitic carbon nitride and 75 Journal of Photochemistry and Photobiology A: Chem. 26 6.31 5.2 "Treatment of paper mult watewater by 168 Journal of Photochemistry and Photobiology A: Chem. 26 6.31 5.2 "Treatment of paper mult watewater by 168 183 Journal of Photochemistry and Photobiology A: Chem. 26 8.17 8.8 "Solar light" (Sudhaik et al. 2005) 183 Chemosphere 2.5 8.17 8.8 "Solar light induced and TO ₂ assist degradation of 389 389 Journal of Colloid and Interface Science 24 8.9 11.0 "Ultralong Cu(OH) ₂ and CuO nanowire bundles: 88 Journal of Colloid and Interface Science 24 8.3 "Optimization of an and Partification Technology 78 Separation and Purification Technology 24 33 "Optimization of and novice bundles: 88 Total ysis Today 24 33 8.3 "Optimization of and Partification Technology 78	<u>`</u>	Applied Surface Science		781	8.7	"Preparation of photocatalytic Fe ₂ O ₃ -TiO ₂ coatings in one step by metal organic chemical vapor deposition" (Zhang and Lei 2008)		Elsevier
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Chemosphere 25 817 8.8 "Solar light induced and TiO ₂ assisted degradation of 389 Journal of Colloid and Interface Science 24 859 11.0 "Ultralong Cu(OH) ₂ and CuO nanowire bundles: 88 Journal of Colloid and Interface Science 24 839 "Ultralong Cu(OH) ₂ and CuO nanowire bundles: 88 Separation and Purification Technology 24 433 8.3 "Optimisation of an annular photoreactor process for catalytic performance" (Li et al. 2010) 78 Separation and Purification Technology 24 433 8.3 "Optimisation of an annular photoreactor process for catalytic performance" (Li et al. 2010) 78 Catalysis Today 22 672 9.5 "Optimisation of Congo Red using a newly synthesized titain impregnated kaolinite nano-photocatalyst" (Chong et al. 2009) 132 Desalination and Water Treatment 22 672 9.5 "Solar photocatalysis as a tertiary treatment to remove the filtenst" (Bernahou et al. 2011) 27 Desalination and Water Treatment 22 129 2.7 "Removal of polycyclic aromatic hydrocarbons from the filtenst" (Salihoglu et al. 2012) 27 Desalination and Water Treatment 22 129 2.7 "Removal of polycyclic aromatic hydrocarbons from the filtenst" (~	Journal of Photochemistry and Photobiology A: Chem- istry		631	5.2	"Treatment of paper pulp and paper mill wastewater by coagulation – flocculation followed by heterogeneous photocatalysis" (Rodrigues et al. 2008)	183	Elsevier
Journal of Colloid and Interface Science2485911.0"Ultralong Cu(OH)2, and CuO nanowire bundles:88Separation and Purification Technology244338.3"Optimisation of an annular photoreactor process for degradation of Congo Red using a newly synthesized titania impregnated kaolinite nano-photocatalyst"88Separation and Water Treatment226729.5"Solar photocatalysis as a tertiary treatment to remove emerging pollutants from wastewater treatment plant effluents" (Bernabeu et al. 2011)132Desalination and Water Treatment221292.7"Removal of polycyclic aromatic hydrocarbons from municipal sludge using UV light" (Salihoglu et al. 2012)27	~	Chemosphere		817	8.8	"Solar light induced and TiO ₂ assisted degradation of textile dye reactive blue 4" (Neppolian et al. 2002)	389	Elsevier
Separation and Purification Technology244338.3"Optimisation of an annular photoreactor process for degradation of Congo Red using a newly synthesized triania impregnated kaolinite nano-photocatalyst"78Catalysis Today226729.5"Solar photocatalysts as a tertiary treatment to remove form wastewater treatment plant effluents" (Bernabeu et al. 2011)132Desalination and Water Treatment221292.7"Removal of polycyclic aromatic hydrocarbons from 2012)27Desalination and Water Treatment221292.7"Removal of polycyclic aromatic hydrocarbons from 2012)27Desalination and Water Treatment2122.7"Removal of polycyclic aromatic hydrocarbons from 2012)27	0	Journal of Colloid and Interface Science		859	11.0	"Ultralong Cu(OH) ₂ and CuO nanowire bundles: PEG200-directed crystal growth for enhanced photo- catalytic performance" (Li et al. 2010)	88	Elsevier
Catalysis Today 22 672 9.5 "Solar photocatalysis as a tertiary treatment to remove 132 Catalysis Today emerging pollutants from wastewater treatment plant emerging pollutants from wastewater treatment plant Desalination and Water Treatment 22 129 2.7 "Removal of polycyclic aromatic hydrocarbons from 27 Desalination and Water Treatment 22 129 2.7 "Removal of polycyclic aromatic hydrocarbons from 27 Desalination and Water Treatment 22 129 2.7 "Removal of polycyclic aromatic hydrocarbons from 27	-	Separation and Purification Technology		433	8.3	"Optimisation of an annular photoreactor process for degradation of Congo Red using a newly synthesized titania impregnated kaolinite nano-photocatalyst" (Chong et al. 2009)	78	Elsevier
Desalination and Water Treatment 22 129 2.7 "Removal of polycyclic aromatic hydrocarbons from 27 nunicipal sludge using UV light" (Salihoglu et al. 2012)	12	Catalysis Today		672	9.5	"Solar photocatalysis as a tertiary treatment to remove emerging pollutants from wastewater treatment plant effluents" (Bernabeu et al. 2011)	132	Elsevier
	2	Desalination and Water Treatment	22	129	2.7	"Removal of polycyclic aromatic hydrocarbons from municipal sludge using UV light" (Salihoglu et al. 2012)	27	Desalination Publications

Tabl	Table 1 (continued)						
S/N	S/N Journal	ΤΡ	IP TC	Citescore (2019)	Citescore (2019) The most cited article (reference)	Times cited Publisher	Publisher
14	14 Journal of Alloys and Compounds	21	21 376	7.6	"Uniformly distributed anatase TiO ₂ nanoparticles on graphene: Synthesis, characterization, and photocata-lytic application" (Bai et al. 2014)	60	Elsevier
15	Water Research	21	1386 14.5	14.5	"Application of the colloidal stability of TiO ₂ particles for recovery and reuse in solar photocatalysis" (Fernández-Ibáñez et al. 2003)	195	Elsevier
16	Journal of Cleaner Production	20	415	10.9	"Fabrication of fluorine doped graphene and SmVO ₄ based dispersed and adsorptive photocatalyst for abatement of phenolic compounds from water and bacterial disinfection" (Shandilya et al. 2018)	79	Elsevier
17	17 Ceramics International	17	355	6.1	"Morphology controlled hydrothermal synthesis and photocatalytic properties of ZnFe ₂ O ₄ nanostructures" (Dhiman et al. 2016)	51	Elsevier
18	Journal of Materials Science	16	249	6.2	"An investigation on synthesis and photocatalytic activity of polyaniline sensitized nanocrystalline ${\rm TiO}_2$ composites" (Min et al. 2007)	66	Springer Nature
19	Water Science and Technology	15	118	2.9	"Dye photo-enhancement of TiO ₂ -photocatalyzed degradation of organic pollutants: The organobromine herbicide bromacil" (Feigelson et al. 2000)	25	IWA Publishing
20	ACS Sustainable Chemistry and Engineering	14	782	<i>L</i> .6	"Self-Assembly Reduced Graphene Oxide Nanosheet Hydrogel Fabrication by Anchorage of Chitosan/ Silver and Its Potential Efficient Application toward Dye Degradation for Wastewater Treatments" (Jiao et al. 2015)	111	American Chemical Society

ACS Sustainable Chemistry and Engineering journal published by the American Chemical Society with a 9.7 CiteScore is 20th on the list. It has total publications and total citations of 14 and 782 respectively. CiteScore is a metric used in tracking journal performance based on the citation data available in the Scopus database. According to the CiteScore 2019 report, almost all the journals have a CiteScore of more than 5, except for 3 journals; Environmental Science and Pollution Research (4.9), Desalination and Water Treatment (2.7), and Water Science and Technology (2.9).

Leading countries, top institutions, and collaborations

Figure 3 depicts the top 20 most productive countries in the field of photocatalysis for wastewater treatment. Almost 38% of the total publications globally regarding this field are contributed by China, with 516 total publications. India the second-most populous country in the world was also the second-most productive country in the world, having a total publication of 86. Regarding the most productive Institution in China, Jiangsu University can be considered as the most productive with 25 total publications as can be seen in Table 2. However, our result revealed that there are 88 total publications affiliated with the Ministry of Education China, and 39 total publications affiliated with the Chinese Academy of Sciences. Ministry of Education China cannot be regarded as one institution because it comprises so many academic and nonacademic institutions, likewise, since the Chinese Academy of Sciences has 124 branches, comparisons will be hard and prejudiced (Md Khudzari et al. 2018).

In India, however, the most productive institution is Anna University with 5 total publications, the number might appear very small when compared with the total publications in the whole country, which may not be unrelated to the large numbers of academic research institutions in India. Figure 3 shows the relationship between countries. In VOSviewer, the closer countries are situated close to each other the stronger their interaction, and the stronger the link between two countries, the ticker the line connecting them. The highest number of countries per region comes from Asia (25), followed by Europe (17), Africa (8), South America (5), North America (4), and Australia (2).

Meanwhile, co-authorship results showed that China is the most affiliated country linked to 28 countries/territories with 101 times co-authorship. China was followed by Spain (18 links, 34 co-authorships), India (14 links, 32 co-authorships), Malaysia (11 links, 14 co-authorships), the United States (10 links, 43 co-authorships), the UK (10 links, 19 co-authorships), and the rest. China being the most affiliated country may not come as a surprise, because of the rate at which they provide postgraduate scholarships globally through their various academic institutions, and most importantly through the Chinese Academy of Science and Ministry of Education China. This contributes largely to the availability of diverse research partners and the high rate of foreign postgraduates/researchers, which in turn led to a substantial increase in their international collaboration.

Highly cited articles

Citation count is a measure of the impact of academic works, it is generally referring to how many times a journal article, book, or author is cited by other journal articles, books, or researchers. Table 3 presents the 20 most highly cited articles on the usage of photocatalysis for wastewater treatment. The 1st in the list was an article written by Xuming Zhang and coworkers in 2013, even though it was published 8 years

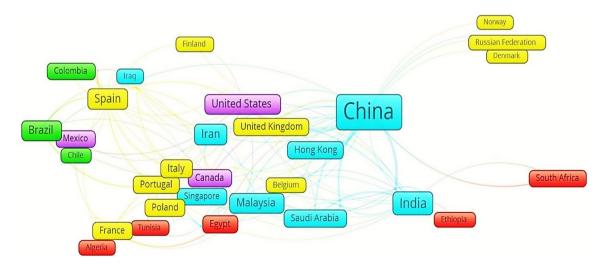


Fig. 3 Bibliometric map based on co-authorships catalysis for wastewater treatment from 1990 to 2020

Table 2Topmost productivecountries with the institutionshaving highest publications

Rank	Country	TP	Affiliation
1	China	516	Jiangsu University (25)
2	India	86	Anna University (5)
3	Iran	55	Tarbiat Modares University (9)
4	Spain	33	Universidad Rey Juan Carlos (7)
5	Brazil	33	Universidade Estadual de Maringa (6)
6	Malaysia	28	Universiti Teknologi Malaysia (8)
7	South Korea	25	Inha University, Incheon (4)
8	Taiwan	16	National Taiwan University (3)
9	Italy	15	Università di Salerno (8)
10	United States	14	University of South Florida, Tampa (2)
11	Canada	12	University of Calgary (2)
12	Australia	10	University of Technology Sydney (3)
13	Germany	10	Universität Bayreuth (2)
14	Egypt	9	American University in Cairo (3)
15	Pakistan	7	University of Agriculture, Faisalabad (2)
16	Hong kong	7	Hong Kong University of Science and Technology (4)
17	Portugal	6	Universidade do Porto (3)
18	France	6	CNRS Centre National de la Recherche Scientifique (2)
19	Saudi Arabia	3	King Saud University College of Science (1)
20	United kingdom	2	Loughborough University (1)

ago, it has a total citation (TC) of 785, out of which global citation (GC) was 783, and local citation (LC) of 2. This is not surprising because plasmonic photocatalysis has recently initiated rapid progress in enhancing photocatalytic activity under visible light, leading to the opportunity of using sunlight for energy generation and environmental wastewater treatment. Another factor that may contribute to such high number of citations is its accessibility, it was pointed out earlier that open-access articles usually receive much more citation, because they are always available for free, unlike close access article that has to be paid before accessibility.

The 2nd on the list is an article by Jian Long Wang and Le Jin Xu in 2012, it receives 636 TC, out of which 629 is for GC, and 7 for LC. However, it is a close-access article that may reduce its number of citations to some extent. The 3rd in the list is a close access article, it is a research article that presents an interesting method of tuning large bandgap photocatalyst (TiO₂) to absorb visible light and reduce its rate of recombination, by employing noble metal (gold). This article was written by X. Z. Li and F. B. Li has attracted a wide range of readers, it receives 627 TC, out of which 625 are GC and 2 are LC.

The rest of the highly cited articles all have a TC range of 380–166, with a range of local citations of 43–0. Interestingly, the article that falls 14th on the list is the only one that has 0 LC. This is interesting because the authors (Angela Claudia Rodrigues and coworkers), tried to bring a hybrid idea of using photocatalysis along with biological treatment (coagulation-flocculation) in the treatment of paper mill wastewater. This has generated a lot of interest and opened yet another novel idea in the treatment of wastewater; as such it generates a lot of GC. It is important to state that out of the 20 most highly cited articles, only 2 are open access, we, therefore, recommend more publications on open access to aid visibility and increase the rate of citations. Likewise, it is worthy of note that review articles receive much more citations than research articles, because of the brainstorming and critical analysis done in review articles leading to the identification of various research gaps and potential areas in need of attention.

Leading authors

Table 3 presents the top 20 most productive authors in wastewater treatment using photocatalysis, the authors are affiliated with 4 countries namely China (11 authors), Portugal (4 authors), Italy (3 authors), and Spain (2 authors). The first publications range from 2001 to 2017. S. Malato from Spain top the list with 18 total publications from 2001, as well as 1218 total citations and 81 h-index. Liugi Rizzo from Italy is the second most productive author, he has a total of 11 publications since 2007, an h-index of 38, and 585 total citations. Guangming Zeng is ranked 3rd on the list, however, he also has 11 total publications but unlike Liugi Rizzo his first year of publication was 2016. Guangming Zeng with an h-index of 136 and 946 total citations is from Hunan University Changsha, China. Looking at the rate of his citations

S/N	Title	Access	Ref	Year LC	GC	TC	Journal
1	"Plasmonic photocatalysis"	Open	(Zhang et al. 2013b)	2013 2	783	785	Reports on progress in physics
7	"Advanced oxidation processes for wastewater treatment: Formation of hydroxyl radical and application"	Close	(Wang and Xu 2012)	2012 7	629	636	Critical reviews in environmental science and technology
n	"Study of $Au/Au^{3+} - TiO_2$ photocatalysts toward visible photooxidation for water and wastewater treatment"	Close	(Li and Li 2001)	2001 2	625	627	Environmental science and technology
4	"Solar light induced and TiO_2 assisted degradation of textile dye reactive blue 4"	Close	(Neppolian et al. 2002)	2002 5	384	389	Chemosphere
5	"An Investigation of TiO ₂ Photocatalysis for the Treatment of Water Contaminated with Metals and Organic Chemicals"	Close	(Prairie et al. 1993)	1993 11	315	326	Environmental science and technology
9	"BiVO4/CeO2 nanocomposites with high visible-light-induced photocatalytic activity"	Close	(Wetchakun et al. 2012)	2012 6	301	307	ACS applied materials and interfaces
٢	"Construction of high-dispersed Ag/Fe ₃ O ₄ /g-C ₃ N ₄ photocata- lyst by selective photo-deposition and improved photocata- lytic activity"	Close	(Zhu et al. 2016)	2016 17	229		246 Applied catalysis B: environmental
×	"Preparation of Au-BiVO ₄ heterogeneous nanostructures as highly efficient visible-light photocatalysts"	Close	(Cao et al. 2012)	2012 9	214	223	ACS applied materials and interfaces
6	"Construction of iodine vacancy-rich BiOI/Ag@AgI Z-scheme heterojunction photocatalysts for visible-light-driven tetracy- cline degradation: Transformation pathways and mechanism insight"	Close	(Yang et al. 2018)	2018 43	179	222	Chemical engineering journal
10	"New perspectives for Advanced Oxidation Processes"	Open	(Dewil et al. 2017)	2017 14	193	207	Journal of environmental management
11	"Application of the colloidal stability of TiO ₂ particles for recovery and reuse in solar photocatalysis"	Close	(Fernández-Ibáñez et al. 2003)	2003 7	188	195	Water research
12	"Preparation and photocatalytic property of a novel dumbbell- shaped ZnO microcrystal photocatalyst"	Close	(Sun et al. 2009)	2009 3	187	190	Journal of hazardous materials
13	"Treatment of petroleum refinery sourwater by advanced oxidation processes"	Close	(Coelho et al. 2006)	2006 4	185	189	Journal of hazardous materials
14	"Treatment of paper pulp and paper mill wastewater by coagulation-flocculation followed by heterogeneous photo- catalysis"	Close	(Rodrigues et al. 2008)	2008 0	183	183	Journal of photochemistry and photobiology A: chemistry
15	"Application of solar AOPs and ozonation for elimination of micropollutants in municipal wastewater treatment plant effluents"	Close	(Prieto-Rodríguez et al. 2013)	2013 10	170	180	Water research
16	"Engineering of solar photocatalytic collectors"	Close	(Rodríguez et al. 2004)	2004 13	163	176	Solar energy
17	"A TiO ₂ /AC composite photocatalyst with high activity and easy separation prepared by a hydrothermal method"	Close	(Liu et al. 2007)	2007 10	161	171	Journal of hazardous materials
18	"Removing pharmaceuticals and endocrine-disrupting com- pounds from wastewater by photocatalysis"	Close	(Dalrymple et al. 2007)	2007 3	167		170 Journal of chemical technology and biotechnology

Table 3 list of the highly cited papers in wastewater treatment using photocatalysis

166 Journal of materials chemistry A

156

10

2014

(Liang et al. 2014)

Close

heterojunction photocatalysts with

enhanced visible light responsive activity and wastewater

Water research

169

161

 ∞

Year 2009

(Rizzo et al. 2009)

Close

detoxification of an urban wastewater treatment plant effluent

contaminated with pharmaceuticals"

Novel Bi₂S₃/Bi₂O₂CO₃

20

treatment'

"Heterogenous photocatalytic degradation kinetics and

Ref

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Journal

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and h-index he may likely top the list of the most productive authors in near future (Table 4).

The authors that fall 4th–7th in the list all have 9 total publications that started from 2012 to 2016, three of the authors namely Yi Li, Wenlog Zhang, and Zhi Zhu are all from China, while the remaining one (Vincenzo Vaiano) is from Italy. The remaining authors all have at least 6 total publications ranging from 2009 to 2017. It is important to know that about 4 productive authors on the list come from Jiangsu University, Zhenjiang (China), and such can be termed as the most productive institution on the list.

Author keywords

A total of 1000 keywords were identified, with 801 (80.1%) being used once, 304 (30.4%) being used twice, and 199 (19.9%) being used three times. After re-labeling single synonyms words and relatable wordings, 785 keywords had at least one occurrence and the largest set of connected items for the mapping in VOSviewer.

Terminology and concept

'Photocatalysis' was found to be the most frequently used keyword as can be seen in Fig. 4, it has 458 occurrences and 249 links to other keywords. 'TiO₂ particles' is the second most encountered keyword with 204 occurrences and linked to 249 other keywords. The third most encountered keyword is 'wastewater treatment' with 203 occurrences and 236 links to other keywords. The rest are 'photocatalytic activity' (164 occurrences, 214 links), 'photocatalysts' (118 occurrences, 158 links), 'visible light irradiation' (109 occurrences, 88 links), 'nanomaterials' (53 occurrences, 88 links), 'ZnO particles' (50 occurrences, 80 links), 'Advanced oxidation process' (49 occurrences, 87 links), 'adsorption' (46 occurrences, 74 links), and others.

The prevalence of TiO₂ and ZnO particles in the most encountered keywords might not be surprising, because TiO₂ and ZnO were among the first photocatalyst known, as such their properties and usage were studied extensively in various photocatalytic applications. To date, there is so much research still on TiO₂ and ZnO photocatalysts, most importantly in using them to produce nanocomposites with other narrow bandgap semiconductors. Hence, the prevalence of nanomaterials is also one of the most encountered keywords. Nanomaterials are usually employed in photocatalysis because of their ability to provide a very large surface area suitable for adsorption during photocatalytic reactions leading to enhanced photocatalytic activity. Likewise, recent research on photocatalysis is focusing on visible-light-driven photocatalysts, because of the abundance of visible light in nature, unlike ultraviolet light which is limited. So it is

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Table 4 List of the most productive authors in photocatalysis for wastewater treatment

S/N	Author	Scopus Author ID	Year of 1st publication	ТР	h-index	TC	Current affiliation	Country
1	Malato, S	57,207,915,948	2001	18	81	1218	CIEMAT-Plataforma Solar de Almería, Almeria	Spain
2	Rizzo, Liugi	9,044,416,100	2007	11	38	585	Università di Salerno, Salerno	Italy
3	Zeng, Guangming	55,454,449,900	2016	11	136	946	Hunan University, Changsha	China
4	Li, Yi	55,881,885,600	2012	9	34	215	Hohai University, Nanjing	China
5	Vaiano, Vincenzo	8,432,129,900	2015	9	33	317	Università di Salerno, Salerno	Italy
6	Zhang, Wenlog	55,063,813,600	2012	9	22	215	Hohai University, Nanjing	China
7	Zhu, Zhi	56,427,214,900	2016	9	19	497	Jiangsu University, Zhenjiang	China
8	Oller, Isabel	8,415,190,600	2009	8	40	480	CIEMAT-Plataforma Solar de Almería, Almeria	Spain
9	Sacco, Olga	55,502,359,200	2015	8	21	300	Università di Salerno, Salerno	Italy
10	Vilar, V.J.P	10,540,195,800	2009	8	45	131	Universidade do Porto, Porto	Portugal
11	Yan, Yongsheng	57,217,677,633	2016	8	38	406	Jiangsu University, Zhenjiang	China
12	Boaventura, Rui Alfredo Rocha R	6,701,822,293	2009	7	57	118	Universidade do Porto, Porto	Portugal
13	Huo, Pengwei	24,366,451,100	2017	7	40	188	Jiangsu University, Zhenjiang	China
14	Li, Shijie	56,257,988,500	2017	7	23	273	Zhejiang Ocean University, Zhoushan	China
15	Liu, Jianshe	15,755,883,100	2012	7	42	311	Donghua University, Shanghai	China
16	Silva, Adrian M.T	56,329,177,700	2013	7	52	313	Universidade do Porto, Porto	Portugal
17	Chen, Fei	55,619,290,134	2016	6	30	366	Hunan University, Changsha	China
18	Dong, Hongjun	55,543,111,300	2014	6	35	459	Jiangsu University, Zhenjiang	China
19	Faria, Joaquim Luis	7,006,045,981	2013	6	55	301	Universidade do Porto, Porto	Portugal
20	Jiang, Wei	56,931,753,200	2017	6	19	214	Zhejiang Ocean University, Zhoushan	China

evident that almost all the 10 most frequently encountered keywords listed above are related to one another.

Topics of interest

As one of the successful strategies for producing efficient photocatalysts, the 'Heterojunction' keyword has 32 occurrences, signifying its frequent usage. Likewise 'Z-scheme heterojunction' has 21 occurrences because a recent research on heterojunction is focused on producing Z-scheme-based photocatalysts. Meanwhile, 'Graphitic carbon nitrate' appeared in 31 occurrences, it is one of the efficient materials currently under investigation for various photocatalytic reactions; as such, there is growing interest in it.

'Semiconductor photocatalysis' was used 13 times (13 occurrences), among the various methods of synthesis of photocatalysts sol-gel methods were frequently mentioned (18 occurrences) and linked to numerous keywords like 'TiO₂ particles, 'ZnO particles, 'calcination temperature', etc. The sol-gel method is one of the efficient methods of synthesis of nanomaterials, it is largely employed in the synthesis of most photocatalysts because of the simplicity and flexibility of the process.

Among the various sources of wastewater, pharmaceutical wastewater appeared the most with 26 occurrences, followed by organic dye wastewater (20 occurrences), textile wastewater (13 occurrences), dyes wastewater (9 occurrences), contaminants of emerging concern (6 occurrences), industrial wastewater (5 occurrences), dairy wastewater (4 occurrences), 'sulfate wastewater' (1 occurrence), and refinery wastewater (1 occurrence). So, cumulatively it can be seen that dyes are the main contributor to the menace of wastewater generation because organic dye wastewater and textile wastewater, and some portion of pharmaceutical wastewater all constitute a large proportion of dyes.

Among the various types of dyes, methylene blue generated a lot of concern as the keyword 'methylene blue photodegradation' has 43 occurrences and is linked to 64 keywords. Methylene blue is a cationic dye known to be resistant to so many remediation techniques, but using photocatalysis, its mineralization can largely be achieved. Other dyes that appeared the most are 'Rhodamine B' (25 occurrences), 'methyl orange' (13 occurrences), and 'congo red' (9 occurrences), while 'Acid orange 7' (2 occurrences) and 'Synazol yellow dye' (1 occurrence) appear a few times.

Other sources of wastewater that appeared most are 'Bisphenol A' (11 occurrences), 'Endocrine disruptors' (11 occurrences), 'carbamazepine' (7 occurrences), 'inorganic pollutants' (3 occurrences), 'arsenic' (2 occurrences), and '4-chlorophenol' (2 occurrences). The keyword 'Degradation; has also been repeated 41 times and linked to about 61 keywords like 'reusability', 'disinfection', 'tetracycline

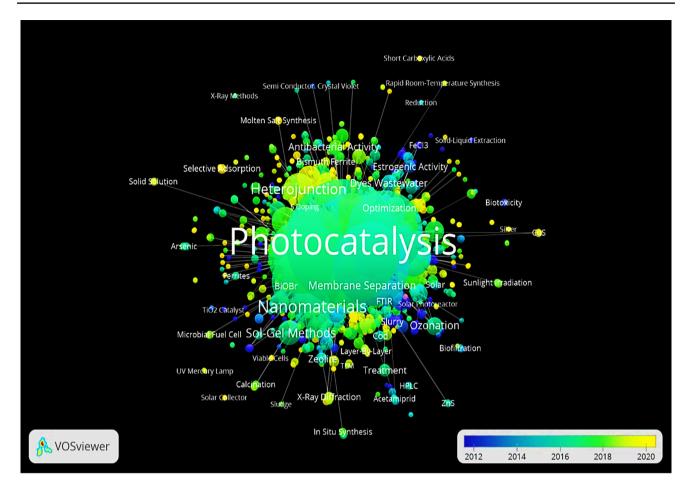


Fig. 4 Bibliometric map based on co-occurrence of author keywords

degradation', and others. The complete degradation of and mineralization of wastewater is desirable, due to the shortage of fresh water, as such, emphasis is given to photocatalysts that can eventually mineralize the wastewater completely, which will enhance the reusability of the water.

Distribution of photocatalysis publications based on the major subthemes

The connections between the outputs of the subtheme search and central theme search were revealed in Fig. 5. Composites with a search phrase: ("photocatalysis*" OR "photocatalyst*" "wastewater treatment" AND composite*) was the most prominent subtheme with a total of 332 articles. This was followed by Semiconductor (132 articles), Heterojunction (94 articles), and conducting polymers (3 articles). The keywords containing semiconductor appeared in 'TiO₂ semiconductor (1 occurrence), 'semiconductor photocatalysis' (14 occurrences), 'alloyed semiconductor' (1 occurrence), and 'semiconducting mineral' (1 occurrence). TiO₂ and ZnO were the first set of semiconductor photocatalysts found; as such research in photocatalysis including semiconductors

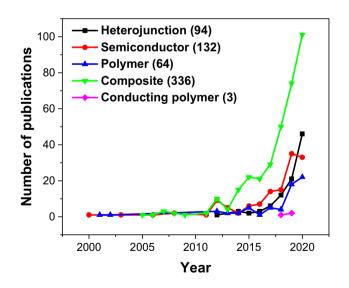


Fig. 5 Research trends of the selected major strategies used in photocatalysis for wastewater treatment

was reported a long time ago, which is why there are relatively higher publications on semiconductors within these years. Earlier semiconductor photocatalysts have wide-bandgap as such their usage is limited to an ultraviolet region of the electromagnetic spectrum.

Likewise, after the advent of photocatalysis, it was understood that single semiconductor photocatalysts are not efficient enough, because of the rapid rate of recombination of electrons and holes after excitation, which subsequently leads to the inactivation of the catalyst. This led to the search for various strategies for improving the activity of photocatalysts, since the effective separation of charges is believed to reduce the rate of recombination and improve the photocatalytic activity, composites are therefore produced with other materials, in order to improve the electron and holes separation as well as tuning the bandgap of the photocatalysts to be active under visible light, which is much abundant than ultraviolet light. That is why there is high research interest in composites evidenced by the highest number of publications within those years.

Heterojunctions are also one of the most promising techniques for the preparation of efficient photocatalysts, due to their feasibility and effectiveness for the spatial separation of electron and hole pairs. Heterojunction refers to the interface between two different semiconductors with unequal band structures, which can result in band alignments. Three types of heterojunctions were identified based on the band structure, there are those with a straddling gap (type 1), staggered gap (type 2), and broken gap (type 3) (Low et al. 2017). The keyword 'Heterojunction' appeared 32 times and linked to 52 keywords. The research on heterojunction has increased drastically from 2015 to date as can be seen in Fig. 5; this is projected to increase in the coming years because of increased interest in Z-scheme heterojunction, which is far more efficient than other types of heterojunction. Z-scheme heterojunction, however, has 21 occurrences and is linked to 28 other keywords.

As pointed out earlier there is also a growing interest in the usage of graphitic carbon nitrate, which is a polymeric material, the keyword 'graphic carbon nitrate" has 31 occurrences and is linked to numerous keywords. This is an indicator that polymers are receiving attention recently, probably due to their resiliency; they can be used in doping, protonation, and molecular functionalization. Polymers such as the graphic carbon nitrate were reported to show enhanced photocatalytic activity in the decomposition of water and degradation of various pollutants.

Conducting polymers are a set of polymeric materials having the properties of inorganic semiconductors, as they provide a similar band structure to most metal oxide semiconductors. They are very stable and easy to synthesize, and their great charge carriers' mobility, as well as compatibility, qualifies them to be used as efficient photocatalysts. The members of this interesting class of polymers include polyaniline (PANI), poly(3,4-ethylenedioxythiophene)(PEDOT), polypyrrole (PPy), and polythiophene (PTh). As can be seen from Fig. 5, their usage in wastewater treatment is very limited, interestingly in the few publications reported on them, they were found to be very effective, as such we strongly recommend their exploration for wastewater treatment. Besides, it was reported that the composites of metal oxide and conducting polymers are more efficient than that of metal oxides or conductive polymers alone (Janáky et al. 2012).

Limitations of the study

The search for the main theme was restricted to "photocatalysis*" OR photocatalyst* "wastewater treatment" from the titles and abstracts, as such the search result will be limited to the application of photocatalysis in wastewater treatment and might not cover all photocatalysis-related articles in Scopus. Although photocatalysis can be used in so many processes like hydrogen generation and other watersplitting reactions but its application in wastewater treatment is increasing tremendously, because of the flexibility and simplicity of the processes. As such, it is recommended that future research analyze the applications of photocatalysis in other processes, and also comparison can be made using the outputs of the available databases like Scopus and Web of Sciences.

Conclusion

This study provides insight into the research trends of the use of photocatalysis in wastewater treatment, based on bibliometric analysis which is rarely seen in Physical Science, using 1373 publications extracted from the database of Scopus. The result revealed that from the year 2002 there was a growing interest in research in that field, with a cumulative increase every year to date. A massive increase in the number of publications was discovered from 2017 to 2020, with an increase of more than 70 publications every year; this is expected to increase rapidly in the coming years. Almost 38% of the total publications globally on this topic were contributed by China, followed by India and others. The majority of the most productive Institutions also come from China, with Jiangsu University as the single most productive institution. China besides its large number of publications, has strong collaborations globally, this will give potential countries and regions ideas for further collaborations to widen their spectrum of research. The most current research is aimed at resolving photocatalyst bottlenecks, such as fast photogenerated electron-hole recombination, limited visible-light response ability, and low specific surface area. The development of composite photocatalyst has gotten a lot of attention, and conducting polymers are playing an important role because of their unique properties of good physicochemical stability and an appealing electronic structure combined with a medium band gap. As a result, their importance as a potential agent for enhancing and modifying the properties of conventional photocatalyst is acknowledged. Different research areas that received increased attention recently were discussed, and hot topics that require urgent consideration like the usage of conducting polymers as a component of nanocomposite photocatalysts were also outlined. This study produced a kind of hybrid review paper that can provide a synopsis of the way forward regarding the usage of photocatalysis in various wastewater treatments, as well as potential opportunities, future research, and collaborations in the field.

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Data availability The datasets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Declarations

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

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