Photocatalytic Degradation of Phenol in Wastewater: A Mini Review

Lawal, A.I.[1*], Muhammad, Z.[2], Obunadike, C.V.[3], Yakubu, Y.Y.[4], Ogunsanmi, A.O.[5], Abdulrazak, O.O.[6], Ayodele, C.O.[7] and Komolafe, F.E.[8]

[1,2] Kaduna State University, Nigeria
[3,6] Osun State University, Nigeria
[4]Kwame Nkrumah University of Science and Technology, Kumasi- Ghana
[5]Kwara State University, Nigeria
[7] Federal University of Agriculture, Abeokuta, Nigeria
[8] Federal university of Technology, Akure, Nigeria
**Corresponding Author*

***Abstract*: A major public health concern in many developing countries, including Nigeria, is the quality of their water supply. Everything a live entity does depends on water, a fundamental component of the biosphere. To ensure that water is safe for industrial and home use, it must be treated before consumption. However, phenolic compounds are found in our water bodies due to the polluted wastewater from industrial, agricultural, and home activities. Nature also has a role in their occurrence. These substances are poisonous and can cause long-term harm to both humans and animals. This paper reviewed research on the photodegradation of phenol utilizing nanoparticles in water treatment. This provides additional information and facts on cost-effective methods of treating wastewater and mineralizing phenol into valuable chemicals.**

***Keywords*: Photocatalysis, Phenol, Pollutants, Wastewater, Metal ions.**

I. INTRODUCTION

Water supply contamination is a growing issue. Most current treatment methods are efficient at cleaning water, but they only move toxins from one medium to another or produce waste that needs to be cleaned up and disposed of [1]. Effective techniques for converting resistant pollutants into less hazardous chemicals or complete mineralization are required. Transferring impurities from one water phase to another is not the best solution. More long-lasting solutions are offered by destructive oxidation processes [2].

Recent developments in oxidation technology have shown promise for treating wastewater and water. Photodegradation is an effective method used to treat toxic and bio-resistant pollutants [3]. The highly reactive hydroxyl radical is the oxidant involved in oxidizing organic molecules. The production of hydroxyl radicals can be accomplished in various ways, each requiring the employment of an oxidant and an activating system [4].

The elimination of organic and inorganic waste from water has a high potential for photocatalytic reactions on irradiation semiconductor powders. Since it is non-toxic, insoluble in water, and reasonably priced, titanium dioxide is a semiconductor commonly employed in investigations on organic breakdown [5].

Both a synthetic chemical and a natural substance, phenol both. When pure, it has no color or is solid and white. The industrial item is a liquid. The smell of phenol is distinctive and sickeningly sweet and tarry. Phenol can be tasted and smelled at concentrations below those that are dangerous. A moderate amount of phenol can dissolve in water to form a solution because it evaporates more slowly than water. The synthesis of phenolic resins, as well as the creation of nylon and other synthetic fibers, are the main uses of phenol. Additionally, it is utilized in medical preparations, as a disinfectant and antiseptic, and in slimicides (chemicals that eliminate bacteria and fungi found in slimes) [6].

Phenol is used to make the intermediates caprolactam and bisphenol A, which are used to make nylon and epoxy resins, respectively. In pharmaceuticals, phenols produce ear and nose drops, mouthwash, throat lozenges, slimicides, and disinfectants [7].

Both developing and developed nations deal with the issue of environmental contamination year-round due to phenol usage [35]. Phenol was among the top 50 chemicals generated annually in the bulk of the housing and building industries in the United States [32].

Human activities are the leading cause of phenol pollution in the environment, particularly in soil, because its mobility in an aqueous environment is limited due to high adsorption onto solid surfaces [32, 36]. Because phenolic chemicals are extensively employed to make wood preservatives, soil regions within sawmills are typically highly contaminated [27]. Since the 1860s, phenol has been utilized in manufacturing [14].

Before dyes, chemical intermediates, and aspirin were invented in the early nineteenth century, it was utilized to manufacture basic plastic resin. The major application of phenol is in the manufacture of phenolic resins, which are synthetic polymers used in the construction, automotive, and appliance sectors, as well as the manufacture of bisphenol A, commonly used in the manufacture of plastics [37], and caprolactam for nylon and synthetic fiber. In addition to its limited usage in the manufacture of paint, tanning colors, lacquers, perfumes, and ink, phenol is employed in the manufacturing of general infection, slimicide, lotion, ointments, and salves for medicinal purposes [38–40].

1.1 Photocatalysis

Photocatalysis is a method for facilitating or accelerating chemical reactions by using both light and catalysts simultaneously. The method of photocatalysis can be utilized for several things, such as the oxidation of organic contaminants in wastewater, the creation of hydrogen, the cleansing of the air, and antibiotic activity. Photocatalysis is expanding quickly and attracting more study interest than other approaches due to its availability, affordability, benefits, efficiency, efficacy, and environmental sustainability abilities [8].

Photocatalysts are divided into two types: homogeneous and heterogeneous processes. [9,10,11]

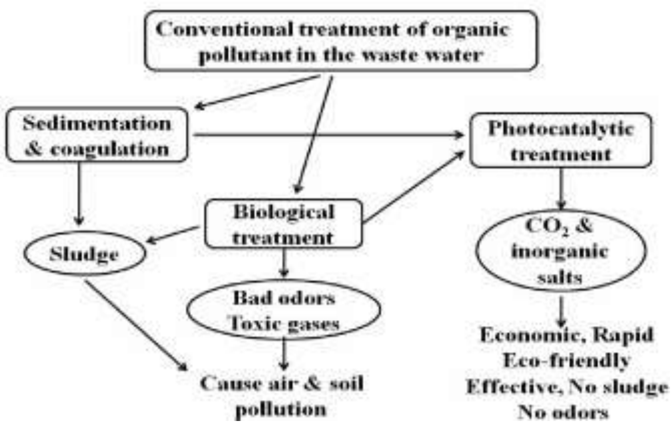

Figure 1: Schematic illustration of the benefits of photocatalysis in the removal of organic contaminants from wastewater.

1.2 Principle of Photocatalysis

1.2.1 Discovery of Photocatalysis

In 1972, Fujishima and Honda first observed photocatalytic splitting of water on a TiO_2 electrode under ultraviolet (UV) light [10], which resulted in heterogeneous photocatalysis. Electrochemists did not accept this discovery because of the use of light as an energy source; they argued that oxygen could not produce a low voltage based on the previous results indicating 1.5–2V and above. This led to the substantial study of the photocatalytic efficacy of TiO_2 and its improvement. These investigations often focus on energy storage and recharging [11,12]. TiO_2-based photocatalysts are a promising method for quickly destroying organic molecules in polluted air and water [9,11,12].

Prof. Fujishima emphasizes that everyone should benefit from research and technology because it builds a society where people can have relaxed lives. The most important thing in science and technology is to Creation of novel ideas that can be used to create goods and services by using the photocatalyst [8,11].

1.3 Types of Photocatalysis

1.3.1 Homogeneous Photocatalysis

They are commonly employed as catalysts with metal complexes (transition metal complexes like iron, copper, nickel, chromium, etc.). The higher the oxidation state of metal ion complexes produced hydroxyl radicals under these photon and temperature circumstances. These hydroxyl radicals react with organic materials, causing hazardous compounds to degrade.

1.3.1 Heterogeneous Photocatalysis

It is a method for degrading different organic contaminants in wastewater. This approach offers various advantages over competing processes such as Complete mineralization, waste management, inexpensive, and temperature and pressure conditions friendly [9,10]. Semiconducting materials (TiO_2, ZnO, SnO_2, CeO_2, and Ni, for example) primarily function as heterogeneous photocatalysts due to their advantageous combination of electronic structures, which include a filled valence band and an empty conduction band, light absorption properties, charge transport characteristics, and excited state lifetime [10-15]. A good semiconductor photocatalyst should be Photoactive., Able to utilize visible and near-UV light., Biologically and chemically inert, Photo stable (i.e., stability toward photo corrosion), Inexpensive, and Nontoxic. Semiconductor photocatalysis seems to be a promising technology that can be used in several ways [10–15].

Photocatalysis is a unique method used in several applications, such as bacterial activity, hydrogen production, degradation of several organic pollutants in wastewater, and air purification [16]. To completely mineralize the pollutant at moderate temperature and pressure, the photocatalytic process has recently become more concentrated in the wastewater treatment industry. When sunshine or near-UV light is used as a source of irradiation, these methods stand out for waste disposal and cost-effectiveness. Photon-assisted production of catalytically active species is referred to as a photocatalyst. A change in the pace of chemical reactions or their creation under the influence of light in the presence of substances known as photocatalysts that absorb light quanta and are involved in the chemical transformations of the reactants is often referred to as photocatalysis [16].

1.4 Description of The Two Mechanisms in Photocatalysis

1.4.1 Description of Oxidation Mechanism

Water is present on the photocatalyst surface and is referred to as "absorbed water." The generation of hydroxyl radicals (OH·) occurs when light irradiation causes positive holes in the valence band due to the electrons shifting to the conduction band (agents with strong oxidative decomposition power). After that, the organic material in the dyes is reacted with by these hydroxyl radicals. When this process occurs in the presence of oxygen, the intermediate radicals in the organic compounds can undergo radical chain reactions and, in some situations, consume oxygen. In this situation, the organic material eventually decomposes and transforms into carbon dioxide and water [13].

In these conditions, organic molecules may react directly with the positive holes, leading to oxidative decomposition. Figure 1.0 depicts the entire oxidation process.

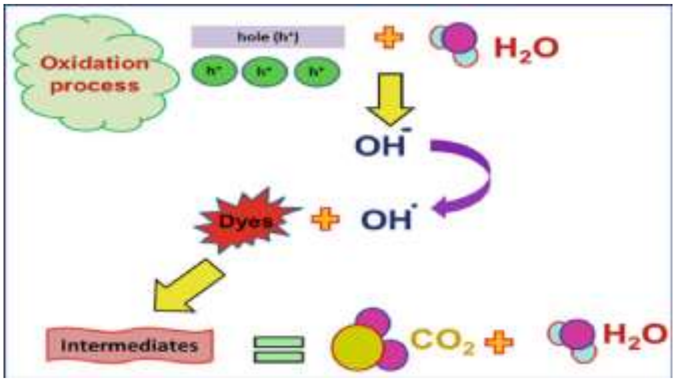

Fig. 2. Schematic representation of oxidation mechanism.

Source: R. Saravanan, Francisco Gracia and A. Stephen. Basic Principles, Mechanism, and Challenges of Photocatalysis

1.4.2 Description of Reduction Mechanism

A pairing reaction results in the reduction of oxygen present in the air. Because oxygen is an easily reducible substance, it is reduced instead of converted into hydrogen. Superoxide anions are produced when dissolved oxygen species interact with the conduction band electrons. During the oxidative reaction, these superoxide anions attach to the intermediate products, creating peroxide or converting to hydrogen peroxide before becoming water. In organic materials rather than water, the reduction is probably more likely to happen. Because of this, there are more positive holes when there is a higher concentration of organic matter. By doing so, carrier recombination is decreased, and photocatalytic activity is increased [15]. The process of reduction is shown in Figure 2.2.

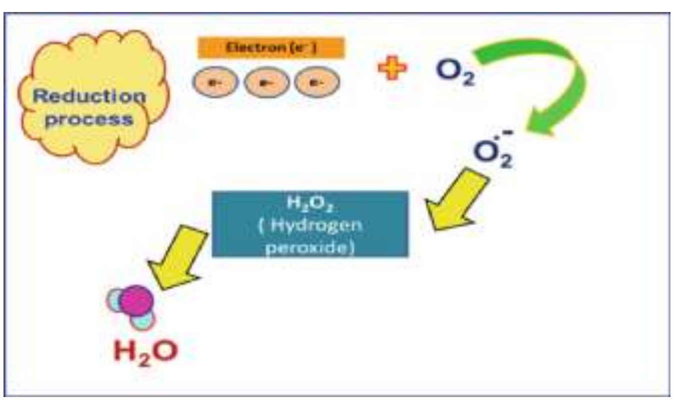

Figure 3. Schematic representation of reduction mechanism.

Source: [8]

II. BACKGROUND HISTORY OF PHENOLS

Phenol is a component of coal tar and was probably first (in part) isolated from coal tar in 1834 by Runge, who called it "carbolic acid" (Karbols are) or "coal oil acid" [17].

Phenol (hydroxybenzene) is a colorless, crystalline substance with a distinctive odor used in the production of chemicals (alkyl phenols, cresols, xylenols, phenolic resins, aniline, and other compounds), oil, coal processing, and metallurgical use are some of its frequent industrial applications. Additionally, phenol is used to manufacture textiles, explosives, pesticides, and dyes. Additionally, it is employed in chemical analysis as a reagent and as a disinfectant. On a large scale, coal tar is used to synthesize phenol. Chemical processes that also result in the production of phenol include the oxidation of toluene, the reaction of chlorobenzene with sodium hydroxide, and the synthesis of phenol from benzene and propylene. [17]

The anthropogenic phenol emissions in the environment are a result of the processes which take place in various industries that are responsible for all anthropogenic phenol emissions in the background. Phenol is also released from fossil fuels used in automobile vehicles. The chemicals enter the environment due to urban or industrial sewage draining onto water bodies. Furthermore, the presence of phenols in the surroundings is caused by the manufacture and application of various pesticides, particularly phenoxy herbicides such as 2.4-dichlorophenoxyacetic acid (2,4-D) or 4-chloro-2-methylphenoxyacetic acid (MCPA), as well as phenolic biocides such as pentachlorophenol (PCP) and dinoseb pesticides. Some phenols may be generated naturally, such as the synthesis of phenol and p-cresol (chlorinated phenols) during organic matter decomposition [18].

They are frequently employed as disinfectants, preservatives, pesticide production raw materials, and alternatives in other processes. Priority phenols, sadly, are now widespread environmental contaminants that can be detected in ambient air, soil, and drinking water. Numerous key phenols, particularly chlorophenols, are infamous for their poisonousness, carcinogenicity, and environmental persistence [18].

2.1 Physicochemical Properties of Phenol Structures

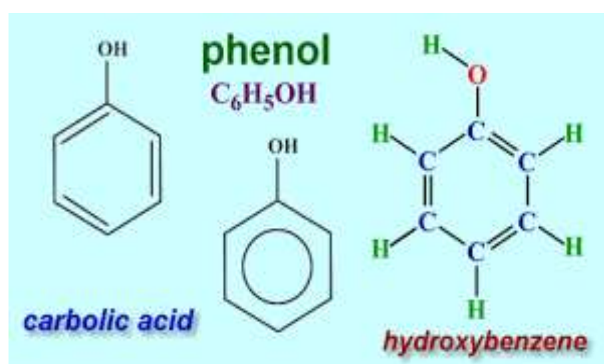

Figure 4. Structural formula of phenol.

Chemical formula of phenol: C_6H_5OH; early name: carbolic acid, hydroxybenzene;

CAS registry number: 108-95-2.

Molecular weight: 94.11 (molecular mass of C_6H_5OH is equal to 94.04186).

Freezing point: 40.91ºC.

Specific heats of combustion: Cp = 3.06Jmol−1 K−1, Cv= $3.07Jmol^{-1} K^{-1}$.

Phenol is very soluble in water and is quite flammable.

2.2 Phenol And Waste Water

The wastes from most chemical industries discharge phenol and phenolic compounds, contaminating various natural water resources [19]. As a result, this contaminant is exposed to humans. One of the main environmental contaminants comes from phenol-using industries' wastewater effluents. Hazardous carbon-based pollutants are formed during chemical and petroleum industries processes, and these pollutants negatively impact the environment. These industries frequently produce aromatic organic compounds in their effluents, which are resilient to natural degradation and remain in our surroundings. They can so travel over great distances and bioaccumulate in both human and animal tissue. A class of substances known as organic pollutants poses a major threat to human health. Numerous aromatic substances exhibit mutagenic, teratogenic, or carcinogenic characteristics. Organic compounds that are not biodegradable must be pre-treated to make them biodegradable or less hazardous. Worldwide, there has been a significant deal of concern over the pollution of water bodies by aromatic organic contaminants like phenol and its similar compounds. The severe toxicity of phenols toward aquatic life, human life, and other living forms is well established. They are regarded as some of the most dangerous contaminants, and they are undoubtedly the most challenging to get rid of. Phenol is a contaminant that is frequently present in wastewater from industries such as those that process coal, and oil, make pulp and paper, manufacture resins and coke, manufacture plastics, and varnishes, manufacture steel, manufacture pharmaceuticals, manufacture pesticides, manufacture textiles, manufacture tanneries, and refine metals [20–21]. Phenol quickly penetrates the skin, can cause severe eye, mucous membrane, and respiratory tract irritation, and can be fatal when consumed, inhaled, or absorbed through the skin. One gram of phenol is said to be disastrous for humans and can seriously harm the liver and kidneys when consumed orally. The number of phenols in wastewater can range from 10-300 mg/l, but in extremely polluted sewage, this can increase to 4.5 g/l. [22]

Additionally, it's likely that when chlorinated water is added to phenol-containing water for disinfection, harmful polychlorinated phenols are created. Phenol and its derivatives have the potential to cause cancer and are poisonous or fatal to aquatic animals (fishes) at doses of 5 to 25 mg/l. Even at a considerably lower quantity of 2µg/l, drinking water has a medical taste and an unpleasant odor. The World Health Organization has established a recommendation of 1µg/l to limit the phenol concentration in drinking water due to these detrimental effects of phenols on human well-being [23]. The U.S. Environmental Protection Agency has designated phenols as priority pollutants and set a water purification standard of less than 1µg/l of phenol concentration in surface waters due to the high use of phenols in the United States and their potential toxicity. The phenol concentration in drinking water is regulated by the European Council Directive, which has a 0.5 µg/l limit established. It is worth mentioning that water policy in the European Union is presently undergoing considerable change. The adopted measures stress the need to stop surface water deterioration, safeguard water bodies, and lessen pollution from hazardous substance discharges by 2015. The UAE has laws that limit the number of total phenols in industrial water that is released into the main water bodies to 0.1 mg/l [24].

Therefore, it is mandatory globally for industries to cleanse their wastewater effluents before safe discharge into the surroundings to preserve the soils and aquatic ecosystems. The elimination of phenol is possible using effective treatment techniques such as activated carbon adsorption, ion exchange, liquid-liquid extraction, and chemical oxidation. But they frequently have significant drawbacks, including being expensive. Additionally, most of these processes transfer phenol to another phase rather than degrading it, which creates dangerous by-products (secondary pollution). However, biodegradation is viewed as a more economical and cost-effective substitute. As a result, the biological treatment of phenols has become a more crucial step in reducing pollution [25].

Additionally, the biodegradation approach of phenol removal is widely chosen over physicochemical methods due to the possibility of complete phenol mineralization, which results in a compound's entire conversion to its inorganic mineral elements. Traditionally, continuously activated sludge techniques significantly reduce processing costs, and their by-products are used to treat effluents containing phenols. However, due to its low capacity to adapt to changes in the phenolic load, the actual applicability of this technique is quite constrained [26]. Novel biological treatment systems were introduced because many toxic pollutants cannot be effectively removed by conventional natural treatment methods [27]. Treating wastewater containing phenolic compounds using biological processes has been the subject of a significant amount of research. Still, there haven't been any thorough evaluations of the published literature. In contrast, [28] researchers have focused on studying microorganisms enhancing phenol biodegradation and the process required, [29] as well as the mechanisms and kinetics of microbial degradation of phenols. We provide a thorough analysis of the literature on the aerobic biodegradation of phenols during the last ten years in this paper, focusing on assessing the field's current state and considering potential directions for future research.

2.3 Ultraviolet and Visible Spectrophotometer

The visible and ultraviolet regions of the electromagnetic spectrum have wavelengths between about 100 and 800 nm. The vacuum ultraviolet (100-200nm) is challenging to measure and has limited application in analytical processes. For both quantitative and qualitative analyses of chemical species, the absorbance or transmittance in the ultraviolet or visible region of the spectrum is measured. Such species are absorbed in two stages, the first of which is $M+hv= Mx$ [32].

This entails the species being excited by photons (hv) with a short lifetime (10–9 seconds) that are absorbed. The second stage involves relaxing by photochemically converting M*x* into new species. The interaction between photons and electrons that both directly partake in the bond formation (and are associated with more than one atom) or are localized around such atoms as oxygen, sulfur, nitrogen, and hydrogen is what causes radiation to be absorbed by organic molecules [32].

2.4 Effects Of Metal Ions On The Photodegradation Of Phenols.

The complex formation between the metal ions and organic species in industrial effluent might slow the degradation of organic pollutants and lower the effectiveness of metal recovery. Many industries produce aqueous effluent streams that are too high to be released into the environment untreated but too low to recover easily from organic contaminants and metal ions. Phenol and its derivatives are regarded as the main polluting components in wastewater due to their high toxicity, high oxygen demand, and low biodegradability [33].

Processes intended to remove phenols from or mineralize water bodies have been reported in terms of efficacy [34]. While biological and chemical oxidation treatment methods have traditionally been favored for the destruction of this type of organic substance, they have been used in phenol recovery operations together with solvent extraction and activated carbon adsorption processes. In the current study, photolytic oxidation and anodic oxidation of phenol in the presence or absence of titanium dioxide as a catalyst and hydrogen peroxide as a chemical oxidant were both taken into consideration. There have been reports [35] comparing various advanced oxidation processes for phenols, discussing how metal contaminants affect some of these processes' efficiencies. In this report, the effects of copper ions on phenol oxidation are discussed.

2.5 Mechanism of Photodegradation of Phenols

Overuse of water resources and rising water pollution have both been blamed for the shortage of water bodies [36]. Due to the growing variety of manufactured goods and the related variations of precursor chemicals that can be disposed of in water resources, industrial wastewater contamination has become a significant and complex concern [37]. In the petrochemical, chemical, and pharmaceutical industries, one of the most poisonous recalcitrant organic chemicals widely utilized is phenol [38]. Advanced oxidation processes (AOPs), which are excellent alternatives, have recently drawn a lot of interest in the removal of phenol. AOPs use a variety of reaction mechanisms, but they all operate on the same basic oxidation principle, which uses hydroxyl radicals as the oxidizing species to eliminate pollutants in water [39]. One AOP that has shown effective at converting carbon-based compounds into easily biodegradable compounds which can be mineralized into carbon dioxide and water is heterogeneous photocatalysis using semiconductor catalysts [40]. The fundamental idea behind photocatalysis is that when UV light excites the motivations, the resulting electrons and holes interact with oxygen or water to produce highly oxidizing free radicals like OH-. The pollutants in water are converted into carbon dioxide and water by hydroxyl radicals.

2.6 Effect of Time On Photodegradation Of Phenols

Photocatalysis is associated with time-exhausted electrons and holes to get to the particle's surface. When the particles are nano-sized, their diameter becomes very miniature, so it is then straight to recharge carriers moving from the inside to the surface and starting redox reactions, thereby resulting in a superior photocatalytic reaction.

III. CONCLUSION

Modern industrial and societal development necessitates extensive research into wastewater treatment. A large number of researchers have worked on this problem. In other way, phenol is an important contaminant from this perspective. Despite all of the studies over the previous decade, phenol remains one of the most common contaminants in the environment. This is owing to the widespread use of phenol as the primary chemical in numerous sectors, which will continue as long as demand continues. Because phenol is a priority pollutant, the risk of phenol pollution cannot be avoided. Hence, It must be eradicated or decreased from the environment by potentially effective and efficient methods. Among all the existing approaches, photocatalysis effectively and efficiently eliminate phenol from water. Hence, photodegradation may be an alternate treatment strategy for pollutants that are resistant to traditional treatment procedures. With the help of affordable and reusable catalysts, photodegradation can be used to mineralize phenol completely. The findings suggest that photocatalytic degradation could be used to remove phenol completely., Photodegradation is a viable and cost-effective treatment option for phenolic wastewater.

REFERENCES

[1] Crittenden, J. C., Lıu, J., Hand, D. W. and Perram, D. L.: 1997, 'Photocatalytic oxidation of chlorinated hydrocarbons in water', Wat. Res. 31, 429–438.

[2] Matthews, R. W.: 1991, 'Photo oxidative degradation of coloured organics in water using supported catalysts TiO_2 on sand', Wat. Res. 25, 1169–1176.

[3] D'Oliveira,J.-C., Al-Sayyed, G. and Pichat, P.: 1990, 'Photodegradation of 2- and 3-chlorophenol in TiO_2 aqueous suspension', Environ.Sci. Technol. 24, 990–996.
[4] Winterbottom, J. M., Khan, Z., Boyes, A. P. and Raymahasay, S.: 1997, 'Photocatalyzed oxidation of phenol in water using a concurrent down flow contactor reactor', Environ. Progress 16, 125–131.
[5] Lakshmi, S., Renganathan, R. and Fujita, S.: 1995, 'Study on TiO_2-mediated photocatalytic degradation of methylene blue', J. Photochem. Photobiol. 88, 163–167.
[6] Agency for Toxic Substances and Disease Registry (ATSDR). 2008. ToxicologicalProfile for Phenol. Atlanta, GA: U.S. Department of Health and Human Services, PublicHealth Service.
[7] Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological Profile for Phenol (Update). Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA. 1998.
[8] R. Saravanan, Francisco Gracia and A. Stephen Basic Principles, Mechanism, and Challenges of Photocatalysis.
[9] Rajeshwar K, Osugi ME, Chanmanee W, Chenthamarakshan CR, Zanoni M, Kajitvichyanukul P, Krishnan-Ayer R (2008) Heterogeneous photocatalytic treatment of organic dyes in air and aqueous media. J Photochem Photobiol C 9(4):171–192
[10] Rehman S, Ullah R, Butt AM, Gohar ND (2009) Strategies of making TiO_2 and ZnO visible light active. J Hazard Mater 170(2–3):560–569
[11] Fujishima A, Rao TN, Tryk DA (2000) Titanium dioxide photocatalysis. J Photochem Photobiol C1(1):1–21
[12] Fujishima A, Honda K (1972) Electrochemical photolysis of water at a semiconductor electrode. Nature 238(5358):37–38
[13] Khan MM, Adil SF, Al-Mayouf A (2015b) Metal oxides as photocatalysts. J Saudi Chem Soc 19(5):462–464
[14] Konstantinou IK, Albanis TA (2004) TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations. Appl Catal B 49(1):1–14
[15] Nakata K, Fujishima A (2012) TiO_2 photocatalysis: design and applications. J Photochem Photobiol C 13(3):169–189
[16] Hagen J (2006) Industrial catalysis: a practical approach/Jens Hagen, 2nd edn. Wiley, Weinheim
[17] F. F. Runge, Ann. Phys. Chem., 31, 65 (1834); F. F. Runge, Ann. Phys. Chem., 32, 308 (1834); C. F. v. Reichenbach, Ann. Phys. Chem., 32, 497 (1834).
[18] Central pollution control board. (ministry of environment, forests & climate change). parivesh bhawan, east arjun nagar, delhi – 110032, website: www.cpcb.nic.in. August, 2016. Compiled by Dr. Yogita Kharayat, Scientist 'B'; Sh. V. K. Verma, SSA; Sh. Bhupander Kumar, Scientist `C' and Dr. C. S. Sharma, Scientist `E'.
[19] Fleeger, J.W., K.R. Carman and R.M. Nisbet, 2003. Indirect effect of contaminants in aquatic ecosystem. Science Total Environments, 3170: 207-233.
[20] Kumar, A., Kumar, S., and Kumar, S. (2005). Biodegradation kinetics of phenol and catechol using Pseudomonas putida MTCC 1194. Biochem. Eng. J. 22, 151–159.
[21] Edalat Manesh, M., Mehrvar, M., and Dhib, R. (2008). Optimization of phenol degradation in a combined photochemical–biological wastewater treatment system. Chem. Eng. Res. Des. 86, 1243–1252.
[22] Nuhoglu, A., and Yalcin, B. (2005). Modelling of phenol removal in a batch reactor. Process Biochem. 40, 1233–1239.
[23] Yan, J., Jianping, W., Jing, B., Daoquan, W., and Zongding, H. (2006). Phenol biodegradation by the yeast Candida tropicalis in the presence of m-cresol. Biochem. Eng. J. 29, 227–234.
[24] Al Zarooni, M., and Elshorbagy, W. (2006). Characterization and assessment of Al Ruwais refinery wastewater. J. Hazard. Mater. A136, 398–405.
[25] Liu, Y. J., Zhang, A. N., and Wang, X. C. (2009). Biodegradation of phenol by using free and immobilized cells of Acinetobacter sp. XA05 and Sphingomonas sp. FG03. Biochem. Eng. J. 44, 187–192.
[26] El-Naas, M., Al-Zuhair, S., and Makhlouf, S. (2010). Batch degradation of phenol in a spouted bed bioreactor system. J. Ind. Eng. Chem. 16, 267–272.
[27] Shourian, M., Noghabi, K. A., Zahiri, H. S., Bagheri, T., Karballaei, G., Mollaei, M., Rad, I., Ahadi, S., Raheb, J., and Abbasi, H. (2009). Efficient phenol degradation by a newly characterized Pseudomonas sp. SA01 isolated from pharmaceutical wastewaters. Desalination; 246, 577–594.
[28] Agarry, S. E., Durojaiye, A. O., and Solomon, B. O. (2008). Microbial degradation of phenols: A review. Int. J. Environ. Pollut. 32, 12–28.
[29] Nair, C. I., Jayachandran, K., and Shashidhar, S. (2008). Biodegradation of phenol. Afr. J. Biotechnol. 7, 4951–4958. https://education.Jlab.org/itselemental/ele028.html.
[30] https://www.fhwa.dot.gov/pavcmcnt/rccmicro.html,"Microsilica-Utilization of Recycled Materials in Illinois Highway construction"
[31] Yilleng, M. T. (2014). Photocatalysis activity of metal
[32] Santos, A., Yustos, P., Durban, B., Garcia-Ochoa, F., 2001. Oxidation of phenol in aqueous solution with copper catalysts. Catal. Today 66, 511-517.
[33] Kulkarni, U.S., Dixit, S.G., 1991. Destruction of phenol from wastewater by oxidation with sulfite-oxygen. Ind. Eng. Chem. Res. 30, 1916-1920.
[34] Brezová, V., Blazžková, A., Borošová, E., Čeppan, M., Fiala, R., 1995. The influence of dissolved metal ions on the photocatalytic degradation of phenol in aqueous TiO_2 suspensions. J. Mol. Catal. A-Chem. 98, 109-116.
[35] T. Teka, A. Reda, Int. J. Technol. Enhance. Emerg. Eng. Res. 2, 2347 (2014)
[36] H. Eskandarloo, A. Badiei, C. Haug, Mater. Sci. Semicond. Process. 27, 240 (2014)
[37] I. Prabha, S. Lathasree, Mater. Sci. Semicond. Process. 26, 603 (2014)
[38] P. Navarro, J. Sarasa, D. Sierra, S. Esteban, I.L. Obelleiro, Water Sci. Technol. 51, 113 (2005)
[39] M.N. Chong, B. Jin, C.W.K. Chow, C. Saint, Water Res. 44, 2997 (2010)