

Sonophotocatalysis

¹Ide Vinayak Sudhakar, ²Shaikh Sameena Ibrahim, ³Jadhav Harshal Dinesh,

⁴Hongekar Shubham Parshuram, ⁵Hoge Avinash Dnyaneshwar

^{1, 3, 4 & 5} Students, B. Pharmacy Final Year Student

² Assistant Professor

Srinath College of Pharmacy, Chhatrapati Sambhajanagar, Maharashtra, India.

vinayakidge84@gmail.com

Abstract: Sonophotocatalysis is described as a combination of two individual processes of photocatalysis and sonocatalysis. It has proven to be highly promising in degrading dissolved contaminants in wastewaters as well as bacteria disinfection applications. It eliminates some of the main disadvantages observed in each individual technique such as high costs, sluggish activity, and prolonged reaction times. The review has accomplished a critical analysis of sonophotocatalytic reaction mechanisms and the effect of the nanostructured catalyst and process modification techniques on the sonophotocatalytic performance. The synergistic effect between the mentioned processes, reactor design, and the electrical energy consumption has been discussed due to their importance when implementing this novel technology in practical applications, such as real industrial or municipal wastewater treatment plants. The utilization of sonophotocatalysis in disinfection and inactivation of bacteria has also been reviewed. In addition, we further suggest improvements to promote this technology from the lab scale to large-scale applications. We hope this up-to-date review will advance future research in this field and push this technology toward widespread adoption and commercialization.

Keywords: Sonophotocatalysis, Sonocatalysis, Photocatalysis, Synergistic effect etc

I. INTRODUCTION

Sonophotocatalysis is a combination of two individual processes of photocatalysis and sonocatalysis. It has proven to be highly promising in degrading dissolved contaminants in wastewaters as well as bacteria disinfection applications. This hybrid technology has gained significant attention due to its ability to accelerate the degradation rate and improve the overall efficiency of the photocatalytic process. Sonocatalysis is a field of sonochemistry which is based on the use of ultrasound to change the reactivity of a catalyst in homogenous or heterogenous catalysis. It is generally used to support catalysis. Photocatalysis is a catalytic chemical reaction that triggers or speeds up specific reduction and oxidation (redox) reactions with an irradiated wavelength that can absorb a specific amount of light related to its bandgap energy⁽ⁱ⁾

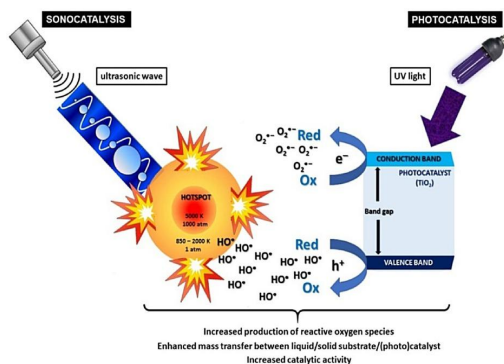


Figure 1: Sonophotocatalysis



Sonophotocatalysis

The mechanisms of activity of sonocatalysis and photocatalysis as well as their synergistic interaction in sonophotocatalysis are detailed below sonocatalysis.⁽ⁱⁱ⁾

1. Sonocatalysis

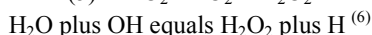
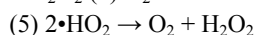
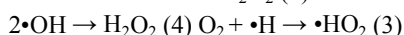
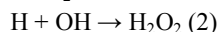
Sonocatalysis is an innovative and highly effective technology that leverages ultrasonic irradiation in conjunction with photoactive materials to degrade pollutants, particularly in wastewater treatment. Unlike traditional photocatalysis, which requires light irradiation to activate semiconductor materials, sonocatalysis operates solely through the application of ultrasound. This method presents several advantages, such as enhanced penetration of ultrasound waves into the liquid medium, which significantly increases its efficiency in breaking down complex contaminants.ⁱⁱⁱ

Principle of sonocatalysis

The combination of sonochemistry with catalysis can be used to accomplish a number of chemical reactions with convenient workup conditions (e.g. shorter reaction times) in contrast to more conventional methods. Heterogeneous reactions follow via ionic intermediates provoked by mechanical effects, whereas radical reaction enhanced mainly by sonication. In the case when radical and ionic mechanisms lead to other products, ultrasound might promote the radical reaction, which can also provide new synthetic pathways. The fundamental rule of sonocatalysis is diffusion and sorption of the main components on a solid surface followed by a series of heterogeneous chemical reactions on active sites. In a heterogeneous reaction system, the improvement of chemical reaction is mainly caused by physical effects. The physical phenomena improve mass transfer from mixing and acoustic streaming, generate cavitation erosion at liquid–solid interfaces, and are responsible for deformation of solid surfaces. The effect of ultrasonic irradiation on a heterogeneous catalyst may cause physical and chemical modifications (e.g. changes in crystallization, dispersion, and surface properties, as well as changes on catalytic reactivity during reaction. The chemical rate increases due to enhancement of external transport phenomena and the increase in temperature at the catalyst surface^(iv)

Mechanism of sonocatalysis

The “hot spots” and “sonoluminescence” resulting from the ultrasonic cavitation phenomenon are thought to represent the main foundation of the sonocatalytic process. Many tiny bubbles can form in liquids when an ultrasonic radiation of a particular frequency and intensity is applied. As these tiny bubbles form, oscillate, expand, contract, and finally collapse, they undergo a number of physical and chemical changes. The creation of light with a variety of wavelengths, known as “sonoluminescence,” and numerous localized “hot spots” with extremely high temperatures (up to ~5000 K) and pressures (up to ~1000 ATM) are encouraged by it. These localized “hot spots” have the potential to pyrolyze H₂O molecules, generating hydroxyl radicals (•OH), which have the ability to efficiently oxidize organic contaminants and even turn them into CO₂ and H₂O by mineralization. Molecular Structures 28 03706 g001 550. Generally speaking, oxidation by both pyrolysis and free radical assault is used in the sonolytic removal of organic contaminants. However, when depending just on ultrasound, rapid degradation frequently cannot take place because of the substantial energy loss that happens during thermal dissipation (exceeding 50%). Due to its many advantages, such as easy handling, affordability, and environmental friendliness, sonocatalysis—the use of ultrasound in the presence of suitable catalysts has become more and more popular in recent years as a means of degrading organic contaminants. Using a sonocatalyst to produce more active ingredients is known as sonocatalytic degradation. Tiv locations for the cavitation effect, which causes more highly reactive radicals to develop. H₂O +))) → •H + •OH (1) These radicals can generally recombine to create H₂O, •OH, H₂O₂, and •O₂– in water^(v)



Sonocatalysis is a crucial technology in the degradation of pollutants, and radicals play an essential role in this process. These radicals can initiate chain reactions that lead to the degradation of pollutants. To enhance the efficiency of the sonocatalytic process, it is essential to understand the underlying mechanisms of sonocatalysis.

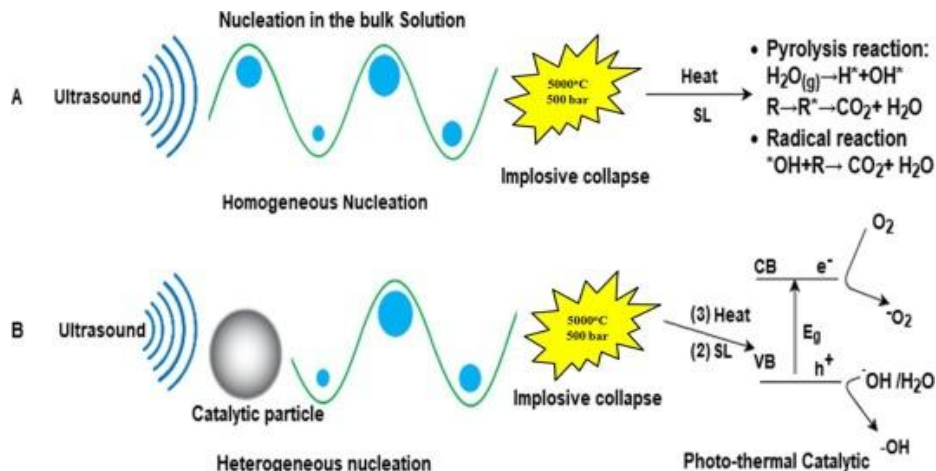


Figure 2; Sonocatalysis mechanism

Mechanism of Heterogeneous Nucleation

It has been noted that semiconductor particles preferentially form nuclei at solid surfaces or phase borders, which increases the production of cavitation bubbles and free radicals such OH. It has been discovered that in sonocatalysis, the phenomena of heterogeneous nucleation are more applicable than homogeneous cavitation. This is because interfaces often have lower thermodynamic nucleation barriers than their bulk equivalents, which encourages surface nucleation. ^(vi)

Mechanism of Photo-Excitation

Collapse of cavitation bubbles results in the light-emitting phenomena known as sonoluminescence (SL). High intensity light with a broad wavelength range, usually between 200 and 700 nm, is released during sonoluminescence. Electrons from the valence band (VB) may be excited to move to the conduction band (CB) when a semiconductor catalyst is present during ultrasonication because the energy of the light produced may surpass the semiconductor's band gap. Because of the excited electrons, this action creates holes in the valence band. Highly reactive radicals are produced when dissolved oxygen reacts with photogenerated electron-hole pairs. Sonocatalysis works similarly to photocatalysis in this regard. ^(vii)

Mechanism of Thermal Excitation

According to the "hot spots" theory, high temperatures in a particular region could cause thermal excitation of the semiconductor, which would lead to the creation of electron-hole pairs. Numerous studies have documented this phenomenon, showing that high temperatures can stimulate the generation of electron-hole pairs in specific semiconductors. TiO₂ exhibits little catalytic activity at ambient temperature, but when heated to temperatures between 350 and 500 °C, its effectiveness greatly increases. The numerous highly oxidative holes that form as a result of semiconductors being thermally excited are responsible for this increase. ^(viii)

Uses of sonocatalysis:

The application of sonocatalytic processes in severely contaminated water has been made possible by the creation of these extremely reactive species. Thus, among other things, the procedure is effective in treating wastewater or effluents that contain a variety of organic contaminants ^(ix)



Sonophotocatalysis is a new treatment method that decreases the need for harsh physical conditions while increasing the overall effectiveness of AOPs and chemical reaction kinetics. By addressing issues with the opacity and porosity of the catalyst support, sonophotocatalysis enhances the efficiency of photocatalytic degradation reactions in comparison to sonolysis and photocatalysis alone.

Environmental remediation: Organic molecules in the environment can be broken down and mineralized using sonocatalysis.

Sonocatalysis has uses in the domains of pharmacology and medicine.

Metallurgy: There are uses for sonocatalysis in this field.

Sonocatalysis has uses in the field of nanotechnology.

Wastewater treatment: Heavy metals, dyes, medications, and pesticides are among the organic and inorganic contaminants that sonocatalysis may remove from wastewater.

II. PHOTOCATALYSIS

Utilizing light energy to promote chemical reactions, photocatalysis is a novel and potent technique that is mostly used to disinfect water and break down organic contaminants. When it comes to solving environmental problems, such as treating wastewater that contains dangerous materials, this technology is especially important. Fundamentally, the process of photocatalysis uses materials called photocatalysts, which are usually semiconductors like titanium dioxide (TiO_2), to encourage redox (reduction and oxidation) reactions on their surface, which eventually result in the degradation of pollutant. ^(x)

Mechanism of Photocatalysis;

The photocatalytic process happens when a semiconductor catalyst is exposed to light with an energy higher than the semiconductor's bandgap. A hole (h^+) may occur as a result of excited electrons in the VB jumping into the CB. After then, energy is released as a result of the electron-hole pairs created by light absorption recombining. This recombination is responsible for the semiconductor's low light-to-energy conversion rates and poor quantum efficiency. Light-generated electron-hole (e^- , h^+) pairs split off and migrate to the material's surface, where they react with ... if the photogenerated carriers do not recombine. ^(xi)

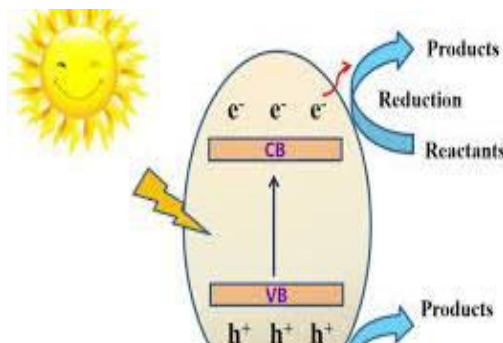


Figure 3: Mechanism of Photocatalysis

Uses of photocatalysis

Utilizing light to accelerate chemical reactions, photocatalysis is a technology with numerous benefits, such as:

Purification of air and water: Toxic ions and contaminants can be eliminated from air and water by photocatalysis. Additionally, it can be used to treat wastewater, remove ethylene from fruits and vegetables, and get rid of odors.

Water splitting: Hydrogen can be produced through water splitting using photocatalysis.

Applications in medicine: Photocatalysts can be utilized in surgical garments, photodynamic therapy, and coatings that are antibacterial, antiviral, and antifungal. Agriculture: Photocatalysts can improve plant growth and seed germination.



Self-cleaning: Materials that are self-cleaning, self-sterilizing, self-degrading, or anti-fogging can be made via photocatalysis. ^(xii)

Comparing the Mechanisms of Photocatalysis with Sonocatalysis

Comparison of the mechanisms of sonocatalysis and photocatalysis can help better understand the unique features and advantages of sonocatalysis in promoting efficient and sustainable chemical transformations. The similarity and difference between these two types of mechanisms are detailed below. ^(xiii)

Similarity:

Semiconductor catalyst plays a vital role in lowering the energy barrier for the formation of cavitation bubbles, which is similar to the way that a traditional catalyst reduces the activation energy of a chemical reaction. This is achieved by providing a surface for the accumulation and stabilization of gas or vapor pockets within the fluid medium, effectively reducing the threshold pressure required for bubble nucleation.

Undoubtedly, photocatalysts have the potential to serve as effective sonocatalysts, leveraging the phenomenon of sonoluminescence generated by cavitation given their inherent properties and unique chemical compositions, photocatalysts can harness the energy released by cavitation bubbles to enhance catalytic reactions and promote efficient chemical transformations. ^(xiv)

Difference:

The formation of cavitation bubbles is primarily driven by physical processes, involving the rapid formation and collapse of small pockets of gas or vapor within a fluid medium. This can occur due to the changes in pressure and temperature that cause the fluid to reach its boiling point, resulting in the generation of these bubbles. The effect of cavitation can be significant, leading to the erosion of solid surfaces and the generation of shockwave that can have profound impacts on the surrounding environment.

Acoustic cavitation is a key phenomenon in sonocatalysis, whereby high-intensity sound wave generates microscopic bubbles in a liquid medium. During the cavitation process, these bubbles release energy in the form of heat, shockwave, and free radicals, which can induce chemical reactions in the solution. As the bubbles collapse, they generate extremely high temperatures and pressures in localized regions of the solution. The sudden and intense energy release can result in large increases in temperature, which can accelerate the rate of chemical reactions in the solution. Moreover, the high temperatures generated by acoustic cavitation can lead to thermal excitation of the catalyst, thereby promoting the generation of reactive species, such as electron-hole pairs. This, in turn, can lead to enhanced catalytic activity and selectivity in sonocatalysis. ^(xv)

Summary of the Synergistic Effect during Sonophotocatalytic Process

In order to compare the effects of sonophotocatalysis with those of separate processes (sonocatalysis and photocatalysis), it is necessary to assess the synergistic contribution to the elimination of organic pollutants during the degradation process by sonophotocatalysis. The synergistic effect of a sonophotocatalysis process can be assessed using the synergistic index. This index is calculated as the ratio of the rate constant of sonophotocatalysis to the sum of the rate constants of the individual processes, and is commonly employed to analyze the degree of synergistic enhancement in dye decolorization. ^(xvi)

The synergistic effect of sonophotocatalysis in organic pollutant degradation has been demonstrated in many studies. Mosleh et al. reported that the pseudo-first-order rate constant for sonophotocatalytic degradation of trypan blue was $26.33 \times 10^{-2} \text{ min}^{-1}$, while the sum of the rate constants of photocatalysis and sonocatalysis was only $9.88 \times 10^{-2} \text{ min}^{-1}$, resulting in a synergistic index of 2.53. Babu et al. reported a synergistic index of 3.7 for the sonophotocatalytic degradation of Methyl orange using CuO-TiO₂/rGO nanocatalysts. The authors concluded that the high synergy probably resulted from the combined action of hydroxyl radicals generated by the sonolytic and photocatalytic systems. Benomara et al. reported that the pseudo-first-order rate constants for the degradation of methyl violet 2B were 6.8×10^{-3} for sonocatalysis, 22.9×10^{-3} for photocatalysis, and $39.7 \times 10^{-3} \text{ min}^{-1}$ for sonophotocatalysis, demonstrating



the significant synergistic effect of sonophotocatalysis. Ahmad et al. investigated the degradation of Rhodamine B (RhB) in photocatalytic, sonocatalytic, and sonophotocatalytic systems, and found that the sonophotocatalytic process exhibiting a higher rate constant compared to the sum of the photocatalytic and sonocatalytic processes. Sonophotocatalytic process was more effective in degrading RhB compared to photocatalytic and sonocatalytic processes due to the presence of more reactive radicals and the increased active surface area of the ZnO/CNT photocatalyst. Together, these findings highlight the potential of sonophotocatalysis as a promising approach for the efficient degradation of organic dyes in wastewater.

During the sonophotocatalytic process, the combination of ultrasonic wave, light, and photocatalyst can lead to synergistic effect that enhances the degradation of organic pollutants in wastewater. The synergistic effect is attributed to several factors, including the increased production of reactive radicals and the improved mass transfer of the pollutants to the photocatalyst surface. One of the key advantages of sonophotocatalysis is the increased production of reactive radicals, such as $\bullet\text{OH}$, which is highly effective in breaking down organic pollutants. Ultrasonic wave can induce cavitation, which generates high-energy bubbles that collapse and release shockwave and heat, leading to the formation of reactive radicals. Similarly, when a photocatalyst is illuminated with light, electrons are excited, leading to the production of reactive radicals. The combination of ultrasonic wave and light in sonophotocatalysis can lead to a higher production of reactive radicals, as the ultrasonic wave can promote the separation of electron-hole pairs, which are the precursors of reactive radicals, while also enhancing the mass transfer of the pollutants to the photocatalyst surface. Another factor that contributes to the synergistic effect of sonophotocatalysis is the improved mass transfer of the pollutants to the photocatalyst surface.

In traditional photocatalysis, the efficiency of pollutant degradation is often limited by the mass transfer of the pollutants from the bulk solution to the photocatalyst surface. The use of ultrasonic wave in sonophotocatalysis can enhance the mass transfer of the pollutants by promoting the formation of micro-scale streams and turbulence, which increase the contact between the pollutants and the photocatalyst surface. In summary, the synergistic effect of sonophotocatalysis in the degradation of organic pollutants can be attributed to the increased production of reactive radicals and the improved mass transfer of the pollutants to the photocatalyst surface. ^(xvii)

III. CONCLUSION

One new and promising treatment method that greatly improves the effectiveness of Advanced Oxidation Processes (AOPs) is sonophotocatalysis. Sonophotocatalysis has a synergistic impact that enhances chemical reaction kinetics, allowing for the quicker degradation of pollutants and organic contaminants in a variety of situations by fusing the benefits of both ultrasound and photocatalysis. In addition to speeding up the entire degrading process, this technology eliminates the requirement for harsh physical conditions like high temperatures or pressures, which are sometimes necessary for conventional procedures.

Sonophotocatalysis's capacity to overcome the difficulties that separate therapy modalities like sonolysis and photocatalysis encounter is one of its main advantages. For example, problems with catalyst supports' opacity and porosity frequently arise in photocatalysis, which can restrict light penetration and decrease

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