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Photoactive Catalysts for Treatment of Air Pollutants: A Review through Bibliometric Analysis

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Abstract

In recent years, photocatalysts are becoming attractive to researchers in exploring their application for treatment of air pollutants. Exposure to Ultra-Violet Visible (UV-VIS) light on photocatalysts often makes them active in decomposing various toxic materials into less or environment-friendly products. Thus, the identification, as well as simple synthesis and processing of photocatalysts, could ultimately lead to the technologies for the cost-effective mitigation of environmental hazards. A bibliometric analysis has been carried out here to understand and assess the current trend in photocatalyst research. The data retrieved from the Scopus database on the topic for 2000–2020 were analysed to investigate the research activities of the past to foresight the future. Various facets of bibliometry were investigated to produce this holistic review. The contribution of various countries, institutions and authors were investigated. Numerous facets of photocatalyst such as types of photocatalysts, their modification through metal and nometal doping, their pollutants treatment potency, types of reactors for photocatalysis, factors influencing treatment performance and models used for designing reactors were examined. Substantial growth in the publication has been identified in the last two decades. The research trends, problem statements, adopted strategies, and materials explored on the photocatalysis for air pollution treatment over the recent years across the world could be insightful to the researchers and eventually will be beneficial to formulate new research strategies.

1. Introduction

Air quality in outdoor and indoor environments remains the primary concern for healthy lifestyle (Dinh *et al.*, 2021). In recent years, the use of fuels indoors, construction of high-end office buildings, and continuous upgradation of interior furniture are leading to an increase in the deterioration of indoor air quality (Sheehan et al., 2017; Grigoryan et al., 2018; Perez-Padilla, 2018; Luo, 2020). Due to poor microclimatic conditions and considerable use of air conditioners, the closed office buildings cause sick building syndrome because of several volatile organic compounds such as ethanol, propanol, acetone, toluene, formaldehyde, etc.(Lv et al., 2016; Sun et al., 2019). These have led to a surge in many health-related issues including but not limited to respiratory diseases, low immunity, allergies, and cancer (Sheehan et al., 2017; Grigoryan et al., 2018). According to World Health Organization (WHO), approximately 3 billion people cook using kerosene, biomass, and coal-fueled stove, which causes indoor air pollution (Simkovich et al., 2019). These result in the premature death of 4 million people every year globally (Devien et al., 2018). Several techniques have been brought in to deal with the situation. Some studies have demonstrated the efficacies of advanced oxidation processes in degrading organic pollutants. Among them, the photocatalytic oxidation technique that emerged in the 1980s has gained momentum recently because of its promising features, which include low-cost and complete mineralization of pollutants. A photocatalyst is a material that accelerates the reaction when activated under the exposure of light without being consumed. The bandgap, defined as the energy difference between the valence band (measure oxidation potential) and conduction band (measure reduction potential), determines if the material is a metal, a semiconductor, or an insulator (Pawar et al., 2018). When light energy (equal to or higher than bandgap) is incident on the surface of a semiconductor, electron/hole pair is formed, unlike in metals and insulators. Therefore, semiconducting metal oxides are suitable materials for photocatalysis.

Both oxidation and reduction reaction occurs at the surface of semiconducting metal oxide (Madima et al., 2020). The leading role is played by the catalyst which decomposes the toxic agents into less toxic products.

Fujishima et al. (1972) first demonstrated titanium dioxide as a photo electro-catalyst for water splitting (Liet al., 2020). Since then, primitive titanium dioxide (TiO_2) based materials remain the most exhaustively studied photocatalysts mainly because of their low cost, chemical stability and environmental compatibility. However, to obtain more effective photocatalysts, TiO_2 has also been doped with either cationic or anionic counterparts by the researchers (Basavarajappa et al., 2020). Researchers have also explored ZnO and other simple and complex metal oxides as photocatalysts (Lee et al., 2016).

Although initially TiO_2 photocatalysts were applied for water treatment; in recent years, it has been shown that the photocatalytic detoxification of organic compounds is generally more efficient in the gas phase compared to the liquid phase(Carpet al., 2004). Thus, attention to applying this technology for air treatments has increased. The organic compounds degraded include alkanes (methane, ethane, hexane), alkenes (ethylene, propylene, butylene), alkynes (acetylene, methylacetylene), aromatics (benzene, toluene, xylene), alcohols (methanol, ethanol), aldehydes (formaldehyde, acetaldehyde), or ketones (acetone, methyl-ethyl-ketone) and sulphur containing compounds (hydrogen sulphide, SO_x, diethyl / dimethyl sulphide) and nitrogen-containing compounds (NO_x, diethyl amine, propylamine or pyridine) (Portela and Hernández-alonso, 2013).

Significant volumes of literature are mostly devoted to the laboratory-based photocatalytic performances of materials. The basic principles and underlying science of photocatalysts can easily be found in peer-reviewed journals like Nature, Energy and Buildings, Environmental Research, Environmental Pollution and many more (Paz, 2010; Carpet al., 2004). These articles are produced by researchers who have contributed towards studying various photocatalysts and their application for pollution treatment. Predicting the current research trend and gaining knowledge on the utility and prospects of this interdisciplinary research field seems complicated until the enormous number of scattered literatures are collected and analysed systematically. Despite the large number of papers on photocatalysts, only few (Zhanget al., 2010; Qui*et al.*, 2020; Yue et al., 2020) have made attempts to compile and analyse systematically the world scientific publications towards understanding the current research trend and future directions on photocatalysts through the manual review process which scans through only limited literature. Limited study exists on bibliometric analysis which aggregates the large volume of existing information to be analysed in one place for better understanding. The scientific community widely uses this tool for statistical analysis of scientific research publications(Long et al., 2020). Bibliometric tools can include various types of data like academic research publications, book and proceedings etc. for analysis (Moral-muñoz et al., 2020). Some of these tools are Bibexcel, CitNetExplorer, SciMAT,Sci^2Tool, VOSviewer, etc. (Sangam and Mogali, 2014). The data is extracted from the several databases with reference to the relevant keywords. These tools are then used to carry out the bibliometric analysis. Databases such as Web of Science, Scopus, PubMed etc. and various reference managers such as EndNote, Mendeley, etc. can be used. The data is extracted in the formats like txt, .csv, ris etc. which has to be supported by the respective tool.

In the present work, bibliometric analysis has been carried out to understand and assess the current trend in the research activities related to photocatalysts for air treatment. The data from the Scopus database for the 2000–2020 year on the topichas been used for the purpose. The research trends, problem statements, adopted strategies, and materials explored on the topic over recent years throughout the globe could be insightful to the researchers and eventually will be beneficial to formulate new research strategies.

2. Methodology

The method adopted for the bibliometric analysis is illustrated in Fig. 1. The Scopus database (www.scopus.com) was used to acquire the data for twenty years, from 2000 to 2020. The primary keywords, excluding duplicates, from over 100 related publications (Table S3) on topic (details included supplementary,Table S1) were extracted manually. These and their numerous combinations with various boolean operators were used to filter relevant publications from the database(((for example, “photocatalysis” OR “photo-degradation” OR “TiO_2” OR “titania” OR “Titania” OR “titanium dioxide” OR “Titanium dioxide” OR “semiconductor photocatalyst”) AND (“indoor air pollution”) OR (“household air pollution”) OR (“urban environment”)) AND PUBYEAR > 1999 AND PUBYEAR < 2021) (to name a few) to acquire secondary keywords (Table S2).Such various combinations of the secondary keywords were formulated to extract the data from the database. Details of the few search combination used to extract the data are provided in supplementary (Table S4).The searches were targeted to pick the terms present in the title, abstract, and keywords for acquiring relevant publications. The literature mined in languages apart from English was excluded. When reading the abstract as and when needed, the choice criteria were applied and excluded the publications that didn't comply to the theme of this work. The extracted document information, author details, keywords, document type, the affiliation of organizations, journal, citations, subject class etc. were gathered to assess various facets of photocatalyst in the field of air pollution treatment like types of photocatalyst used, their modifications to reinforce degradation potency, models and reactors used etc.VOS viewer (www.vosviewer.com) tool was further accustomed to perform the bibliometric analysis.

3. Results And Discussion

This section is divided into several subsections for the detailed analysis of publication structure, citations and collaboration. It contains information on several types of photocatalysts and modifications that were made to improve their performance in treating air pollutants. Different types of reactors, as well as their design, modelling, and numerous aspects impacting their performance are addressed.

3.1 Publication Structure Analysis

In this section, the analysis of publication structure is performed by the following aspects: annual publication, productive countries and institutions.

3.1.1 Annual publication

The trend of annual publication for year 2000 to 2020 is illustrated in Fig. 2. Publication in the field started with few in the year 2000, followed by an exponential increase since then (Fig. 2). There were a total of 5439 publications obtained using the different combination of keywords that belonged to the research topic. These are classified to six different document types. Original research articles were the most commonly utilized document type, accounting for 58.7% of total creation, followed by reviews (32.3%). Book Chaps. (5%), conference papers (3.4%), short surveys (0.4%) and books (0.2%) were among the less significant categories.

3.1.2 Productive countries

The publishing information was confined to 51 of 111 countries by fixing the minimum number of documents per country to 50. The top twenty countries/regions and their annual publications are exported (Fig. 3) to arrange them into a manageable number further. It can be seenthat China, USA, Japan, South Korea and India were the 5 leading nation for research on this field..

3.1.3 Productive institutions

The publishing information of institutions was confined to 150 of 9492 institutions by fixing the minimum number of documents per institution to 7. To further sort them into manageable number, the leading twenty institutions and their annual publications are exported and depicted in Table 1.It was found that University of Chinese Academy of Sciences, Kyungpook National University and Soochow University were the significant contributor, followed by many others.

Table 1
The Top 20 productive institutions

Rank	Organization	Country	Publications
1	University of Chinese Academy of Sciences	China	42
2	Kyungpook National University	South Korea	18
3	Soochow University	China	13
4	Wuhan University of Technology	China	12
5	Iran University of Medical Sciences	Iran	11
6	Tianjin University	China	10
7	Sun Yat-Sen University	China	10
8	Curtin University	Australia	10
9	Tsinghua University	China	10
10	North China University of Science and Technology	China	10
11	Gdansk University of Technology	Poland	9
12	Shandong University	China	9
13	Jiangnan University	China	8
14	University of Tabriz	Iran	8
15	Chinese Academy of Sciences	China	8
16	Fuzhou University	China	8
17	University of Seoul	South Korea	8
18	Ocean University of China	China	8
19	Boreskov Institute of Catalysis	Russia	7
20	Polish Academy of Sciences	Poland	7

3.2Analysis of Citations

To demonstrate the influence of the publications, the citation analysis is carried out and split into citation analysis by countries/regions, organizations and authors.

3.2.1 The most cited countries and regions

Almost 111 countries have published at least one paper in the area, and 50 of them have published at least ten papers, which have been cited over a hundred times. The citation network of the 50 countries/regions is illustrated in *Fig.S1 (supplementary)* which shows the co-citation network of the countries/regions in the said field. The joined nodes represent the countries/regions cited along, and the node's size indicates the number

of citations of corresponding countries/regions. The large node size indicates a larger citation number. The thicker link indicates the higher frequency of collaboration and subsequent higher co-citations. The top 20 most cited countries/regions are depicted in Fig. 4.The countries/regions are ordered and ranked by the number of citations. China, USA, Spain and Japan have produced larger number of documents and their citations are also impressive. Nations like Germany, South Korea, Hong Kong, U. K., Taiwan, Greece and poland have produced relatively less documents in decreasing order but their link strength is significant.

3.2.2 The most cited organizations

In this section, the citation network of the organization is analyzed. Almost 9492 institutions have published papers on the topic of research. Among these, 53 have published a minimum of 5 papers and have been citedto almost 100 times.The co-citation relationship of institutions is classified into eight clusters in different colors (*Fig.S2, supplementary*). The connection between the two nodes represents the coupled institute' publications. The thickness of the link indicates the strength of the co-cited relationship. The large node size indicates larger institution's publications citations.

To further sort them into manageable numbers, the top 20 most cited institutions having more than 100 citations were extracted and the same is depicted in Fig. 5. As seen in this figure, majority of the 20 institutions are from China, 3 of them are from South Korea. Citations of Chinese institutions are also higher relatively. Although, total link strength (TLS) appears to be distributed randomly (Fig. 5).

3.2.3 The Authors with the most impacts

This section demonstrates the citation of authors and their co-cited relationship. Overall, 11,570 authors have published papers on the topic, and 337 have published a minimum of ten papers. Besides, 337 authors have been cited more than 100 times. *Fig.S3 (in supplementary)* shows the most extensive co-cited network with 337 authors which are clustered in different colors. The node size represents the author's citations and the line joining two authorsare the co-citations. Thicker is the line, larger the co-citations of authors. Figure 6 shows the relative information of the top 20 authors with citations not less than 1000. Chinese authors are the significant contributor to the topic of research. Wang X, Li H and Li J have the highest total link strength.

3.2.4 The most potent publications

On the topic, 5439 papers have been published in total. The co-citation relationship is depicted in *Fig. S4 (in supplementary)*.The top five most cited publications (citations > 700) and the corresponding information are listed in Table 2. With 1413 total citations, the work by Xiang et al. (2011) on graphene's visible light photocatalytic H_2 generation activity was the most cited. Applied Catalysis B: Environmental Journal had the most articles (277), followed by Chemical Engineering Journal (173) among many others, as seen in Fig. 7 (a). Journal of the American Chemical Society (5686) was highly cited journal followed by Environment Science and Technology (4610) and many others as depicted in Fig. 7 (b).

The published output knowledge of photocatalytic research was spread in eleven subject classes throughout the last twenty years, based on the classification of subject classes. The five most fruitful subject areas were Environmental Sciences (31.3%), Chemistry (17%), Chemical Engineering (15.5%), Engineering (9.5%), and Material Science (7.3%).

Table 2
The Top 5 most influential publications

Rank	Document	Author	Publication year	Citations	Links
1	Preparation and enhanced visible light photocatalytic H_2 production activity of graphene/C_3H_4composites	Xiang q, Yu- j, Jaroniec m	2011	1413	8
2	TiO_2 -graphene nanocomposites for gas-phase photocatalytic degradation of volatile aromatic pollutant	Zhang y, Tang z, Fu-x, xu-y	2010	1386	27
3	Fe-g-C_3N_4-catalyzed oxidation of benzene to phenol using hydrogen peroxide and visible light	Chen x, zhang j, fu x, antonietti m, wang x	2009	807	21
4	Generation and detection of reactive oxygen species in Photocatalysis	Nosaka y, nosakaa.y	2017	783	17
5	Enhanced photocatalytic performance of direct z- scheme g-C_3H_4 TiO_2photocatalysts for the decomposition of formaldehyde in air	Yu j, wang s, low j, xiao w	2013	772	27

3.3 Evaluation of Collaboration

The cooperation networks of nations, organizations /institutions and authors are investigated to analyse the cooperation relationship. In this section, P represents the number of publications.The total link strength (abbreviated as TLS) denotes the whole duration the article collaborated with others, and the link represents what fraction the object works with.

3.3.1 Country cooperation network

By setting the minimum number of documents of a country as 10, 51 of 111 countries were filtered for the collaboration networks analysis; the bibliometric map of the same is depicted in *Fig.S5 (supplementary)*. All the fifty-one countries are grouped into 6 clusters, in different colors. The link between two nodes indicates their cooperation, and the link dimension represents the link strength, i.e., the frequency of cooperation. The dimension of the node is known as the TLS of the node, which is derived from the summation of all the link strengths of the node. In this, the USA, China and India are the three countries with the higher TLS (*Fig. S5,in supplementary)*.The link strength between the USA and China is the strongest.

For the focused study of the collaboration relationship, the top 20 countries/regions with the highest total link strength and most substantial cooperation relationship are depicted in Fig. 8 (a) and Fig. 8 (b) respectively. Total cooperation strength is derived by the ratio of Total Link Strength to publication,which indicates the degree of cooperation in percentage. The country with thesignificant TLS signifies the most cooperative country/region. Chinaand USA havehighest links and TLS but the cooperation strength of China is relatively

lesser then USA. In fact, China appears to be the least cooperative country.Co-operation strength of countries like Saudi Arabia, Switzerland, Greece,Australia, United Kingdom, Hong Kong, Germany is higher but TLS is smaller.

3.3.2 Institutional Cooperation network

In line with the analysis, 150 of 9492 institutions have published a minimum of 7 publications on the topic of interest. Of 150, approximately 15 institutions comprise the most extensive coupled network, as demonstrated in *Fig. S6 (supplementary).* The top 20 institutions, along with the related information having highest total link strength and cooperation strength, are shown in Fig. 9 (a) and (b) respectively.University of Chinese Academy of Sciences has the highest total link strength, followed by many other institutions but appears to be least cooperative compared to others.

3.3.3 Authors' Relationships of Collaboration

The co-operation relationship among authors was investigated in this section. It was found that 11,570 authors had published papers on the topic. Approximately 3570 authors comprised the most extensive author cooperation network with 12,480 Link and 21,302 TLS within the network, as shown in *Fig. S7 (supplementary).*

To extract the most relevant authors, the top 20 authors having better Total Link Strength (TLS) and their relative information are listed in Fig. 10. The TLS of the following authors:Wang X, Li J, Zhang Y are significant, followed by many others. Yu J, Liu, Zhang and Malato S are the leading authors having considerably high link.

3.4 Photo-catalysts facets

This section investigates the various aspects of photocatalysis. Following related subtopics are investigated in its subsections: Photocatalyst, modification in photocatalyst, air contaminants degraded by photocatalyst, their treatment summary, factors affecting photocatalysis, photocatalytic reactors and models.

3.4.1 Photocatalyst

The prime component of the photocatalysis treatment technique is photocatalyst. Photocatalysts are the compounds such as TiO_2, ZnO, Fe_2O_3, CdS, SiC etc. The entire list of the investigated photocatalysts for air treatment is depicted in *Fig.S8 (supplementary)*. The top photocatalysts ranked by their occurrences in the documents are depicted in Fig. 11.

The most preferred photocatalyst is Titania (Fig. 11.) because of its merits like high photocatalytic activity, excellent physical and chemical stability, low cost, non-corrosive, non-toxic, reusability, eco-friendliness and high availability (Jianget al., 2012; Baloyi et al., 2015; Dong et al., 2015; Tasbihi et al., 2017). Despite these advantages, it has drawbacks that limit its applications in the field. Firstly, the probability of recombination of photogenerated electrons and holes is high (Riboni et al., 2013; Etacheri et al., 2015). Its large bandgap requires ultraviolet radiation for photo-activation, which restricts the use of solar light as UV light constitutes only 5% of the broad solar spectrum (Dong et al., 2015; Szczepanik, 2017). Titanium dioxide particles can undergo agglomeration and aggregation, hindering photo-activation (De Temmerman et al., 2014; Ivanovaet

al., 2016; Melcher et al., 2017; Pellegrino et al., 2017). Carbon-based nanomaterials have gained tremendous attention in applications of photocatalysis in the environment. Among different carbon-based nanomaterials, graphene oxide (GO) and graphitic carbon nitrate (g-C_3N_4) are primarily used owing to their exceptional properties (Madima et al., 2020). The superior qualities of graphene, such as fast electron transfer, high adsorption capacity, and light absorption range, make it suitable for photocatalytic degradation of organic pollutants. Still, it has poor chemical stability (Kemp et al., 2013).

ZnO is often unstable in illuminated conditions. The capabilities of CdS, ZnS, and iron oxides, among others, have been investigated. On the other hand, all of those materials have corrosive qualities (Reddyet al., 2011). One of the materials with exceptional photocatalytic performance is bismuth-based chalcogenides. This is because they have band gap energies that allow them to absorb light in the visible range of the solar spectrum. They are non-toxic, photostable, photoactive, re-usable, chemically and physiologically inert, and non-toxic (Ajiboyeet al., 2021). Due to their low production cost, high optical absorption, and excellent optical bandgap for visible-light-driven photocatalytic activity, copper oxides (CuO and Cu_2O) are considered the most promising photocatalysts for the photo-degradation of organic contaminants. On the other hand, copper oxides are limited by their high recombination rate and low charge collection (Khiaviet al., 2019). Manganese oxide materials have a high adsorption capacity and require low band gap energies (Ristig *et al.*,2015).

3.4.2 Photocatalyst modification

In recent years, people started modifying the photocatalyst to improve their efficiency for photodegrading the pollutants by mainly metal and non-metal doping. They introduced impurities in photocatalyst to enhance visible light absorption. The prime metal and non-metal dopants, as considered by researchers are listed in Fig. 12. The metal dopants are used extensively to increase light absorption, thereby improving the efficiency of a photocatalyst. It was found that when TiO_2 nanoparticles were doped with Na, Ti existed as Ti^{3+} and Ti^{4+} and the conversion between Ti^{4+} and Ti^{3+} prevented the recombination of e^-/h^+(Zhao et al., 2017). In Pt-doped samples, Titania's surface area was increased, resulting in enhanced photocatalytic efficiency. Also, the bandgap of TiO_2 was reduced to 2.34eV from 3.00eV (Guayaquil-sosa et al., 2017). Noble metals like Ag (Mwcntet al., 2018), Pt (Guayaquil-sosa et al., 2017), Pd (Lavorato et al., 2017) and Au (Zhang et al., 2016) can reduce the recombination rate of electron and hole due to Schottky barrier at metal-titania interface which in turn increases the contact time of pollutants with the photocatalyst.The overlap of the conduction band due to the Ti (d orbital) of TiO_2 and the metal (d-orbital) orbital of Fe^{3+} ions has been proven to decrease the band gap of TiO_2 lattice when Fe^{3+}ions are doped in it. Furthermore, it is widely recognized that doping Fe^{3+} ions cause the development of novel electronic states ($Fe^{4+}$and Fe^{2+}) that broaden TiO_2's band gap. Furthermore, these electronic states may operate as electron and hole trapping sites, reducing electron and hole recombination and, as a result, increasing photocatalytic activity(Ali et al., 2017). Due to the size difference between the host and guest ions, the solid will exist in a strained state with high lattice energy when a dopant with a larger ionic size (such as Sn^{4+}, Mn^{2+}, Ag^+, Zr^{4+}, and Ln^{3+}) substitutes the Ti^{4+} ion in the TiO_2 lattice. As a result, more oxygen may escape from the lattice, trapping photogenerated holes and forming hydroxyl radicals, thus preventing electron-hole recombination. When the dopant ionic radius was near 80 pm, TiO_2 nanoparticles doped with various metal ions (V^{5+}, Mn^{2+}, Fe^{3+}, Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) show increased photocatalytic activity (Kumar and Devi, 2011).

The visible light absorption of photocatalyst is enhanced more when doped with non-metals than metals (Jaiswal et al., 2015; Lee et al., 2017). The C-doped (Fig. 12) TiO_2 is more active than N-TiO_2, thereby receiving much attention (Yang, 2015). Carbon doped on titania affected the structural properties of photocatalyst, a reduction in the bandgap was also observed (Ji et al., 2017). The N-doped TiO_2 increased the crystallinity of photocatalyst and the fast separation of photogenerated carriers (Zeng et al., 2016). The surface modification of sulphur as sulphate, which plays a critical role in electron trapping, is responsible for strong S- TiO_2's photocatalytic activity. S- TiO_2 exhibits a considerable increase in surface area, decreased crystallite size, increased surface acidity, visible light absorption, and photogenerated charge carrier lifespan extension (Devi and Kavitha, 2014).

3.4.3 Photocatalyst and Treatment Summary

Photocatalysis is a powerful technique for eliminating contaminants from the air. This process has also been shown to operate in actual conditions, particularly in less humidified indoor environments. *Fig.S9 (supplementary)* depicts the near-complete list of contaminants considered by researchers. The prime pollutants degraded are shown in Fig. 13 and Table 3. Several indoor contaminants can contribute to various chronic health issues. The volatile organic compounds (VOC), including several others are prevalent indoor air pollutants that can be efficiently photo-degraded. In Table 3, it can be seen that the predominant light sources for photocatalyst is UV.

TiO_2 is also effective at deodorizing indoor air. Some contaminants and their treatment efficiency are used as a reference (Table 3) to show how effective it is against various kinds of pollutants released from diverse sources.

Table 3
The Treatment Condition of Contaminants Degraded by Photocatalysis

Photocatalyst	Pollutant	Reported efficiency (%)	Initial concentration	Lamp condition	Reference
TiO_2	NOx	14.1	1 ppm	UVA (peak at 365 nm)	(Szatmáry et al., 2014)
pCN/TiO_2	NOx	25.8	-	Visible light	(Huang et al., 2019)
TiO_2	Formaldehyde	95	460 ppm	UVA (peak at 365 nm)	(Chinget al., 2004)
TiO_2/Poly(dimethysiloxane)	Acetaldehyde	50	100 ppm	4 W UV bulb (peak at 352 nm)	(Iketani et al., 2003)
$TiO_2/Al_2O_3.SiO_2$	Acetaldehyde	100	100 ppm	UV (peak at 253 nm)	(Yuan et al., 2008)
$ZnO + Zn_2TiO_4$	Benzene	95	110 ppm	UV (peak at 254 nm)	(Hernández-García et al., 2016)
TiO_2 loaded silica	Ethanol	47	106 ppm	UV (peak at 365 nm)	(Adjimi et al., 2014)
Fe_2O_3/ TiO_2	NOx	12.5	100 ppb	Visible + UVA	(Wood et al., 2020)
WO_3 decorated ZnO	NO	12	150 ppb	Visible + UVA	(Gasparotto et al., 2018)
TiO_2	Acetaldehyde	100	60 ppm	UV (peak at 365 nm)	(Yamagishi et al., 2003)
$ZnFe_2O_4$	Toluene	60	900 ppm	36 W fluorescent or 8 W UV lamp	(Mehrizadeh et al., 2017)
SnO_2/ TiO_2	NO	40	450 ppb	300 W Xenon lamp (> 420 nm)	(Huy et al., 2019)
Fe doped TiO_2	Dichloro-methane	95	96 ppm	310–385 nm	(Hung et al., 2007)

3.4.4 Photocatalytic Reactors

The closed system in which the photocatalytic oxidation reaction occurs is a photocatalytic reactor. Reactor design aims to degrade pollutants as much as possible while using as little energy. *Fig.S10 (supplementary)* depicts the numerous reactors utilized in this technique. Figure 14 shows the primary reactors (sorted by most occurrences in the scanned documents) utilized in photocatalytic oxidation. The photocatalytic reactors used

in air treatment can be broadly classified according to the way in which photocatalyst is introduced into the reactor or the geometry of the photocatalytic reactor. Various reactors are available according to the photocatalyst type and reactor arrangement (Paz, 2010). Fluidized bed reactors are widely used in air treatment due to their high throughput and low-pressure drop. In glass fibre filters, glass fibres are used to transmit light and support the catalyst, but higher airflow is needed to properly operate the reactor (Minzae et al., 2012).

According to the geometry, the reactors are categorized as annular and flat plate reactors. Annular reactors are simple in design where photocatalyst is coated on the reactor wall but low air throughput is obtained; hence are less commercially viable. In a flat plate reactor, the catalyst is coated on the interior surface of the glass plates but the low surface area and poor utilization of light reduce the photo-degradation (Imoberdorf et al., 2007). The catalyst is coated on a particular number of channels in a honeycomb monolith reactor. Low-pressure drop and a high surface area to volume ratio are two of its advantages. Optical fibre reactors use optical fibres to transmit light over long distances and to provide strong support for the photocatalyst. It reduces absorption and scattering losses associated with external light sources, allowing photons to be used more efficiently, while the geometry and structure give a large surface area (Birnie et al. 2006). Because of its ease of operation, the fixed-bed reactor (also known as a thin film reactor) with TiO_2 on the surface of supporting materials is the most often used type of photoreactor (Minzae et al., 2012).

3.4.5 Photocatalysis Influencing Factors

FigureS11 *(supplementary)* depicts the variables that influence Photocatalysis. Figure 15 lists the essential elements impacting process efficiency. It shows that the foremost influencing parameter is the photocatalyst, next to light source. The efficiency of photocatalyst is directly affected by the intensity of the light source. An increase in absorptivity of light enhances the charge separation, increasing the photocatalytic efficiency (Karunakaran and Senthilvelan, 2005). Kogo (1980) illustrated that the quantity of absorbed photons affects the photocatalytic reaction (Kogo et al. 1980). It means the surface morphologies such as particle size, shape and stability of photocatalyst impact the reaction (Dinget al., 2005). Because all chemical reactions occur at the surface, its surface area is critical for its use as a photocatalyst. The photocatalyst's surface area accelerates photo-degradation. This is because materials with a large surface area include more active sites than those with a small surface area (Kumar, 2017).

The concentration of pollutants influences photocatalytic activity in terms of reaction rate. Also, the inlet concentration and concentration of pollutant over the surface of the photocatalyst differs. Hence, to minimize the concentration disparities, it is preferred to increase air-flow rate (Huang et al., 2016). Hydroxyl groups can be generated from water molecules adsorbed on the surface of photocatalyst (Hisahiro *et al.*, 2001). A decrease in photocatalytic activity is observed in the presence of water vapor. Humidityincreases competition between water molecules and organic pollutants, which can retard photocatalysis (Park et al., 1999; Cao et al., 2000). An increase in reaction temperature often accompanies increased photocatalytic activity; however, temperatures above 80°C encourage charge carrier recombination, while temperatures below 0°C increase apparent activation energy. As a result, the desired temperature range for optimal photo mineralization of organic material has been estimated as 20–80°C (Kumar, 2017). The morphology of photocatalysts is affected by reaction time, as may be seen elsewhere (Konget al., 2017). Photocatalyst deactivation is caused

by catalyst toxicity. Noble metal catalysts (Pd/TiO_2), in particular, are easily deactivated by trace levels of poisoning species (H_2S)(Kakoet al., 2005).

3.4.6 Modelling of Photo-reactors

Though photocatalysis is a promising technique for air treatment, its commercialization is slow. A major issue among many is the scaling-up of the reactor (Kowalska and Rau, 2010). The broad application requires a systematic approach for photocatalytic reactions. Mathematical models such as the fluid dynamic model, absorption-scattering model and kinetic model are developed to solve the complex matrix of radiation transport equations (Cassano and Alfano, 2000; Romeroet al., 2003;Duran, 2015). *Fig.S12 (supplementary)* shows the kinetic models used to build the photocatalytic reactors. Figure 16 summarises the most commonly used models with their occurrences. Computational fluid dynamics (CFD) is an emerging engineering tool that can study the geometry of reactor and reaction flow mixture co-jointly to design and optimize the photoreactors. Therefore, many researchers have focused on CFD modeling to simulate reactor performance (Jović et al., 2012). Langmuir- Hinshelwood models are based on the adsorption of reagent (pollutant) on the surface of photocatalyst (Ollis, 2005; Sannino et al., 2013). Different open-source CFD simulation tools such as OpenFOAM, FEATFLOW and commercial tools like COSMOL Multiphysics and ANSYS Fluent are also available (Janczarek and Kowalska, 2021).

4. Limitations And Future Directions

There are several gaps in material research for practical use. Although modified TiO_2 had shown promise in the remediation of pollutants, the majority of the experiments were carried out on a small laboratory scale and modified materials are difficult to recycle or break down naturally. Their extraction, recuperation, and usage have grabbed elated attention. The materials utilized for alteration, such as heavy metal ions or hazardous organics, may damage the environment. The physicochemical features of modified TiO_2 are now limiting the performance of the materials. Materials for modifying TiO_2 that are environmentally friendly and can be employed in big designs must be discovered or synthesised. Developing a premium separation method with an appropriate photocatalyst immobilization strategy can save money and reduce pollution problems. A good reactor can boost light usage while decreasing electricity costs. As a result, prior to the experiment, a good reactor design is required. In field toxicity testing with modified TiO_2 will be much more useful than lab analysis in some circumstances. While engineered TiO_2 can degrade pollutants effectively in the lab, real-world applications must take into account the catalysts' durability and recyclability. Faced with the challenges of complex types of contaminants and limited duration of treatment, the environmental sector is moving toward a thorough utilization of advanced pollutants treatments.

5. Conclusion

The essential aspects of the worldwide research trend on photocatalysts for air pollution treatment from 2000 to 2020 were investigated in this study. Photocatalyst's research publications have increased rapidly; a large number of countries and institutes were involved in the research. Contribution of China, USA, Japan and India was larger in exponentially expanded number research documents. Large number of Chinese university and particularly the University of the Chinese Academy of Sciences (China) contributed majorly to the research.

Most of the publications were published in Applied Catalysis B: Environmental Journal, the topic's main journal. The keyword analysis demonstrated that Titanium dioxide was the hotspot in photocatalytic research with 1,194 publications. TiO_2 has received enormous research interest due to its high efficiency in degrading pollutants, durability, low cost, stability and less toxic features. Due to its high bandgap, the application of Titania is often limited to a practical approach as usage of UV irradiation increases the cost of treatment. Therefore, research has focused on using solar light with a more visible light spectrum. Another way to enhance its efficiency is to modify the parent photocatalytic material using doping with transition metal and non-metal and hybridizing. Silver and Carbon among many others are the main dopants for photocatalysts improvement. Toluene, Formaldehyde and benzene among many others were the most studied pollutants for the air treatment. Reactor design aims to degrade pollutants as much as possible while using as little energy. The fluidized bed reactor and the glass fibre reactor among several others were the main reactors. Several other parameters influence photocatalysis process, among many, the types of photocatalysts, types of light and initial pollutants concentrations were the major ones. Computational Fluid Dynamics and the Langmuir-Hinshelwood model were the primary models used for reactor design. The recent developments, underlying issues, suggested approaches and materials investigated on photocatalysis for air treatment in past years may be enlightening to researchers. In turn, it may help formulate innovative research strategies.

Declarations

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Availability of Data and Material

All the data used to carry out this research can be found in the article or in its supplementary

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The authors have no competing interest to declare that are relevant to content of this article.

Credit Author Contribution Statement

Akanksha Nema: Formal analysis, Writing - original draft, Writing - review and editing

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Figures

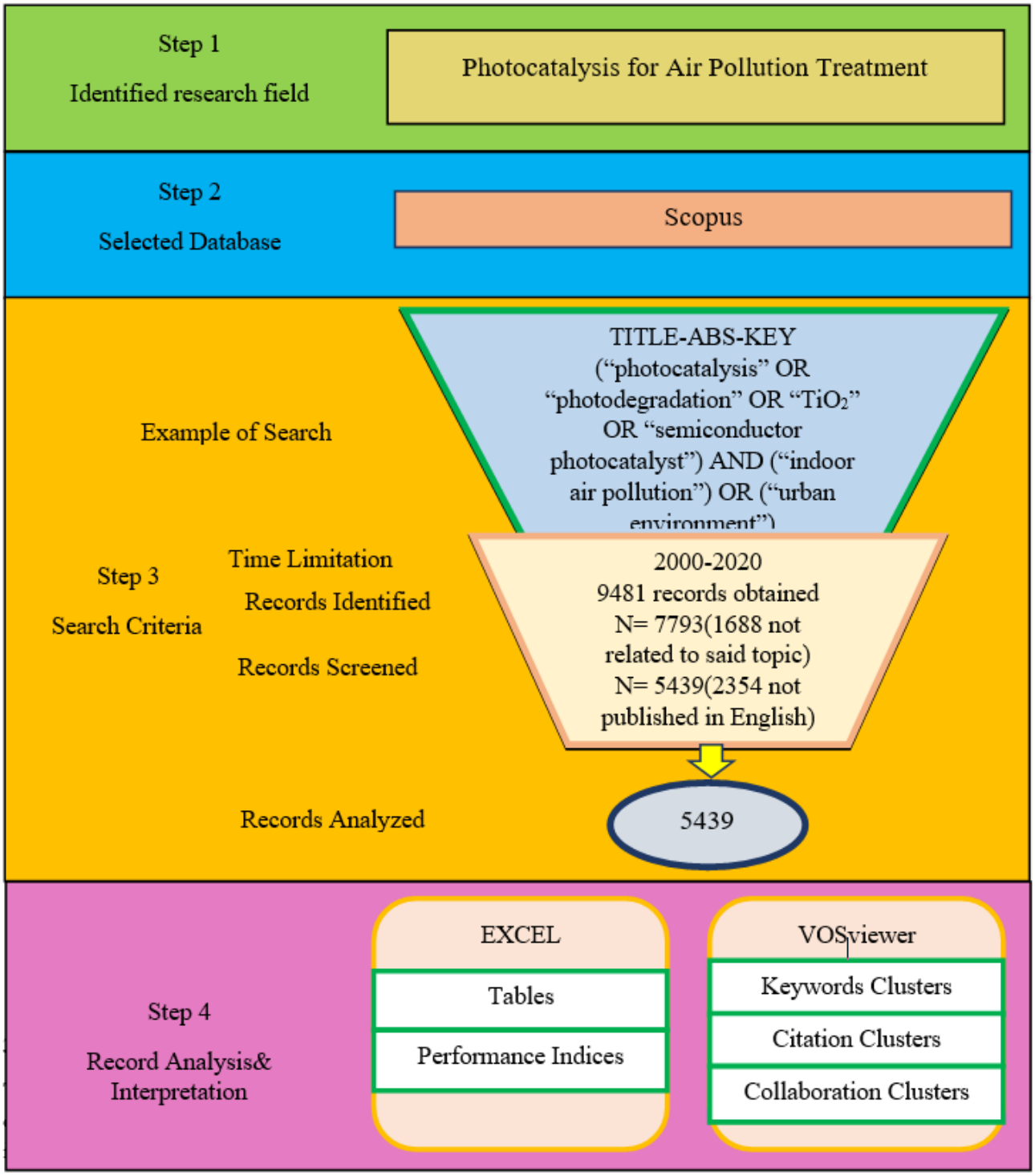


Figure 1

Schematic of bibliometric analysis procedure

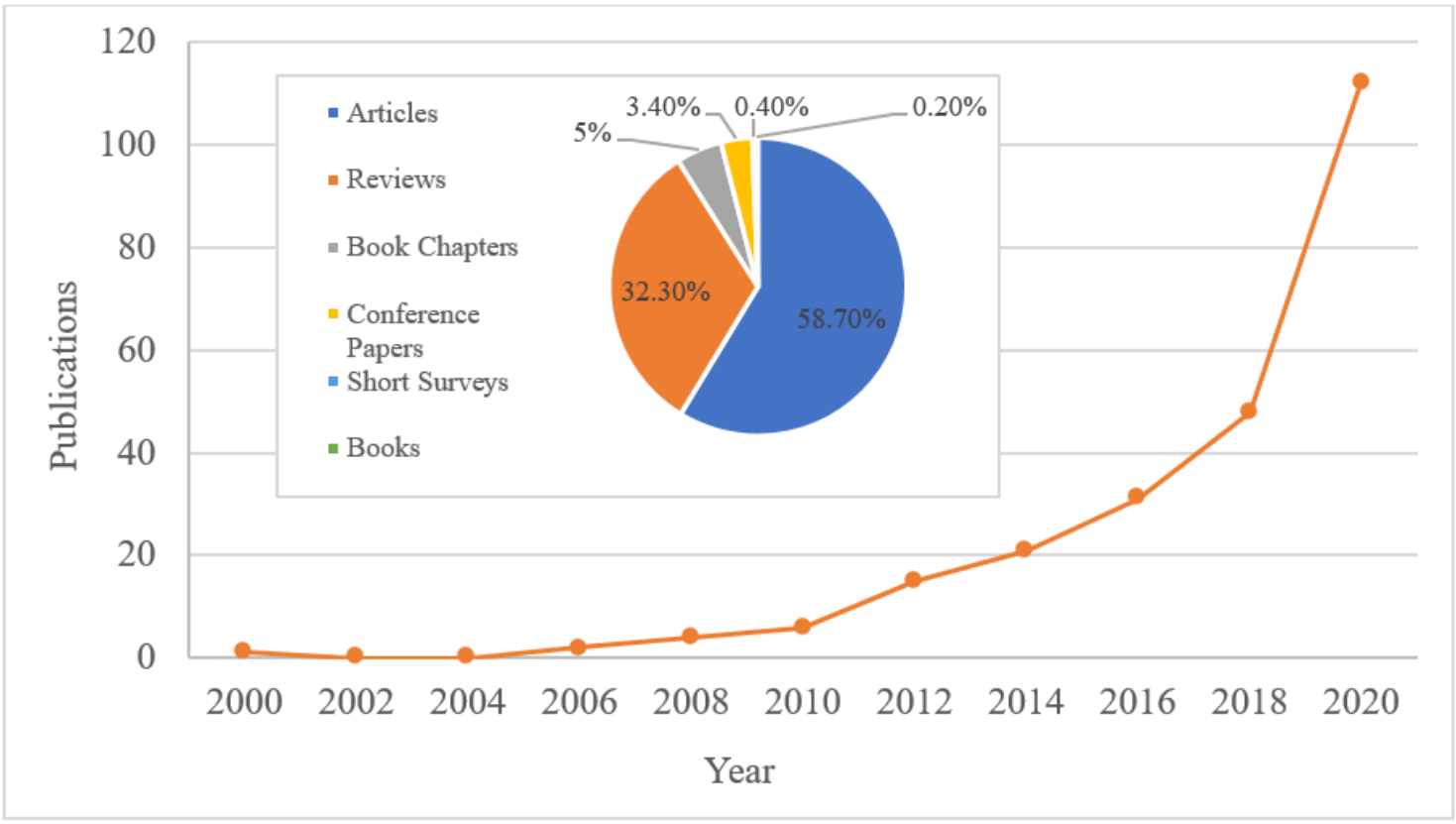


Figure 2

Annual publication in the field of photocatalysis for treating air pollutants using TiO2

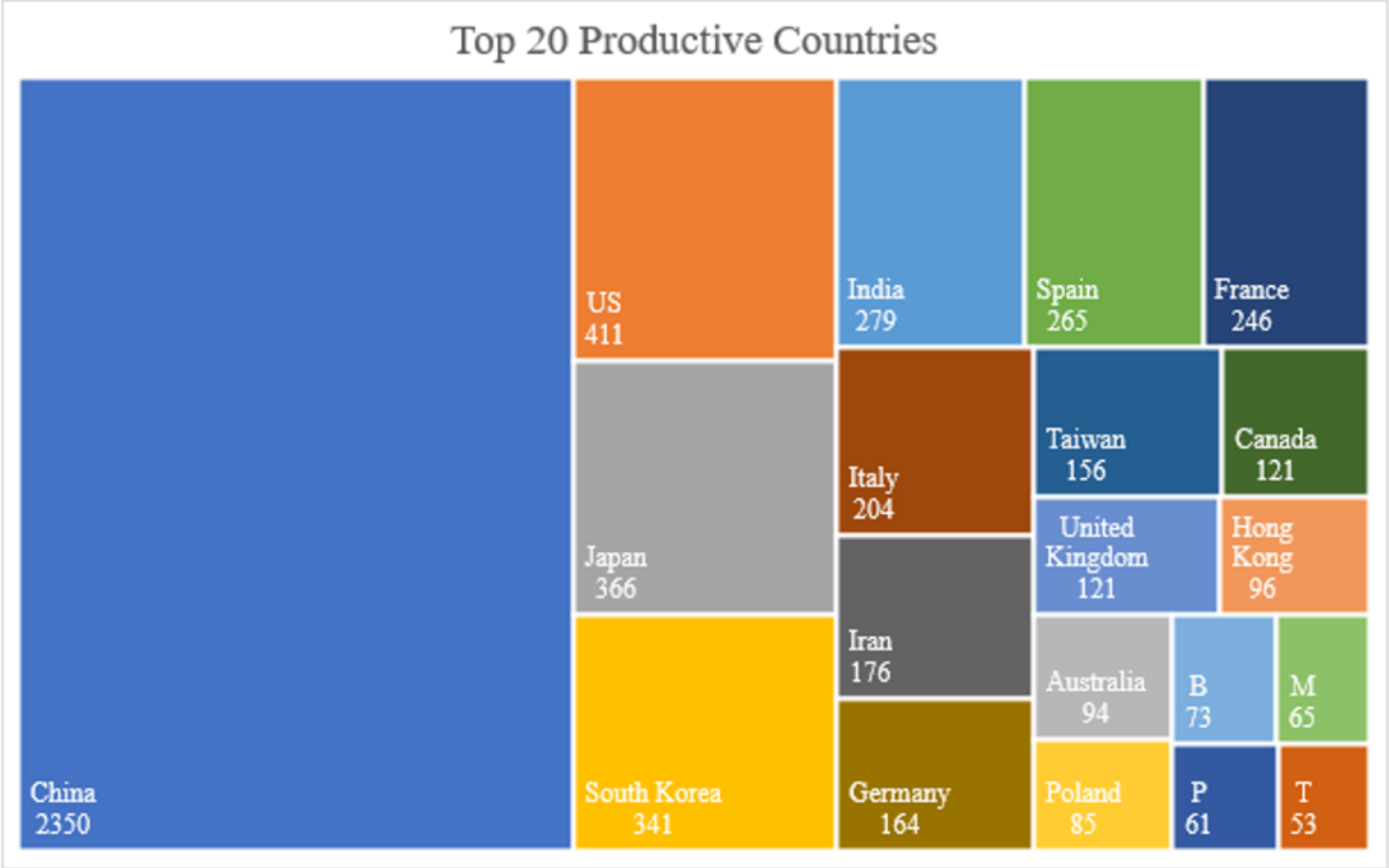


Figure 3

The top 20 productive Countries ranked by number of documents (numbers inside the rectangular region) produced (Abbreviations: B: Brazil; M: Malaysia; P: Portugal; T: Thailand)

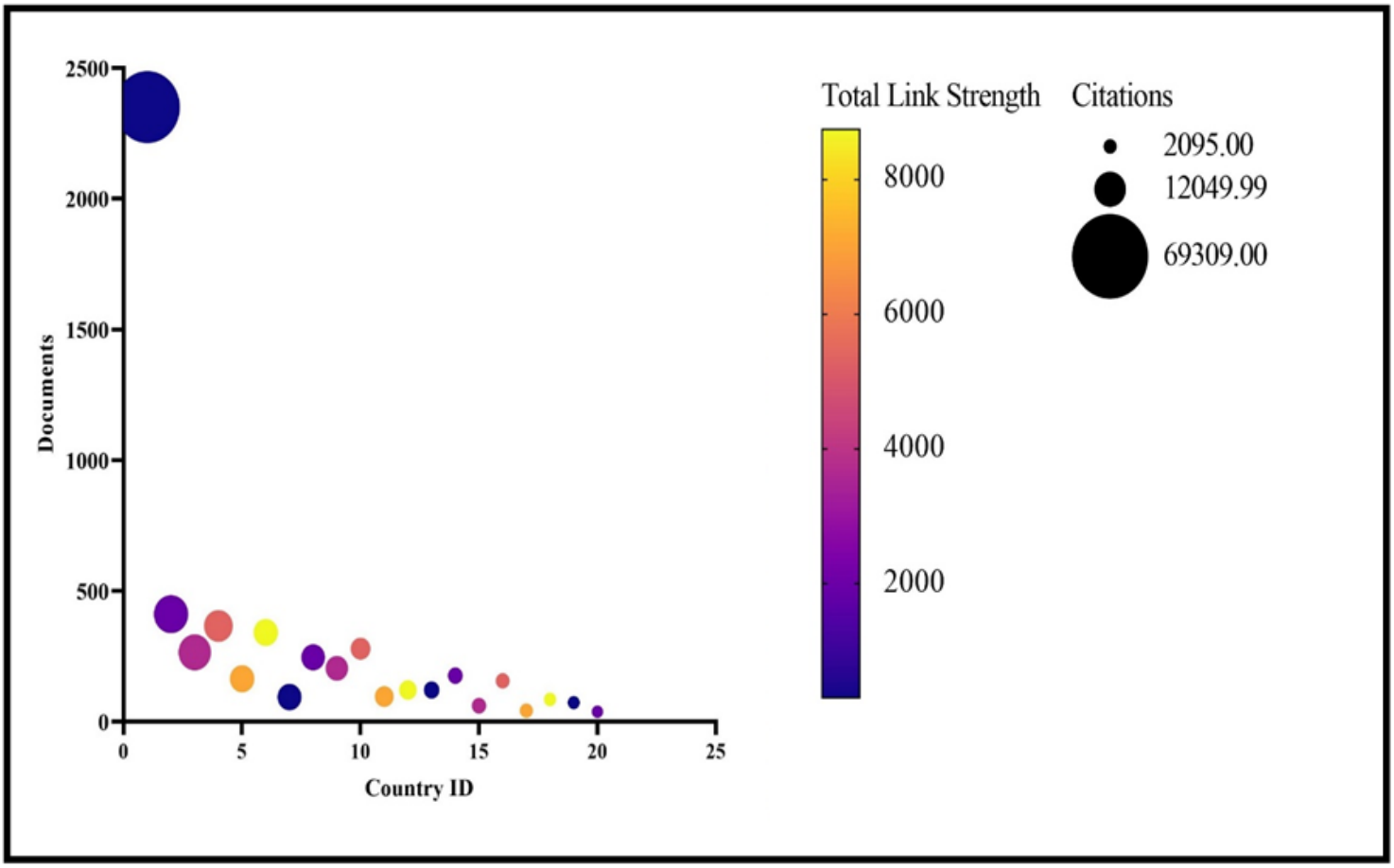


Figure 4

The top 20 most cited countries/regions(Country Id: Country >> 1: China; 2: United States; 3: Spain; 4: Japan; 5: Germany;6: South Korea; 7: Australia; 8: France; 9: Italy;10: India; 11: Hong Kong; 12: United Kingdom; 13: Canada; 14: Iran; 15: Portugal; 16: Taiwan; 17: Greece; 18: Poland; 19: Brazil; 20: Singapore) (The countries/regions are ordered and ranked by the number of citations.)

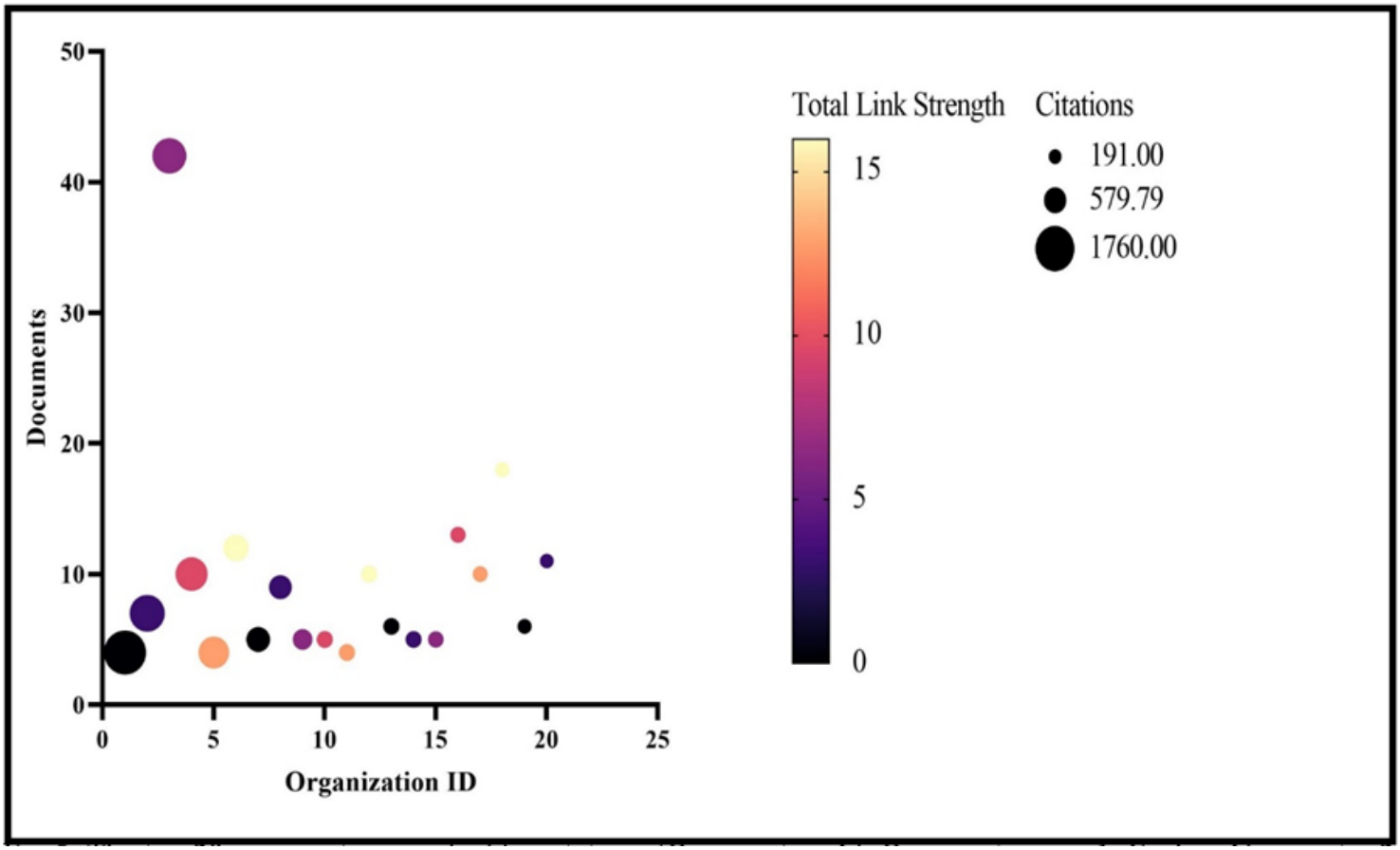


Figure 5

The top 20 organizations ranked by citations (Organization Id: Organization >> 1: Fuzhou University; 2: Zhejiang University; 3: University of Chinese Academy of Sciences; 4: Tsinghua University ; 5: The Hong Kong University of Science and Technology; 6: Wuhan University of Technology; 7: Ewha woman's University; 8: Shandong University; 9: Concordia University;10: Sichuan University; 11: Huazhong Agricultural University; 12: Curtin University; 13: Pohang University of Science and Technology; 14: Ahvaz Jundishapur University of Medical Sciences; 15: Vietnam Academy of Science and Technology; 16: Soochow University; 17: Sun yat-sen University; 18: Kyungpook National University; 19: China University of Mining & Technology (Beijing); 20: Iran University of Medical Sciences)(The Organizations are ordered and ranked by the number of citations)

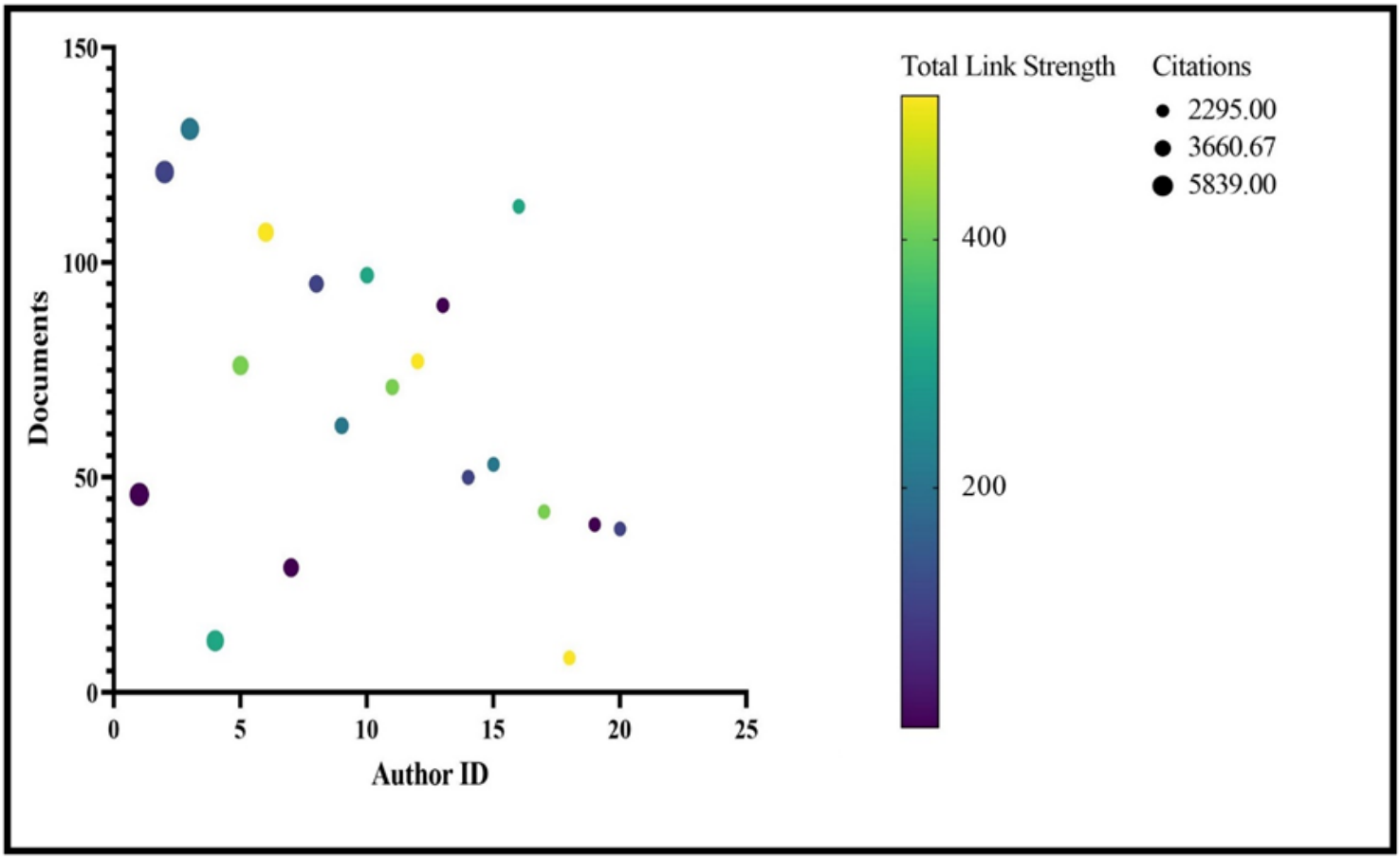


Figure 6

The 20 most cited authors ranked by citations (Author Id: Author>> 1:Fu X; 2: Zhang Y; 3: Wang X;4: Malato S;5: Zhang L;6: Li Y;7: Yu J;8: Liu Y;9: Wang S;10: Wang Y;11: Li H;12: Zhang X;13: Li X;14: Huang H;15: Liu J;16: Li J;17: Chen X;18: Xu Y.-J;19: Wu Z;20: Li D)



Figure 7

(a) Top 20 productive journals; (b) Top 20 cited journals

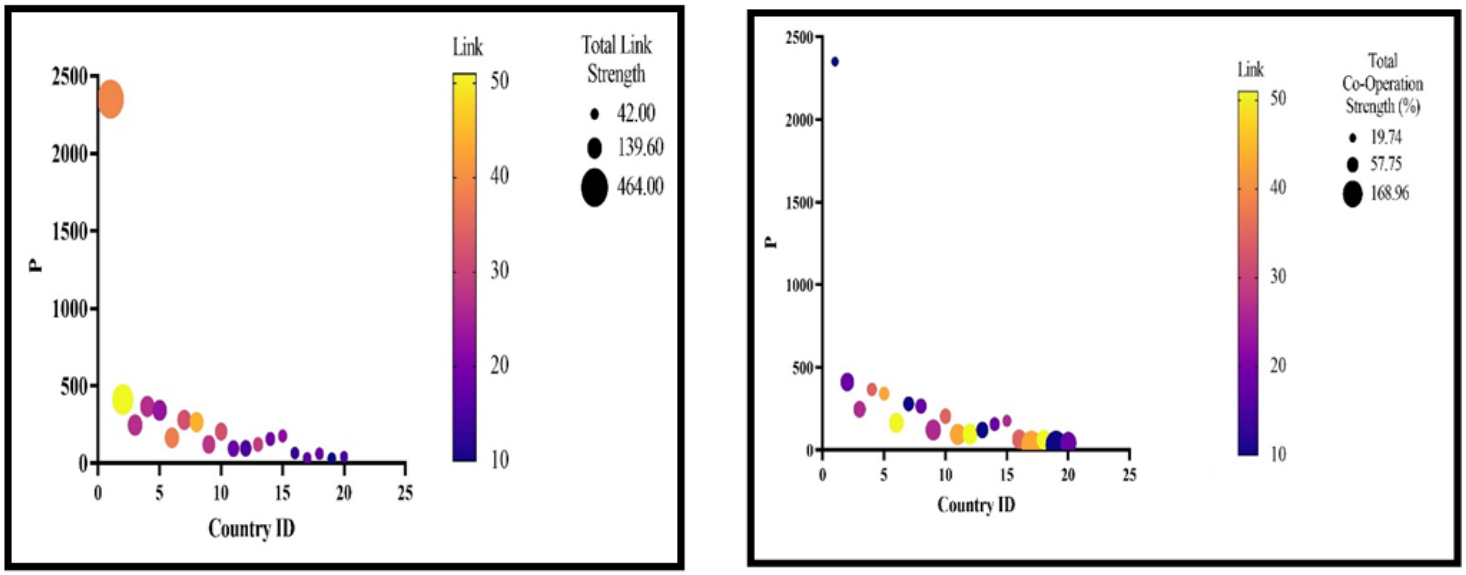


Figure 8

(a) The top 20 countries with the highest total link strength; P: number of publications; (b) The top 20 countries with total cooperation strength; P: number of publications (Country Id: Country >> 1: China; 2: United States; 3: France; 4: Japan; 5: South Korea;6: Germany; 7: India; 8: Spain; 9: United Kingdom;10: Italy; 11: Australia; 12: Hong Kong; 13: Canada; 14: Taiwan; 15: Iran; 16: Malaysia; 17: Switzerland; 18: Portugal; 19: Saudi Arabia; 20: Greece)

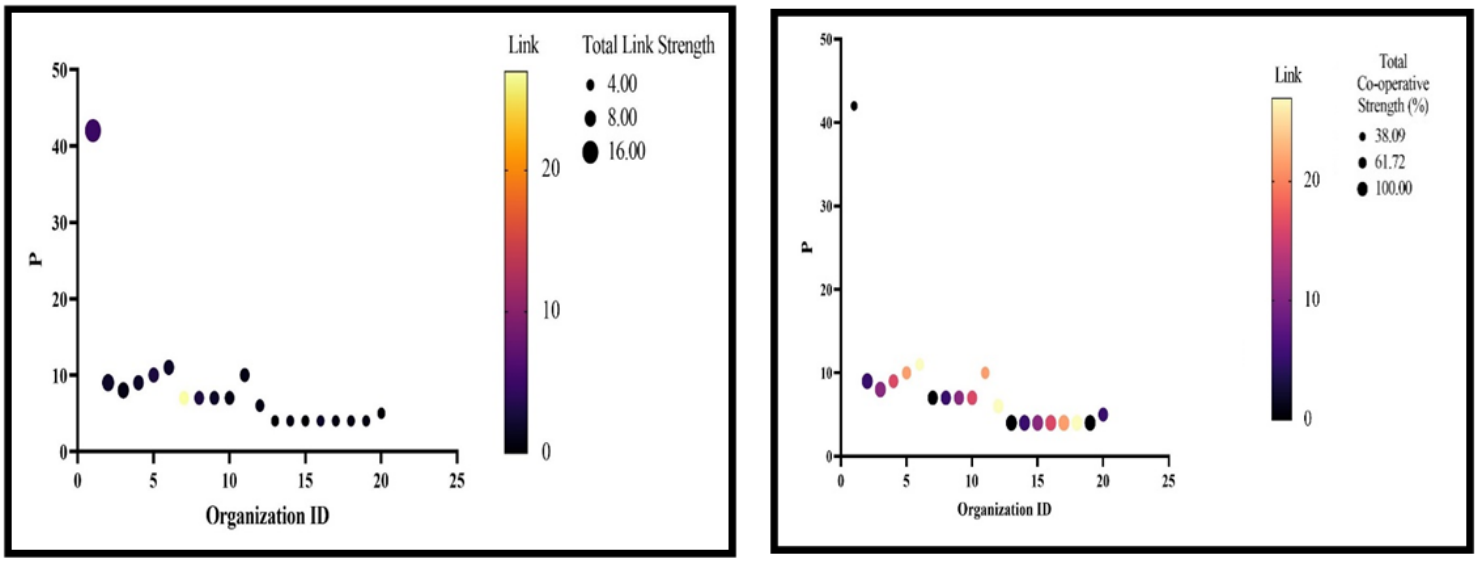


Figure 9

(a) Top 20 organizations with the highest total link strength; P: number of publications;(b) Top 20 organizations with the total cooperation strength; P: number of publications (Organization Id: Organization >> 1: University of Chinese Academy of Sciences; 2: Gdansk University of Technology; 3: Jiangnan University; 4: Iran University of Medical Sciences; 5: Tianjin University; 6: Iran University of Medical Sciences; 7: Boreskov Institute of Catalysis; 8: Collaborative Innovation Center of Chemical Science and Engineering; 9: Polish

Academy of Sciences;10: Novosibirsk State University; 11: Sun yat-sen University; 12: Wuhan Institute of Technology; 13: Hefei University of Technology; 14: Jiangsu College of Water Treatment Technology and Material Collaborative Innovation Center; 15: Korea Institute of Materials Science; 16: University of Electronic Science and Technology of China; 17: Beijing University of Civil Engineering and Architecture; 18: Hunan University; 19: Ministry of Education; 20: Sungkyunkwan University)

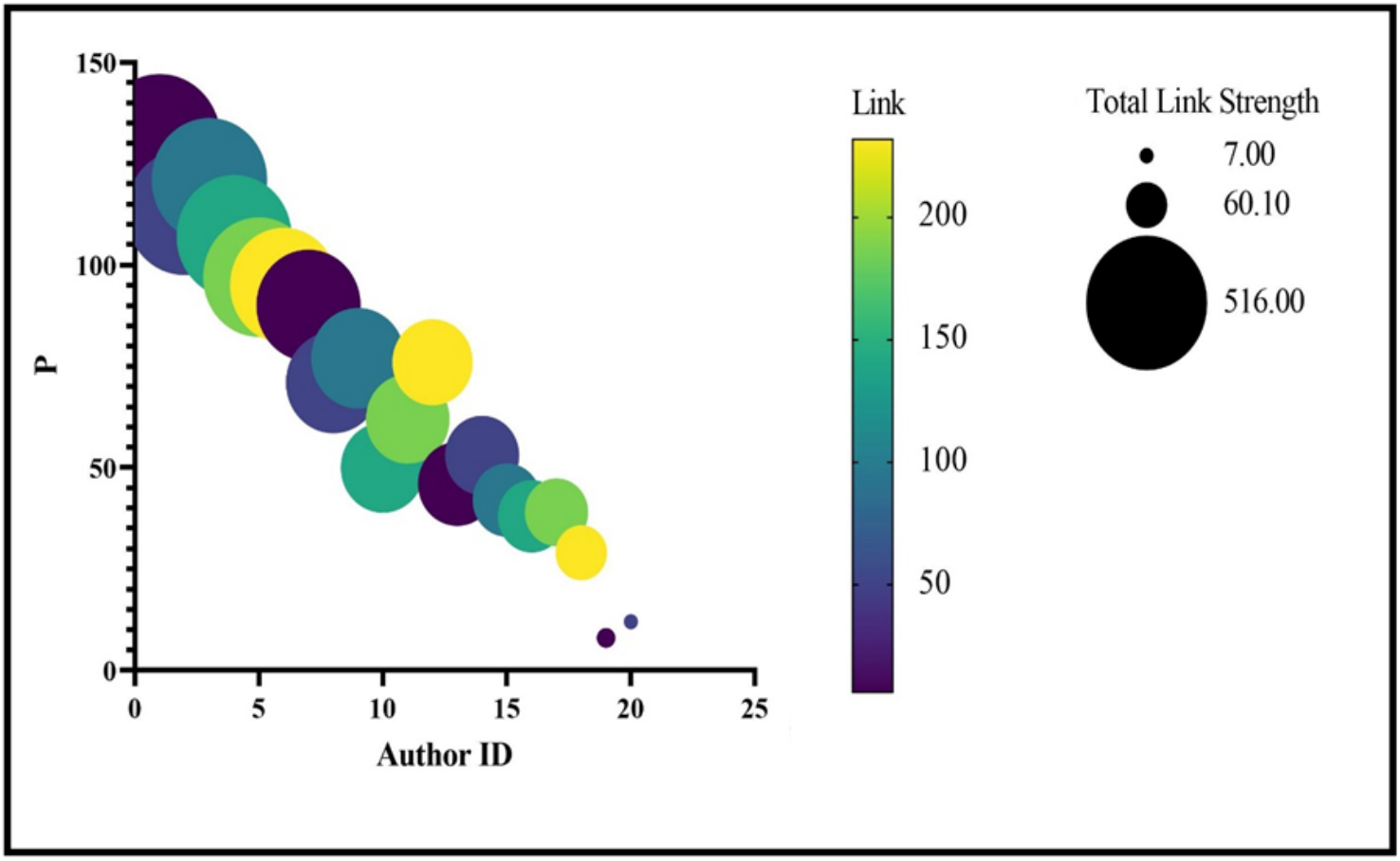


Figure 10

The top 20 authors with the highest total link strength, P-number of publications (Author Id: Author >> 1: Wang X; 2: Li J; 3: Zhang Y; 4: Li Y; 5: Wang Y; 6: Liu Y; 7: Li X; 8: Li H; 9: Zhang X; 10: Huang H; 11: Wang S; 12: Zhang L; 13: Fu X; 14: Liu J; 15: Chen X; 16: Li D; 17: Wu Z; 18: Yu J; 19: Xu Y.-J; 20: Malato S)

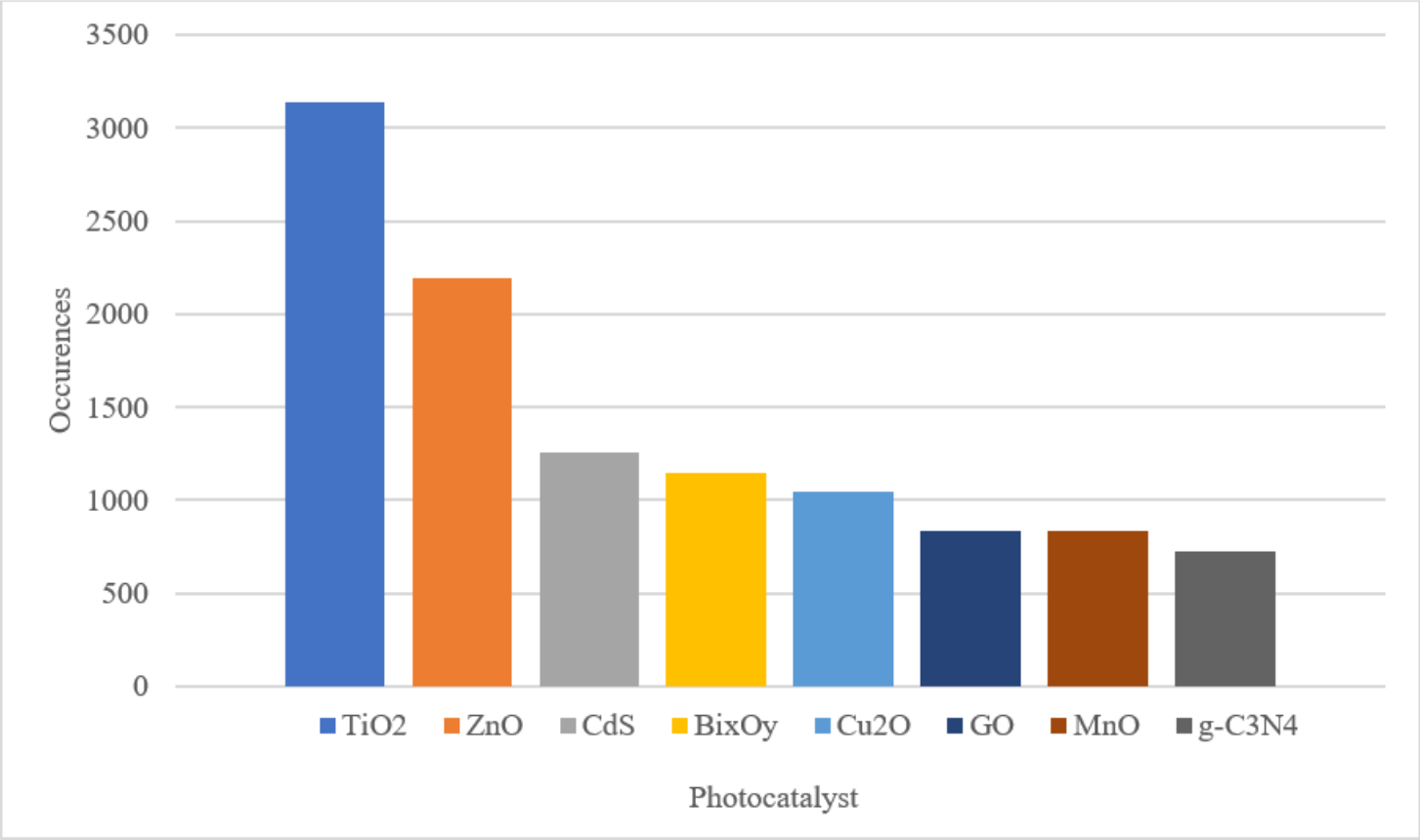


Figure 11

Main photocatalysts considered by researchers

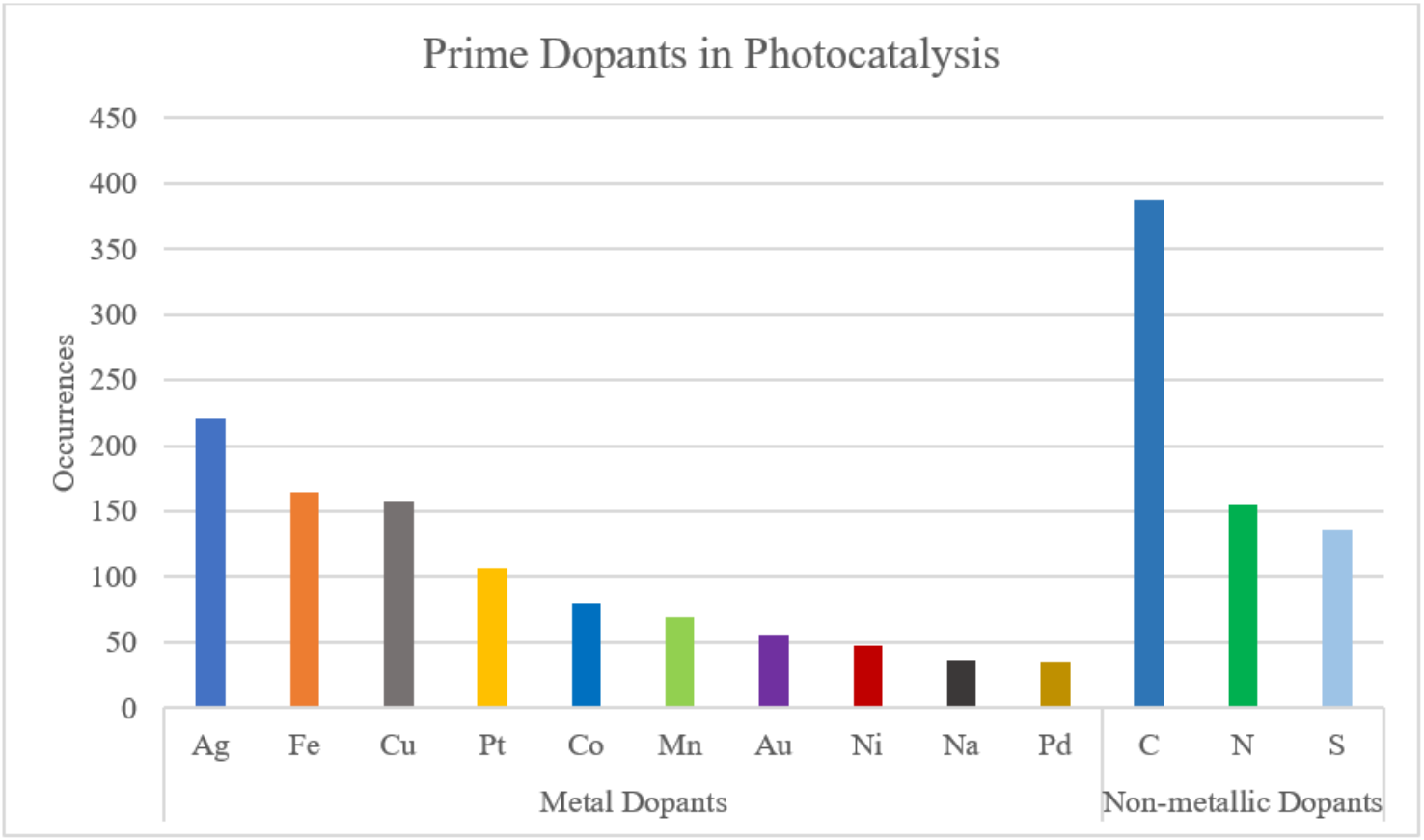


Figure 12

The main metal/non-metal dopants in photocatalysts considered by researchers

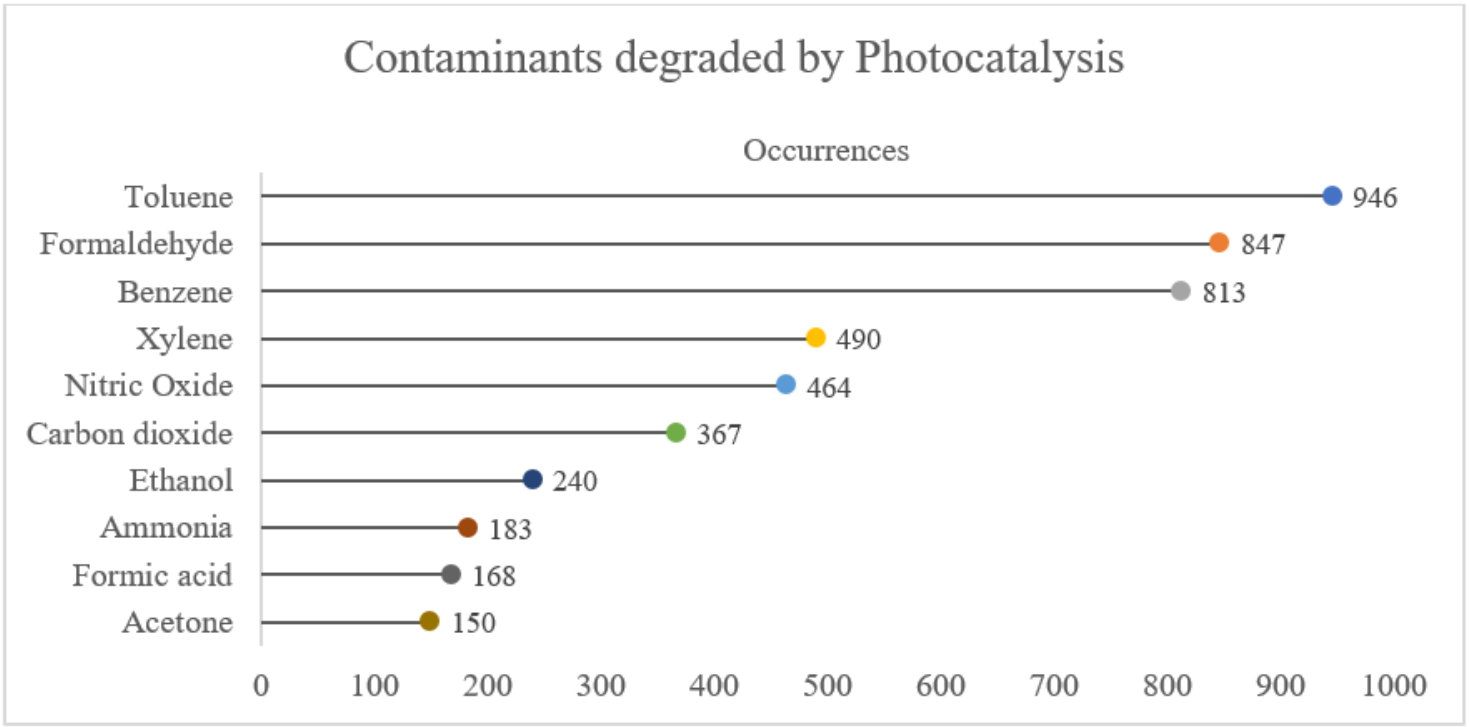


Figure 13

The Main contaminant degraded by photocatalysis

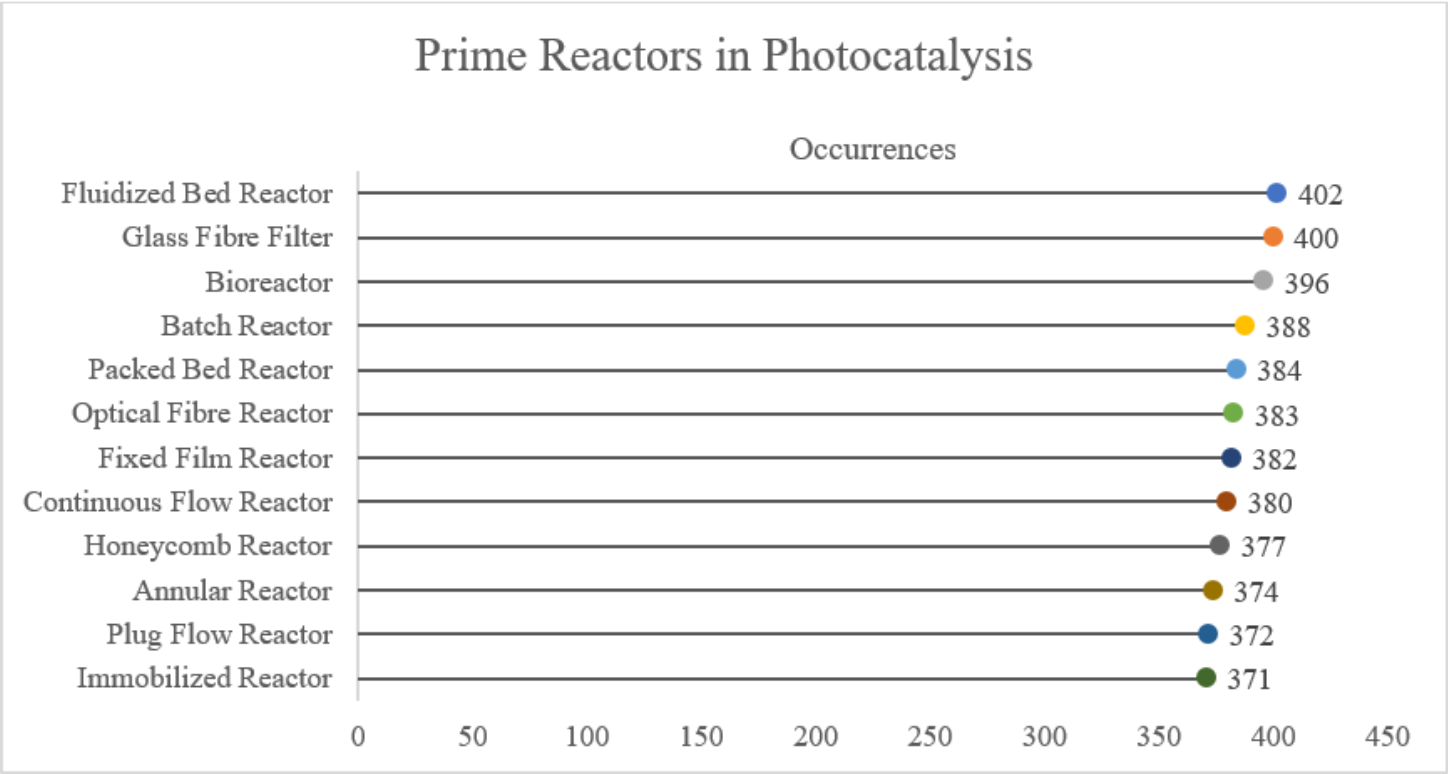


Figure 14

The Prime Reactors for Photocatalysis

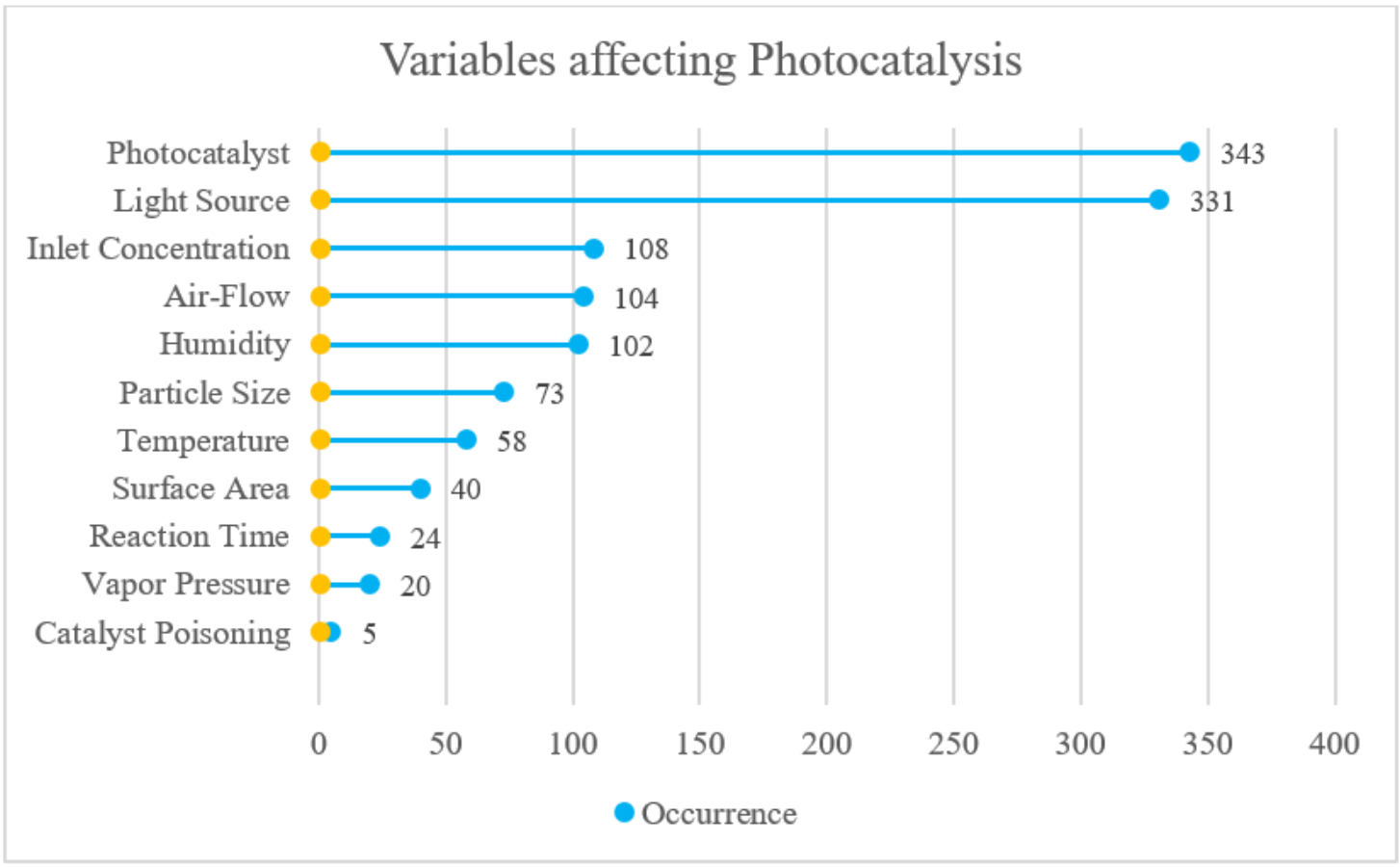


Figure 15

The variables affecting photocatalysis

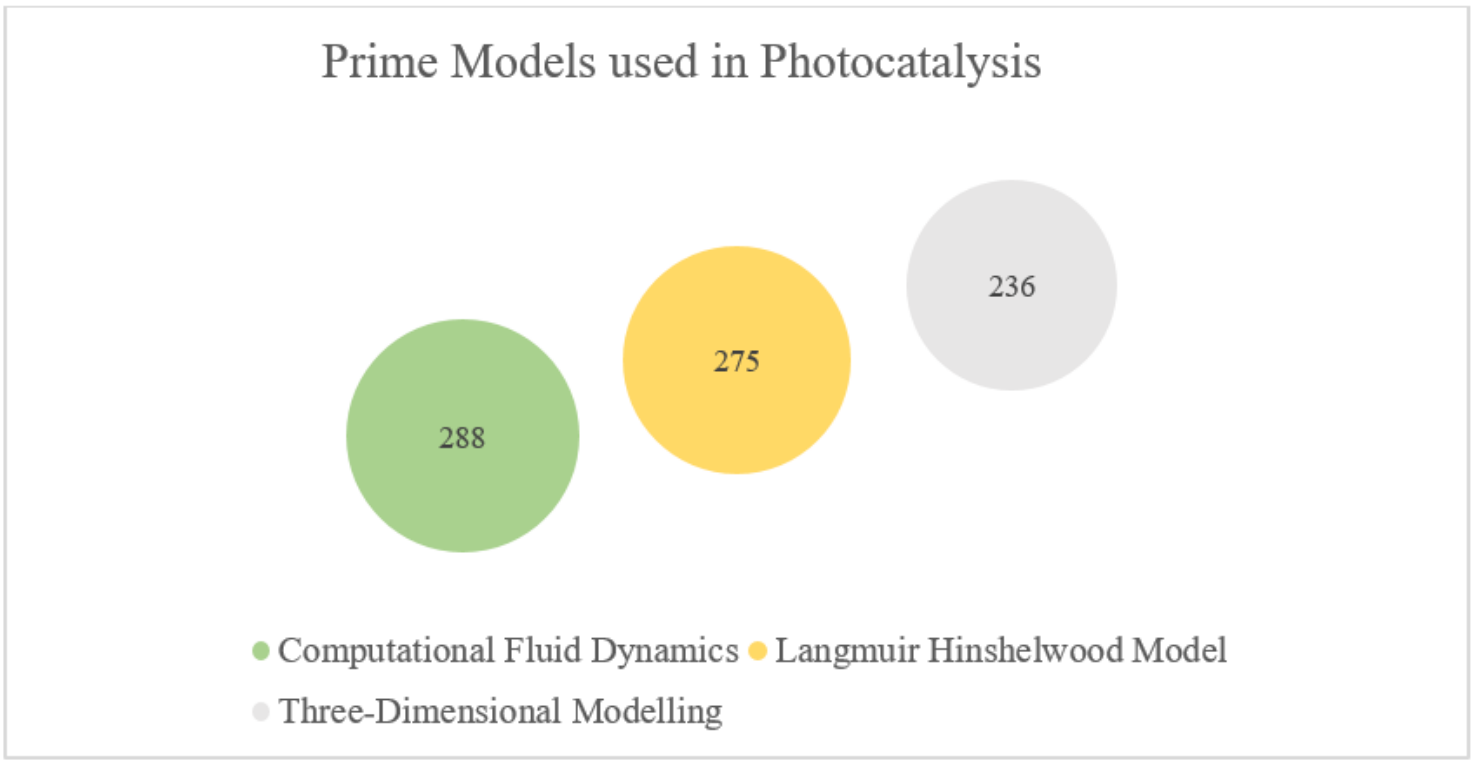


Figure 16

The prime models used for modelling in reactor photocatalysis process

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