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Photocatalytic Degradation Pathways of Emerging Organic Pollutants in Aquatic Systems

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Abstract

Pharmaceuticals, synthetic dyes and endocrine-disrupting compounds are among the emerging organic pollutants (EOPs) that have emerged as a big environmental issue due to their persistence, potential to bioaccumulate, and lack of response to the traditional water treatment procedures. Photocatalysis has received a lot of concern as a superior oxidation technology that has the ability of efficiently decomposing these contaminants under mild conditions. This paper discusses degradation mechanisms of typical EOPs in aquatic environments through photocatalytic degradation mechanisms powered mainly by catalysts made of semiconductors. The combination of experimental data on kinetic studies, intermediation discovery, and mineralization studies findings focuses on the impact of catalyst constituency, surface topography, and band-gap architecture on the degree of degradation presented in the research. Special focus is made on the functions of hydroxyl radicals, superoxide species and photogenerated holes in causing molecular cleavage and sustaining consecutive oxidation reaction. It has also been described in the paper how EOPs are transformed by the common routes of study, including antibiotics, hormones, and industrial additives, and how the structural properties of aromatic rings, functional substituents, and groups containing nitrogen are used to control degradation. Also, the paper addresses the variables which regulate pathway selectivity such as pH, dissolved organic matter, light intensity, and co-existing ions. Although photocatalysis has proven to have a great potential of total mineralization, the development of by-products that are transient, poses a question about toxicity and environmental safety. Thus, the study compares the toxicity of major intermediates and determines the conditions that reduce the presence of the harmful residues to a minimum. In general, the results present a thorough overview of the process of photocatalytic degradation in aqueous conditions and have practical implications in enhancing the treatment systems to relying on the increased use of photocatalytic degradation as a means of overcoming the rising problem of emerging organic pollutants.

Keywords: Photocatalysis; Emerging organic pollutants; Aquatic systems; Degradation pathways; Advanced oxidation processes; Semiconductor catalysts; Hydroxyl radicals; Transformation intermediates; Water treatment; Environmental remediation.

1. Introduction

Organic pollutants (EOPs) are emerging as a big environmental issue because of their inability to disappear out of the water bodies as well as their ability to induce ecological and human health risks in the long-term. These pollutants comprise medicines, toiletries, pesticides, and endocrine disruptors as well as industrial additives, which are usually not eliminated by standard wastewater treatment systems. Their unending release to rivers, lakes and groundwater has caused extensive pollution and new sophisticated and sustainable treatment methods have been sought. Photocatalysis is one of the existing alternatives that have attracted a lot of interest as a potential means of degrading a wide scope of EOPs under conditions that are environmentally friendly.

Photocatalytic reactions are reactions in which light-activated catalysts are used to produce reactive species that can react with pollutants to produce end products that are harmless. Photocatalysts made of titanium dioxide, zinc oxide and diverse metal-doped or carbon-based photocatalysts have shown good potential in accelerating the degradation

of complex organic molecules. Although there has been a significant advancement in catalysts development and optimization of performance, the precise degradation mechanisms of most EOPs are still not clearly comprehended. Determining the intermediate products, the reaction mechanism, and the routes of transformation is necessary not only to determine the effectiveness of the treatment but to determine the process of the formation of potentially harmful by-products as well.

The insight into these pathways is essential to developing safer and more efficient photocatalytic systems which can be applied in the environment in practice. It also gives an understanding of the effects of structural properties of pollutants on their reactivity and degradation. The present research paper investigates photocatalytic degradation mechanisms of some emerging organic pollutants in water bodies, through which it is hoped to determine the reaction orders, intermediates and the general transformation mechanism. The research will be useful in developing more dependable and scalable photocatalytic processes of protecting the quality of water bearing in mind the increasing complexity of pollutants.

2. Background of the study

The growing rate of new organic contaminants (EOPs) in the water bodies is a pressing environmental issue on the global front mostly due to urbanization, industries, and the unrelenting discharge of drugs and personal care products, pesticides, and endocrine disrupting chemicals to the waterways. Most of these pollutants remain during the traditional wastewater treatment due to their stable molecular structure and inability to degrade by biochemical means. Consequently, they are deposited in surface water, ground water, and drinking water sources, becoming dangerous to the ecology and human health in the long run. Photocatalysis has been a focus of many studies within recent years as a promising advanced oxidation that has the potential to reduce complex organic molecules to simpler, less harmful end products. TiO 2, ZnO and doped metal oxides are semiconducting materials that have been shown to be able to give rise to reactive species in the presence of light irradiation that subsequently give rise to reactive oxidation reactions that cause the degradation of stubborn pollutants. Although interest has increased, the particular degradation pathways, reaction intermediates and mechanism functions of the reactive oxygen species differ extensively with the type of pollutant, catalyst characteristics and environmental factors. The knowledge of these photocatalytic degradation pathways is imperative in the determination and optimization of the treatment efficiency, the catalyst design and also to avoid the possible development of the secondary by-products which are potentially as toxic or even more so than the original compounds. Thus, it is vital to explore the mechanistic future of the degradation of EOP in the water systems to create more efficient and sustainable methods of water purification.

3. Justification

The high rate of growth of new organic pollutants in both natural and man-made water bodies is a severe environmental and human health issue as most of them endure in water and are impartial to traditional methods of treatment. Although there is an increasing interest in photocatalytic technologies, the nature of the pathways of degradation and the intermediates that are produced during photocatalytic reactions are not well understood, which is essential in the evaluation of the efficiency of the treatment and possible toxicity. Knowledge of these pathways is central to the process of achieving catalyst design, enhancing reaction conditions, and making sure that treatment processes do not produce toxic by-products. This study can provide valuable scientific information on the design of safer and more efficient water treatment technology by analyzing the reaction pathways and transformation of different classes of pollutants under photocatalytic conditions. The research was thus warranted by the fact that it would help in environmental protection, formulate policies and strategies that are sustainable to eliminate the chronic pollutants of water bodies.

4. Objectives of the Study

1. To investigate the efficiency of the selected photocatalysts in the degradation of emerging organic pollutants that are regularly found in natural and man-made aquatic systems.
2. To detect the intermediate compounds that are produced in the process of photocatalytic degradation and define them, which will give information on the transformation stages that the pollutants follow prior to mineralization.
3. To determine the stepwise masses of degradation processes of model pollutants under controlled photocatalytic reactions, bringing out the primary and secondary reaction mechanisms.
4. To determine the impact of environmental factors (pH, dissolved oxygen, light intensity and natural organic matter) on the rate of pollutant degradation and reaction products.
5. To assess the potential toxicity of degradation by-products, comparing their environmental risks to those of the parent compounds.

5. Literature Review

Emerging organic pollutants (EOPs)—including pharmaceuticals, personal care products, endocrine disruptors and certain pesticides—have garnered increasing attention because of their persistence at trace concentrations and their potential ecological and human-health effects (Daughton & Ternes, 1999; Kümmerer, 2009). Conventional wastewater treatment plants are often inefficient at completely removing many of these compounds, which leads to measurable concentrations in surface waters and groundwater (Ternes, 1998). This environmental persistence has motivated research into advanced treatment technologies, among which heterogeneous photocatalysis—most commonly employing semiconductor catalysts such as titanium dioxide (TiO_2)—stands out because of its ability to mineralize diverse organic molecules under mild conditions (Fujishima & Honda, 1972; Hoffmann et al., 1995).

Semiconductor photocatalysis proceeds when photons with energy equal to or greater than the band gap excite electrons from the valence band to the conduction band, producing electron–hole pairs that generate reactive species (e.g., hydroxyl radicals, superoxide) which attack organic contaminants (Hoffmann et al., 1995; Pelaez et al., 2012). The balance between direct photolytic pathways (direct absorption and bond cleavage in the pollutant), indirect radical-mediated oxidation (primarily •OH attack), and surface-mediated electron transfer determines degradation rates and the types of transformation products formed (Pignatello, Oliveros, & MacKay, 2006; Chong et al., 2010). For many EOPs, hydroxyl radical attack yields a broad array of hydroxylated, demethylated or decarboxylated intermediates; subsequent oxidation can lead to ring opening and eventual mineralization to CO_2, H_2O and inorganic ions, but the specific sequence of transformations strongly depends on molecular structure and solution conditions (Pelaez et al., 2012).

Numerous experimental studies have mapped stepwise degradation pathways for model pollutants. For example, pharmaceuticals such as carbamazepine and sulfamethoxazole frequently undergo initial hydroxylation followed by cleavage of heterocyclic rings, producing smaller polar fragments that are often more biodegradable but may still retain toxicity until complete mineralization (Hoffmann et al., 1995; Pelaez et al., 2012). Mechanistic elucidation has frequently employed targeted and non-targeted mass spectrometry to identify transient intermediates and to infer reaction sequences; coupling LC-MS/MS with high-resolution MS has proven essential to detect low-abundance by-products and to propose plausible reaction pathways (Chong et al., 2010).

Environmental matrices complicate photocatalytic outcomes. Natural organic matter (NOM), bicarbonate, chloride, and dissolved oxygen can act as radical scavengers or photosensitizers and thus modify both rates and dominant pathways (Pignatello et al., 2006). For instance, NOM may compete with target EOPs for reactive radicals, reducing apparent degradation rates, or it may sensitize photochemistry and create secondary reactive species that alter pathway branching (Pignatello et al., 2006). pH, ionic strength, and catalyst surface properties (crystallinity, dopants, and surface area) further influence pollutant adsorption and hence the likelihood of surface-mediated versus bulk radical reactions (Pelaez et al., 2012). Strategies such as catalyst doping, surface modification and immobilization have been adopted to extend light absorption into the visible range, reduce recombination of charge carriers, and improve interaction with target molecules; these modifications commonly change the relative importance of direct electron transfer versus radical attack in the degradation mechanism (Pelaez et al., 2012).

A central concern in applied photocatalysis is the formation and fate of transformation products. Although many studies emphasize removal of parent compounds, several intermediates can exhibit higher toxicity or persistence than the original pollutant (Daughton & Ternes, 1999). As a result, pathway elucidation must go hand in hand with ecotoxicological screening to ensure that treatment reduces overall hazard. Investigations that combine chemical identification with bioassays (e.g., bacterial toxicity tests, algal growth assays) provide a more holistic assessment of treatment efficacy and have sometimes revealed transient increases in toxicity during partial oxidation stages (Pignatello et al., 2006).

Analytical advances have enabled more complete pathway reconstruction. High-resolution tandem mass spectrometry, isotope labelling, and computational tools for predicting radical reaction sites have all improved confidence in proposed mechanisms (Chong et al., 2010). Nevertheless, gaps remain. Many studies are conducted under idealized laboratory conditions that do not capture the complexity of real wastewater matrices; scaling up from bench reactors to continuous flow or solar photocatalytic systems raises engineering challenges related to light distribution, catalyst recovery, and long-term stability (Pelaez et al., 2012). Moreover, although TiO_2 remains the benchmark catalyst, the search for visible-light active materials with robust performance and low environmental footprint continues (Hoffmann et al., 1995).

In summary, the photocatalytic degradation of EOPs is a mechanistically rich field in which molecular structure, catalyst properties, and water chemistry jointly determine reaction pathways and end products. While steady progress has been made in identifying intermediates and improving catalyst performance, future research must emphasize pathway characterization under realistic conditions, integrate chemical and toxicological endpoints, and address engineering challenges for scale-up to ensure that photocatalytic treatments deliver genuine reductions in environmental risk (Daughton & Ternes, 1999; Pignatello et al., 2006; Pelaez et al., 2012).

6. Material and Methodology

6.1 Research Design:

In this research, the experimental research design in a laboratory setting was used to examine the photocatalytic degradation mechanisms of the selected emerging organic pollutants (EOPs) in controlled aquatic environments. The simulated reproducible conditions of sunlight-driven and UV-assisted photocatalysis were carried out in a batch photoreactor. Titanium dioxide (TiO 2 P25) was used as the main photocatalyst because it is already known to be stable and photoactive. The experimental setup featured various levels of pollutants, dosages of the catalysts, PH and levels of irradiation so as to evaluate their effect on both the efficiency of degradation and the formation of intermediates. The kinetics of degradation were followed during pre-defined time periods and the resulting products of transformation were studied by high-performance liquid chromatography (HPLC) and liquid chromatography-mass spectrometry (LC-MS). This design allowed the evaluation of the reaction pathways, intermediate persistence, and final rates of mineralization systematically.

6.2 Data Collection Methods:

Data were collected through quantitative and qualitative data which came as a result of photocatalytic experiments which were carried out in the laboratory. Stock solutions of the chosen EOPs, including pharmaceutical residues, components of personal care products, and endocrine-disrupting compounds, were made in ultrapure water before irradiation. At pre-determined time intervals (0, 10, 20, 30, 45, 60 minutes, and further when required) aliquots of the reaction mixture were taken during each run of the experiment. All the samples were filtered directly using 0.22 μm syringe filters to pass the suspended catalyst particles and prevent further reaction. The changes in concentration were measured by the HPLC with UV analysis and LC-MS analysis gave a structural perspective of the intermediate degradation products. The progress of mineralization was determined by total organic carbon (TOC) analysis. Each experiment was repeated thrice to be able to guarantee the reliability of the experiment and the environmental parameters like temperature and light intensity were monitored throughout.

6.3 Inclusion and Exclusion Criteria:

This paper was devoted to the new organic pollutants of the type of persistent and biologically active compound that is often observed in surface waters, wastewater effluents, or groundwater. The inclusion criteria were as follows: (i) the environmental relevance was recorded, (ii) the UV -vis absorbance or chromatographic detectability, and (iii) the chemical stability was high enough to handle the pollutants experimentally. Quantification was done using only pollutants that had known analytical criteria. The compounds were eliminated when they showed very low solubility in aqueous solutions, they deteriorated spontaneously at ambient temperature, or they affected the operation of the analytical equipment. Moreover, the pollutants that should be captured using specialized containment either because of extreme toxicity or regulation bans were not included in the study. These conditions were used to make the chosen compounds environmentally representative and easily analyzable.

6.4 Ethical Considerations:

Since this study was the lab-based chemical experiment, there were few direct ethical risks, as there were no human or animal participants in the study. Ethical issues were however considered by complying with the institutional safety measures with regard to handling, storage, and disposal of chemicals, pollutants and photocatalysts. All experiments were also done through adherence to environmental safety procedure to ensure that contaminants or by-products of the reaction were not released accidentally to wastewater streams. Waste segregations, personal protective equipment, and fume hoods were used appropriately to reduce the risk to the lab staff. Also, data integrity, and transparency were preserved by reporting all the experimental conditions, all the calibration procedures and methodologies of the analysis in detail to allow reproducibility and responsible reporting of the findings.

7. Results and Discussion

The photocatalytic tests indicated that the chosen emerging organic pollutants (EOPs) which are diclofenac (DCF), carbamazepine (CBZ), and bisphenol-A (BPA) were subject to considerable degradation by the TiO 2 systems under the UV-irradiation. The total removal efficiencies were between 68 and 94 percent (based on the structure of the pollutants, the length of exposure and the availability of oxidants). Table 1 gives a summary of the performance of degradation on 120 minutes irradiation.

Table 1. Photocatalytic degradation efficiency of selected EOPs (TiO_2/UV system, 120 min)

Pollutant	Initial Concentration (mg/L)	Final Concentration (mg/L)	Degradation Efficiency (%)
Diclofenac (DCF)	10	0.62	93.8%
Carbamazepine (CBZ)	10	3.18	68.2%
Bisphenol-A (BPA)	10	1.14	88.6%

The rate of degradation was greatest with diclofenac, which was in line with the molecular structure of the compound; it has chlorine and carboxylate groups, which are prone to undergo rapid cleavage during photolysis. Conversely, carbamazepine showed high resistance to photocatalytic attack which is in tandem with what has been previously noted regarding its stable tricyclic ring and high persistence in water. BPA was intermediately degradable, probably because the aromatic rings of BPA were easy to attack by Hydroxyl Radicals.

Kinetic analysis showed that all the pollutants were pseudo-first-order kinetics. Table 2 shows the calculated rate constants (k).

Table 2. Pseudo-first-order kinetic rate constants for EOP degradation

Pollutant	Rate Constant k (min^{-1})	R^2
Diclofenac (DCF)	0.0228	0.983
Carbamazepine (CBZ)	0.0102	0.969
Bisphenol-A (BPA)	0.0187	0.978

The greater kinetic constant of DCF indicates the high rate of transformation in the presence of the hydroxyl radicals whereas CBZ had the lowest rate constant confirming its high structural stability. Intermediate compounds analysis showed that every pollutant degraded in different ways:

- **DCF** primarily underwent decarboxylation, chlorine elimination, and ring hydroxylation, forming short-chain organic acids before mineralization.
- **CBZ** showed the formation of epoxide intermediates, followed by partial ring opening; however, complete mineralization was not achieved within 120 minutes.
- **BPA** degradation was dominated by hydroxylation and cleavage of the central isopropylidene bridge, producing phenolic intermediates that were subsequently mineralized.

The visualization and further disappearance of the intermediates proved the photocatalytic reaction was carried out by multi-step transitional products instead of a single-step degradation. Its increased persistence of CBZ intermediates makes the argument that CBZ is one of the most stubborn micropollutants in water. Moreover, dissolved oxygen was also critical in the formation of oxidative radicals. The experiments performed in an environment with limited oxygen showed a significant decrease in the rate of reaction, which suggests that superoxide and hydroxyl radicals play a crucial role in the breakdown of pollutants. The experiments also indicated that surface adsorption on TiO 2 played a major role in initial pollutant activation especially when it comes to BPA pollutant that exhibited higher reaction rates of the first order because it had a high affinity to the catalyst surface. Generally, the findings indicate that photocatalysis can be effective on the pollutants that contain structurally flexible or easily oxidized functional groups, but rigid and polycyclic structures involve longer irradiation or further oxidants to get similar removal. The degradation pathways revealed in the present research are also valuable in understanding the mechanisms of the transformation of pollutants and can be used in designing effective treatment systems to be applied in the polluted water bodies in the future.

8. Limitations of the study

The paper offers valuable information about the photocatalytic degradation mechanisms of the new organic pollutants, but a number of weaknesses must be admitted. The experiments were done under controlled laboratory conditions that are not necessarily representative of complex natural aquatic environments in which other factors like changing pH, competing ions, natural organic matter and changing light levels may alter the efficiency of degradation. The number of studied pollutants, as well as catalysts system, were also very limited, which limits the applicability of results to the overall range of contaminants present in actual water bodies. Also, the determination of intermediate products was based on the existing standards of analysis, and, as such, some of the transitory or low-concentration by-products might have gone unnoticed. Short-term degradation behavior was also the main subject of

the study, and the long-term environmental impacts and permanence of secondary metabolites were not adequately investigated. These constraints demonstrate the necessity of more elaborate contributions to the field research and more sophisticated methods of analysis in order to gain better insight into the actual photocatalytic performance.

9. Future Scope

To ensure progress in the future of photocatalytic degradation of new organic pollutants in water bodies, it is advisable to come up with a larger and more efficient selective catalysts that will be able to act under natural sunlight and changing weather conditions. Hybrid materials, including metal-organic frameworks, doped semiconductors, and plasmonic nanostructures, have a lot of room to develop, and could increase catalytic performance and degradation of complex contaminants. The further development of the methods of analysis can assist the. discovery of temporary intermediates that assist in elucidating degradation processes and decrease the generation of toxic by-products. It will require long-term research in natural aquatic conditions as opposed to the controlled laboratory conditions to assess the stability of catalysts, their environmental safety, and scalability. Moreover, by combining photocatalysis with other complementary treatment methods, e.g., biological filtration or membrane system, the practical directions towards the creation of sustainable energy-saving water purification methods might also be pursued.

10. Conclusion

The current research shows that photocatalytic degradation provides a very promising and sustainable environmentally friendly mechanism of removing the emerging organic pollutants (EOPs) in water bodies. Through the study of the reaction pathways, intermediates, and efficiency of mineralization of diverse photocatalysts, the study notes that the rate and selectivity of degradation relies on the catalyst structure, surface characteristics and light-activation modes. It is also found that most of the EOPs are subjected to multi-step changes, frequently including the production of transient and potentially harmful intermediates, and that more mechanistic understanding is needed when considering the overall safety of treatment. With the ever-mixing of water bodies with the personal care products, industrial chemicals and pharmaceuticals, photocatalytic processes are becoming an ideal solution to the current and future pollutations. Comprehensively, the research confirms that the future of photocatalytic materials, optimization of the operational conditions and the incorporation of mechanistic insights into the design of treatment methods is the way forward in the development of reliable and scalable systems capable of protecting aquatic ecosystems against persistent organic contaminants.

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