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Review

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New Generation Energy-Efficient Light Source for Photocatalysis: LEDs for Environmental Applications

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Supporting Information

ABSTRACT: In this review, current progress in the area of photocatalysis using energy efficient Light Emitting Diodes (LEDs) as an irradiation source is discussed. LEDs are small in size, robust, do not contain mercury, have a longer life span than conventional light sources, and can operate on a direct current. These properties of LEDs offer a new alternative to traditional ultraviolet sources and open new possibilities for photocatalytic degradation with reduced power consumption, along with greater freedom in the design of various types of photocatalytic reactors. The present review mainly focuses on the photocatalytic degradation of organic compounds and dyes as well as the sterilization of microrganisms which are present in water and air, using irradiation by various types of LEDs, photocatalytic reactors, and catalysts. In addition, future prospects and challenges for the application of LEDs for to photocatalytic environmental pollutant degradation have been highlighted.

1. INTRODUCTION

Environmental pollution and remediation on a global scale have drawn attention to the vital need for new environmentally friendly, clean chemical technologies, and processes, as one of the most important challenges facing chemical scientists in the field of environmental chemistry. The main causes of water contamination are industrial discharges, excess use of pesticides, fertilizers (agrochemicals), pharmaceutical residues, and land-filling of domestic wastes.[1−11] Similarly, air pollution due to human activity arises mainly due to industrial processes, such as petrochemical production, storage and distribution, solvent usage, and motor vehicle emissions.[12−14] Wastewater treatment is usually based upon multiple mechanical, biological, physical, and chemical processes. Processes such as filtration, flocculation, sterilization, or chemical oxidation of organic pollutants are usually combined, depending on the treatment requirements for a given wastewater.[15−18] The removal of toxic gases has been mainly performed through the use of adsorbents.[19] However, in the treatment of both water and air, one phase of a pollutant is often concentrated or converted to another.[20] Semiconductor photocatalysis is emerging as an advantageous technique for the treatment of many effluents.[21−29] After the discovery of the photocatalytic properties of TiO_2 by Fujishima and Honda,[30] the advanced oxidation technology to remove low levels of persistent organic pollutants and to sterilize microorganisms in water has been widely demonstrated using traditional ultraviolet light and, later, using solar light, each being applied to environmental remediation processes.[31−41] Many photocatalysts have been synthesized and tested for their photocatalytic degradation of various pollutants present in air and water. The photocatalysts were designed to achieve higher photocatalytic activity under ultraviolet and visible light, for the generation of electron hole pairs which are capable of degrading organic pollutants.[9,11,17]

Photocatalytic degradation of pollutants is mainly achieved through the application of conventional ultraviolet lamps. The conventional ultraviolet light sources are mainly mercury vapor lamps (whether of low, medium, or high pressure) which have a relatively high energy consumption, contain hazardous mercury, require cooling, have a relatively short life-span, and can be difficult to operate.[42,43] In the case of solar light, a very large area is needed for its effective application, and the associated high cost of installation and limitation to daylight hours are significant drawbacks. These factors have greatly hampered the development of photocatalytic reactors development and the effective application of photocatalytic processes.[42]

Energy is necessary for the development of society, and, as such, it is present in all areas of everyday life as well as being the foundation of a large fraction of global economic transactions and industries. In order to survive the potential energy crises of the future, the utilization of energy efficient sources for the development of more efficient and commercially viable processes for various applications is the key. Recently, solid state technology has resulted in the development of compact, lower cost, and environmentally friendly light emitting diodes (LEDs). An LED is a semiconductor device which emits light in a narrow spectrum, which is produced by a form of electroluminescence. LEDs can emit light of different wavelength (infrared, visible, or near-ultraviolet) based on the composition and condition of the semiconducting materials. It is solid-state technology based entirely on p-n junction devices made of semiconductor materials such as gallium arsenide (GaAs), gallium arsenide phosphide (GaAsP), gallium

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phosphide (GaP), or indium gallium nitride (InGaN). The light output of an LED is directional and linearly proportional to the current within its active region. Other advantages of using LEDs are their small size and relatively long life span (more than 50,000 h) compared to conventional ultraviolet sources. Traditional UV sources have mainly been used in UV curing, disinfection, sensor, and photocatalysis applications. However, LEDs have recently been recognized as an alternative to conventional ultraviolet irradiation sources, and, additionally, solar light can be utilized alongside LEDs for such applications.[44−47]

In this review, we highlight recent developments in the area of photocatalytic decomposition and degradation of organic compounds, dyes, and microorganisms in water and volatile organic compounds in the air, through irradiation using the new generation energy efficient light sources, such as ultraviolet and visible LEDs. In addition to this, we briefly discuss the fundamentals of LED and reactor designs based on the various types of LEDs employed for the photocatalytic degradation of organic compounds, dyes, and microorganism in water and volatile organic compounds in air.

2. PHOTOCATALYSIS

Semiconductor photocatalysis is an advanced oxidation process that couples ultraviolet light with semiconductor technology as a photocatalyst and has been widely studied for the removal of pollutants from air and water.[48] The photocatalytic degradation of organic substances is achieved at various concentrations of pollutants.[49−51] The appeal of this process technology is the prospect of complete degradation of pollutants to environmentally harmless compounds. The carbon-containing pollutants are oxidized to carbon dioxide, while the other elements bonded to the organic compounds, being converted to their respective ions, such as nitrate, sulfate, or chloride. From the literature, it is clear that a number of pollutants, including aliphatic and aromatic compounds, dyes, surfactants, pesticides, and herbicides, can be completely mineralized to harmless substances through this process.[52] When the semiconductor photocatalyst absorbs photons of the ultraviolet bandgap energy, electron−hole pairs are generated.[53] Electrons in this excited-state form a conduction band, and holes in the valence band may recombine and dissipate the input energy as heat, or they may become separated and become involved in electron transfer reactions with species in the solution the photocatalyst is immersed in.[18] In the presence of suitable scavengers or surface defects, electrons become trapped and subsequently enter into redox reactions with species which are adsorbed on the surface or present within the electrical double layer of the charged particles. The holes react with the electrons, for example hydroxyl ions or water, to form hydroxyl radicals. The electrons on the other hand react with an electron acceptor, for example, molecular oxygen. For a reaction to take place, it is necessary that the valence band has a greater oxidizing potential than that of the species in question or that the conduction band is more reduced than the reduction potential of the species. The redox potential of the valence band holes and conduction band in electrons for different semiconductors varies from +4.0 to ±1.5 V vs NHE (normal hydrogen electrode), respectively.[54] Therefore, through this technology, a wide range of species can be converted using the oxidizing power of the activated catalyst. Of the various semiconductor photocatalysts which have been tested, TiO_2 appears to be the most active, stable, and cost-effective photocatalyst.[55] The anatase form of TiO_2 requires photons with energies greater than 3.2 eV (λ < 380 nm) to initiate bandgap excitation. It satisfies the foremost criteria for the degradation of organics, as the bandgap domain of the catalyst lies within the redox potential of the H_2O/OH couple.[54] Besides the advantages of complete destruction of toxic compounds and the use of atmospheric oxygen as an oxidant, TiO_2-based photocatalysis have many advantages over other conventional chemical oxidation methods. TiO_2 is cheap, biologically and chemically inert, insoluble under most conditions, photostable, nontoxic, has a relatively high reaction rate if a large surface area of catalyst is provided, and can be used for an extended period without any substantial loss of its activity.[56] Moreover, it uses ultraviolet light and, additionally, can be activated by sunlight. Recently, new generation light emitting diodes have been used to study the photocatalytic degradation of pollutants which are present in the air and water as well as for hydrogen production.

3. CONVENTIONAL ULTRAVIOLET LAMPS

Conventional ultraviolet lamps have mainly been used as a light irradiation source for studies of the photocatalytic degradation of various organic compounds present in the air and water.[31−42] The most common sources of UV are commercially available low, medium, and high pressure mercury arc lamps. A typical mercury arc lamp consists of a hermetically sealed tube of UV-transmitting vitreous silica or quartz with electrodes at both ends. The tube is filled with a small amount of mercury and an inert gas, usually argon. The electrodes are usually composed of tungsten with a mixture of alkaline earth metals to aid arc formation within the lamp. A gas discharge is struck by applying a high voltage across the electrodes. UV light is emitted from the lamp when mercury vapor, excited by the discharge, returns to a lower energy state. Argon is present as an inert gas to prevent any atmospheric electrochemical influence on the function of the aid lamp, extending the life of the electrode, and reducing thermal losses. Argon does not contribute to the spectral output of the lamp. However, the disadvantages associated with this conventional mercury lamp are its fragility, hazardous mercury content, and problems relating to its disposal after use. Additionally, mercury lamps have a relatively short working life span (500−2000 h) and are prone to gas leaking from the tube due to thermal stresses on the glass to metal seals in the tube or the glass itself. Lamp explosion is a risk associated with medium and high pressure lamps; medium/high pressure UV lamps operate at very high temperatures (600−900 °C) and, hence, need cooling during reaction, thus consuming more energy.

4. LIGHT EMITTING DIODES (LEDS)

As a result of developments in solid state semiconductor technology, there is now a great potential for the use of ultraviolet and visible LEDs as a light source for photocatalytic applications to environmental remediation procedures. The fundamental element of the LED is the semiconductor chip, which is mounted in a reflector cup supported by a lead frame connected to two electrical wires and then embedded in a solid epoxy lens (Figure 1). One of the two semiconductor regions that comprise the junction in the chip is dominated by negative charges (n-type region), and the other is dominated by positive charges (p-type region). When a sufficient voltage is applied to the electrical leads, current flows and electrons move across the junction from the n region into the p region, where the

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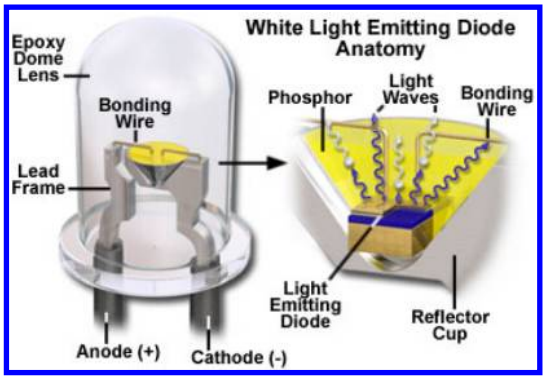

Figure 1. LED construction.

negatively charged electrons combine with positive charges. Each combination of charges is associated with an energy level reduction that may release a quantum of electromagnetic energy in the form of a light photon. The frequency, and perceived color, of emitted photons is characteristic of the semiconductor material (see the Supporting Information), and, consequently, different colors are achieved by making changes in the semiconductor composition of the chip.

Ultraviolet LED (UVLEDs) are mainly employed for the photocatalytic degradation of organic pollutants present in air and water. Recent findings have shown that visible LEDs, like blue, red, green, and white, can also be used for photocatalytic applications. Their spectra are narrow (except in the case of white LEDs), and the peak wavelength can be altered through their design. UVLEDs are currently available with typical outputs of 10 mW to 1 W.

LEDs are available as both chip and bulb types. LEDs are based on p-n junction semiconductors and are robust, safe, compact, cool, do not contain mercury, have relatively low costs of production and operation, and, hence, are environmentally friendly, with a long life span of approximately 100,000 h. LEDs can emit light of different wavelength (infrared, visible, or ultraviolet) based on the composition and condition of the semiconducting materials.[47] As LEDs are energy efficient and mercury free they are considered an environmental source of irradiations, but there is little concern about the waste dispose of LEDs at the end-of-life as it contains various metals and semiconductor materials the same as in some of the electronic waste. It is reported that, according to federal standards, the lead (Pb) leaching from red LEDs is 186 mg/L which is higher than the regulatory limit of 5 mg/L, and other LEDs are not hazardous. However, according to California regulations, excessive levels of copper (up to 3892 mg/kg; limit: 2500), Pb (up to 8103 mg/kg; limit: 1000), nickel (up to 4797 mg/kg; limit: 2000), or silver (up to 721 mg/kg; limit 500) render all except low intensity yellow LEDs hazardous. Still it not clear whether the material content of the LEDs, which generally includes group II−V semiconductors, presents its own set of potential environmental impacts especially when disposed of at end-of-life. It is reported that the white LEDs exhibit relatively low toxicity potential because they contain less copper and do not contain arsenic or lead (Pb).[113]

Energy conversion efficiency or wall plug efficiency (WPE) is an important consideration of any light source. It is defined as the optical power output per electric power input. The germicidal lamp (UVC) has a WPE of 23% and a backlight source (UVA) has a WPE of only 7%. At present, a typical UVLED with an output power of 12 mW, current of 20 mA, voltage of 3.7 V, peak wavelength of 395 nm, and spectrum bandwidth of 26 nm has a WPE of 16.2%. Current research aims to increase the power and WPE of different types of LEDs.[45]

5. PHOTOCATALYSIS USING LIGHT EMITTING DIODES

The first application of UV-LED as an irradiation source for the purification of air was carried out by Johnson, 2003, using TG purple Hi LED and irradiation at a wavelength of 385 nm, which is appropriate for the production of an electron hole pair on the surface of carbon and titanium composite for the purification of air.[46] In 2005 16 UVLEDs, having a peak wavelength of 375 nm and 1 mW output power for each LED, were applied to the photocatalytic oxidation of percholoroethylene.[45]

The photocatalytic removal of pollutants under irradiation of LEDs has been mainly carried out using ultraviolet LEDs. However, some visible LED have also been applied to the degradation of a number of organic compounds in water and volatile organic compounds in air. LEDs of various powers are also under investigations. Presently, LEDs are becoming a promising alternative light source, and a great number of articles are published on the degradation of pollutants in air and water under irradiation by ultraviolet and visible LEDs. Figure 2

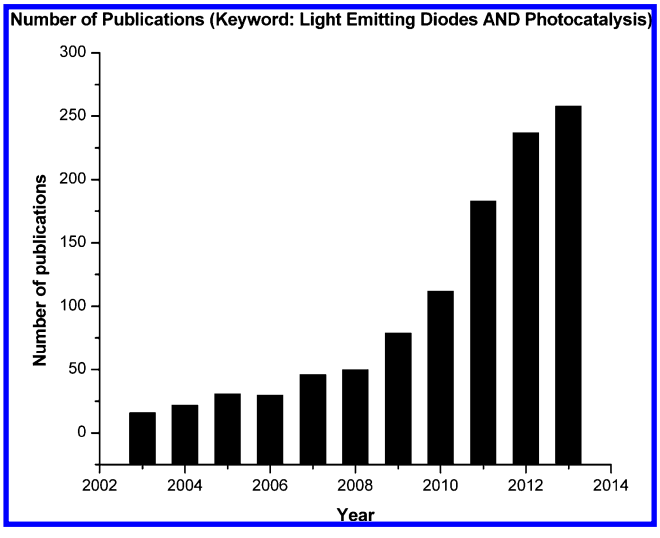

Figure 2. Number of articles published using LEDs as irradiation source (source: SCOPUS).

shows the number of articles published in this area in the last 11 years, which clearly indicates the intended structure photocatalytic applications of LEDs as a source of irradiation. Various studies have demonstrated the feasibility of LEDs as an alternative irradiation source for the photocatalytic degradation of pollutants present in air and water at low level concentrations.

5.1. Degradation of Organic Pollutants in Water. Ultraviolet and visible LEDs have been applied to the removal of various common organic pollutants, such as o-cresol, 4-chlorophenol, formaldehyde, glucose, bisphenol A, Cu-EDTA complex, carbamazepine, aniline, a few known pesticides such as 2,4-dichlorophenoxyacetic acid (2,4-D), 2-methyl-4-chlorophenoxyacetic acid (MCPA and 2,4-dichlorophenol (2,4-DCP), natural organic matter, such as Suwannee River Fulvic Acids-SRFA and emerging contaminants including sulfame-

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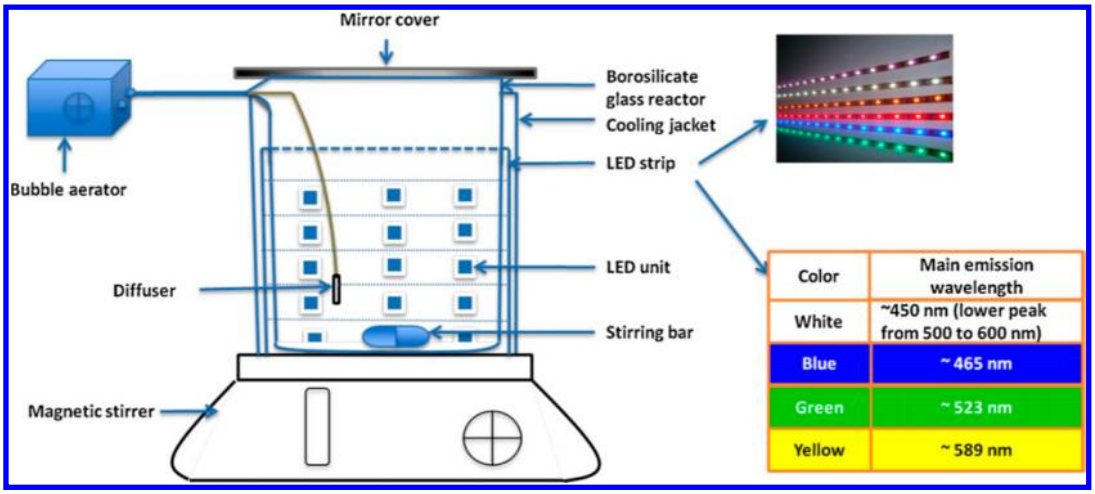

Figure 3. Schematic diagram of photoreactor used for photodegradation of BPA with LED strips as excitation light source.[64]

thoxazole, as well as antibiotic substances such as sulfamethoxazole (SMX) and oxytetracyline (OTC) which are commonly detected in water.[57−76]

Chen et al. studied the effect of controlled periodic illumination on the photonic efficiency and temporal decomposition behavior of o-cresol by the UV/TiO_2 process in a slurry reactor, using LED as the light source.[57] They used Daina B5-437-CVD shorter wavelength UV-LEDs, having a power dissipation of 120 mW, viewing angle of 30, maximum relative intensity of wavelength (peak wavelength) of 395 nm, and bulb size of 5 mm diameter and 8.6 mm length. A 49 mm diameter and 170 mm length cylindrical tube made of polymethyl methacrylate was used as a support for the UV-LEDs. They used 384 UV-LEDs, which were mounted on the outer shell of the cylindrical tube. This was kept in the inner tube of the reactor, and the o-cresol solution was kept in the outer tube. Both tubes were made of quartz and fused silica. The light pulse frequency of LEDs was controlled from 0.1 to 1 s using a Mitsubishi FX1s programmable controller. The decomposition rates increased in a roughly linear manner with increasing average UV light intensity for experiments of periodic illumination and continuous illumination, indicating that the observed reaction rate was a surface controlled photocatalytic reaction. With the similar set up, they also conducted experiments with an initial o-cresol concentrations of 9 mg L^{-1} and pH 3 and found that more than 80% of o-cresol was decomposed after 8 h of irradiation.[58]

Ghosh et al. evaluated the efficacies of LED sources versus conventional Hg lamps and sunlight for the photocataltyic oxidation of 4-CP (4-chlorophenol). The results demonstrated that high intensity LED (436 nm) performance was superior to sunlight, and similar to a conventional lamp for the photocatalytic oxidation of liquid-phase 4-chlorophenol, using a coumarin dye sensitized TiO_2 photocatalyst. To further study the oxidation of 4-CP they used reactors driven by LED and Hg lamp, having powers of 12 and 112 W, respectively.[60] This indicates that the use of LED is more appropriate for the photocatalytic degradation. In addition to this they evaluated four different catalysts, P-25 TiO_2, TiO_2 nanofibers, tin-doped TiO_2 nanofibers under UV light irradiation at 350 nm, and coumarin (C-343) coated TiO_2 nanofibers, for the degradation of 4-CP at 436 nm using light emitting diodes (LED).[61]

Using UVLEDs and a hydrogen peroxide photolytic system, the degradation of phenol was carried out at different viewing angles (15 and 120 °C) and at different wavelengths of 255, 265, and 280 nm. The LEDs used for these experiments were TO-39 LEDs, manufactured by Seoul Optodevice Co., Ltd., Korea. The three distinct LED types, each with viewing angles of 120° (low flat), differed from each other by their emitting wavelength, i.e. 255, 265, and 280 nm. The fourth LED type emitted wavelength of 265 nm, but the viewing angle was 15°, due to the distinct window (flat) of the LED construction. The LEDs were mounted on the plastic cover, and the system was placed on top of a beaker to irradiate the phenol solution contained therein. Phenol concentrations were varied from 25 to 200 mg/L, with corresponding H_2O_2:phenol molar ratios from 5 to 150. The result showed that the quantum yields of phenol degradation (100 mg/L) were 0.33, 0.24, 0.23, and 0.22 for 255, 265, 280, and 265 nm (viewing angle: 15°) reactors, revealing the most efficient wavelength to be 255 nm. This result demonstrated that the possibility of degradation of organic compounds under irradiation of UVLEDs in combination with hydrogen peroxide.[62]

The photocatalytic (PC) and photoelectrocatalytic (PEC) oxidation of glucose by TiO_2 and Pt-TiO_2 films separately under similar conditions using a UV-LED array was carried out by Gan et al. Four UVLEDs (NCCU033(T), Nichia Corporation) of 365 nm wavelength were used with 25 mW cm^{-2} UV light intensity impinging on the surface of the electrode. The concentration of glucose in the reaction solution was 0.05 mM, which also contained 2.0 M $NaClO_4$ as an electrolyte. An initial glucose concentration of 0.05 mM 20% (0.0016 μmol) was mineralized by the undoped-TiO_2 film during a reaction time of 20 min. For the same initial glucose concentration (0.05 M), Pt-TiO_2 films were prepared using 0.1, 0.5, and 1.0 mM; Pt solutions oxidized 37% (0.003 μmole), 50% (0.004 μmole), and 28% (0.0022 μmole) of glucose, respectively. This clearly indicated that the increased Pt deposition on the TiO_2 film surface exhibited a net beneficial effect for the photocatalytic degradation of glucose under irradiation of UVLEDs. It is observed that the overall oxidation efficiency of the PEC process was better than the PC process, for both TiO_2 and Pt−TiO_2 films at similar conditions.[63]

Photocatalytic degradation (PCD) of bisphenol A (BPA) by carbon and nitrogen codoped TiO_2 was synthesized via a facile solvothermal method using a locally fabricated vis-LED photoreactor.[64,65] The flexible strip of white, blue (λ = 465 nm), green (λ = 523 nm), and yellow (λ = 589 nm) LED lights

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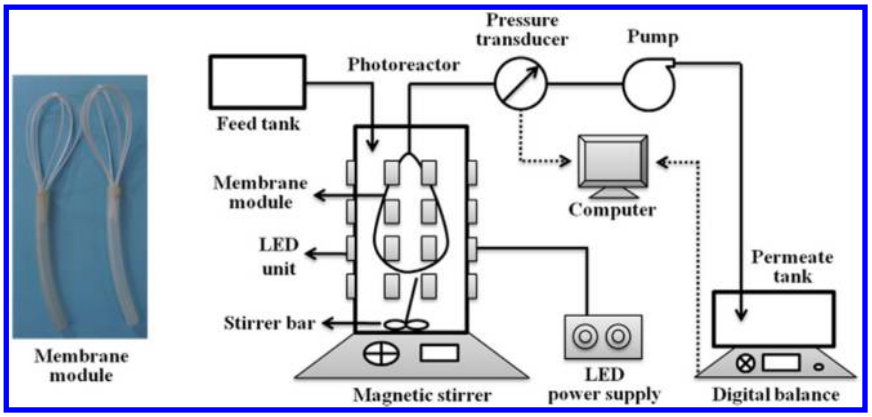

Figure 4. Schematic diagram of the submerged membrane photoreactor (sMPR) combining a visible LED photoreactor.[68]

were used as irradiation sources to study the degradation of bisphenol A, and it was observed that the photocatalytic degradation rates were >99%, >99%, 84%, and 24%, respectively, while the corresponding percentages of degradation were 70%, 60%, 45%, and 9%, respectively. The photocatalytic degradation of bisphenol A was carried out using a vis-LED photoreactor which was comprised of a 500 mL borosilicate glass reactor with a 2 m flexible LED strip (SMD 5050, 30 pcs/m, 7.5 W/m) wrapped around it (Figure 3). Four different LED strips were used in this study, emitting blue, green, and yellow, while the spectrum of white LED light emitted at about 450 nm, and further broadband Stokes-shift light was emitted at roughly 500−600 nm. From the findings it is clear that in the absence of sunlight, LEDs with versatile configuration have the potential for an optimized optical solution, exhibiting uniform illumination, an inherently compact form, and higher photon efficiency in a photoreactor systems. They also tried to compare the photocatalytic efficiency of the synthesized photocatalyst in the presence of white LEDs, solar light, and UV light and found that BPA was completely mineralized within 4 h under UV and solar simulator irradiation, whereas under irradiation of white LED only 65% total organic carbon was removed because of the formation of aliphatic carboxylate ion and their slow degradation.

The adsorption and photocatalytic degradation of the nerve agents isopropyl methylphosphonofluoridate (IMPA) and Sarin (GB) was studied on powdery TiO_2 film under irradiation of UVLED irradiator (ZUV-C30H, OMRON, center wavelength: 360 nm), and the UV intensity on the film was 2.0 mW·cm^{-2}. The adsorbed GB and IMPA were quickly decomposed by TiO_2 photocatalysis to give isopropyl alcohol, acetone, formate, and methylphosphonic acid and, finally, were completely mineralized to phosphoric acid, water, and carbon dioxide. They also elucidated a plausible adsorption structure and photocatalytic decomposition mechanism of GB at the surface of the TiO_2 photocatalyst.[67]

A hybrid submerged membrane photoreactor (sMPR) combining a photoreactor irradiated with visible LED and a submerged hollow fiber PVDF microfiltration (MF) membrane module was investigated in a continuous flow-through reactor, for the degradation of carbamazepine using C−N−S tridoped TiO_2. The reactor setup is shown in Figure 4. A 4 m long visible LED flexible strip comprising 240 vis-LED units (size 4 × 4 mm, SMD 5050, 60 unit/m, 15 Wm^{-1}, blue light emitted at about 450 nm and more broadband Stokes-shift light emitted at roughly 500−600 nm). The powers of visible light intensity applied were ca. 2, 4, 8, 11, and 15 Wm^{-2}. This study also investigated the effect of inorganic anions, including silica, phosphate, nitrate, bicarbonate, sulfate, and chloride.

Photocatalytic degradation of phenol (10 ppm) by titanium dioxide illuminated by high photonic efficiency LED (number of LED used = 1, wavelength = 375 nm, diameter = 5.4 mm, optical power = 1 W) in a batch photocatalytic reactor is also reported. The effect of catalyst loading, catalyst type, phenol−hydrogen peroxide ratio, pH, initial phenol concentration, and radiance by applying pulse width modulation (PWM) was studied. It was observed that an increase in the distance between the light source and target component led to a dramatic drop in the irradiance value. Furthermore, at optimal chemical conditions, such as a phenol concentration of 10 ppm, a hydrogen peroxide−phenol molar ratio of 100, pH of 4.8, and LED fwhm angle of 120°, a degradation rate of 42% was achieved after 4 h. A decrease in fwhm angle to 40° increased the degradation rate to 87% within 4 h of the start of the experiment.[70]

Langford et al. (2014) also studied the degradation of four known pesticides [2,4-dichlorophenoxyacetic acid (2,4-D), 2-methyl-4-chlorophenoxyacetic acid (MCPA), 4-chlorophenol (4-CP), and 2,4-dichlorophenol (2,4-DCP)], in aqueous solution under UVLED, and compared the efficacy of the LED system with mercury discharge lamp irradiation (350 nm). Irradiation of the different pesticides with a 365 nm LED light source led to their complete degradation upon prolonged exposure, and the mercury discharge lamp was determined to be more efficient than the LED source.[72] The degradation of two antibiotics, namely, sulfamethoxazole (SMX) and oxytetracyline (OTC) as well as an endocrine disruptor hormone (17-α-ethynyl estradiol), was also studied under 365 nm LED irradiation.[73]

Photoelectrochemical properties and photoelectrocatalytic (PEC) degradation of an environmental pharmaceutical acyclovir were also studied in bulk and thin-layer photoelectrochemical reactors by Nie et al., with the use of highly ordered titanium dioxide (TiO_2) nanotube arrays. The experiment was conducted using A UV-LED (NCCU033 (T), Nichia Corporation) with a wavelength of 365 nm, and light intensity of 10 mW cm^{-2} was used as light source, and 0.2 mol L^{-1} $NaNO_3$ was used as the aqueous solution electrolyte. They concluded that the degradation efficiency of acyclovir by photoelectrocatalytic was higher than photocatalytic or electrocatalytic degradation due to the enhanced separation of electrons and holes through photoelectrocatalysis promoting a higher degradation efficiency.[74]

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Other than TiO_2, Bi_2MoO_6 was also explored as a photocatalyst for the photocatalytic degradation of Rhodamine B (RhB) and phenol under irradiation with blue LED. The effects of H_2O_2 on the photodegradation of RhB and phenol were determined. More importantly, the photocatalytic mechanisms in the degradation of RhB and phenol were investigated by introducing TBA as an $^{\cdot}OH$ trap and EDTA as a hole sink.[69] Eskandari et al. used CdS as a photocatalyst for the degradation of nitrobenzene. The degradation of aniline was also carried out using 3 W LED irradiation sources (blue, green, yellow, and red) by Antoi et al. They studied various factors, including adsorption, wavelength, aniline concentration, and pH, in order to determine their impact on the photocatalytic activity of synthetic TiO_2 and the degradation of aniline.[76] This shows that the photocatalyst other than TiO_2 also can be used for the degradation of pollutant under irradiation of LEDs light.

5.2. Degradation of Dyes. Different class of dyes, such as azo, mono azo, thiazin, triarylmethane, and triphenylmethane, at different concentrations in aqueous solution were degraded under LED irradiation. These dyes include, methylene blue (MB), malachite green (MG), Rhodamine B (RhB), phenol red (Pr), methyl red (MR), methyl orange (MO), basic red (BR), Congo red (CR), reactive red 22 (RR-22), and reactive black.[44,47,77−90] Some of the reported work is discussed below, including the type of LED, photocatalyst, and reactor which were used for the degradation of dyes.

The degradation of methylene blue (concentration of 10−100 mg/L) dye was studied using ultraviolet and visible LED irradiation, using both standard P-25 Degussa and synthesized TiO_2 as photocatalysts.[47,77,78,83,86,87,89] Tayade et al. used UVLED for the degradation of MB, MG, RhB, and CR dyes using irradiation with 5 LEDs and P-25 Degussa as a photocatalyst, to optimize parameters including concentration of dye, amount of photocatalyst, pH of the reaction mixture, and the addition of different metal ions.[47,81] They also locally fabricated the reactor, where the amount of coated TiO_2 was ca. 2 mg on quartz tube inner surface and 15 UVLEDs to evaluate the photocatalytic degradation of RhB dye and to propose a degradation pathway. Additionally, they reported that the optimum conditions for RhB photocatalytic degradation were a catalyst, dye concentration, and pH of 1.6 g/L, 6.26×10^{-5} M, and 3.05, respectively, while for MB they were 1.2 g/L, 3.12×10^{-5} M, and 8.84, respectively. Using this reactor they found that the order of photocatalytic degradation of dyes was MG > RhB > MB. The degradation path was similar to the degradation carried out in the presence of UV lamp irradiation. In another attempt, they have used highly ordered titanium nanotube grown on the surface of a titanium metal plate to investigate the degradation potential of CR dye using 4 UVLEDs.[82] The results revealed that the initial rate of degradation was 0.77×10^{-7} mol L^{-1} for CR dye in the presence of UV-LED source/TNA. In the case of low pollutant concentrations, the appropriate figure-of-merit is the electrical energy per order (E_{EO}), defined as the number of kW h of electrical energy required to reduce the concentration of a pollutant by 1 order of magnitude (90%) in 1 m^{-3} of contaminated water. The consumption of electrical energy (E_{EO}) for the degradation of Congo red dye was 228 kW h m^{-3} $order^{-1}$ using a titanium nanotube array calcined at 450 °C, while the initial rate of degradation under irradiation by ultraviolet light alone was 0.03×10^{-7} mol L^{-1} and the electrical energy was 14,285 kW h m^{-3} $order^{-1}$. The developed photocatalytic surface showed good reusability, and the degradation potential for Congo red dye was found to decrease by only 5% after five repeated uses.

Another study was carried out by Dai et al. using a plasmonic Ag/AgBr heterostructure as a photocatalytic material. They used a 5 × 20 LED array (wavelength = 450 nm, Wuxi Chengtian Co., Ltd.) printed on a copper clad laminate as a light source, and a reactor containing 100 mL of 10 mg L^{-1} MB and 0.05 g of photocatalyst at room temperature. The distance between the LED light source and the reactor was 1 cm, the light intensity reaching the reactor was 400 μW cm^{-2}, and the reaction mixture was stirred continuously during photocatalytic degradation. They found that 95% of MB dye degradation took place with the plasmonic Ag/AgBr heterostructure as a photocatalyst in 240 min.[90]

White and blue LEDs were used as irradiation sources for photocatalytic degradation using N-doped titanium dioxide. Sacco et al. used a strip composed of 30 white light LEDs (nominal power: 6 W), with wavelength emission in the range 400−800 nm, or a similar number of blue light LEDs (nominal power: 6 W) with wavelength emission in the range of 400−550 nm. The LED strips were positioned around the reactor so that the light source illuminated the reaction volume in a uniform manner. The results demonstrated that the highest photocatalytic degradation of MB (7.5 ppm) was obtained for photocatalysts with a bandgap of 2.6 eV. They also used the same setup for the degradation of methyl orange to verify the photocatalytic activity.[87]

Another approach for the degradation of dyes utilizes ultraviolet (UV)/H_2O, UV/O_3, or UV/Fenton's reagent, and UV/peroxydisulfate for the oxidative degradation of contaminants. Rasoulifard et al. studied the degradation of basic red-46 (BR46) using LED and peroxydisulfate on a laboratory scale. They used 6 × 1 W UVLEDs (TO-18, manufactured by Seoul Optodevice Co., Ltd.); almost no degradation of the dye was achieved through the use of UV LED alone, whereas 43% degradation was obtained in the presence of peroxydisulfate. More than 90% of the dye content was eliminated over 30 min through the simultaneous use of UV LED and peroxydisulfate simultaneously. They found the optimum parameters of peroxydisulfate concentration, dye concentration, pH, and current to be 180 mM, 5 ppm, 6.43 and 720, for the degradation of BR46 dye. Furthermore they calculated the electrical energy efficiency (EEO) to be 42.67 kW h/m^3 for UV LEDs and 125.23 kW h/m^3 for a 30W UV lamp for the degradation of 100 mM peroxydisulfate, indicating that the use of LEDs is more economical than traditional UV lamps.[84] Different wavelength sources of UV light (UVA, UVC, and UVLED) were utilized to study the effect of different wavelengths on the photcatalytic degradation of Rhodamine B dye by Aliabadi et al. (year), who reported that the order of degradation efficiency for RhB dye using different light sources was UVC > UVA > UVLED.[112]

A lab-scale closed-circulating test system (Figure 5) for photocatalytic wastewater treatment was reported by Nickels et al., and its stability in operation and dependence of the reaction rate on initial concentration, light intensity, and liquid volume to the catalyst surface was reported for the photocatalytic degradation of methyl orange. They used 15 Ultra Bright Deep Violet LED370E UVLEDs, sourced from Thorlabs, with a main emission peak at 375 nm, line width of approximately 10 nm, and optical power of 2 mW at a drive current of 20 mA. A blue LED (Hyper blue LED LB3333 from OSRAM Opto Semiconductor GmbH) was applied to an in-stream sensor

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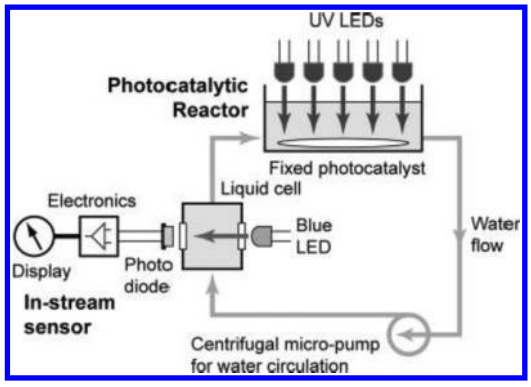

Figure 5. A lab-scale closed-circulating test system for photocatalytic wastewater treatment.[85]

unit. The photocatalytic surface used in this study was glass wafers which were coated with Evonik TiO_2 Aeroxide P25 TiO_2 by a spin-casting method. The total area of the coated wafer was 45.6 cm^2.[85]

A photocatalytic microreactor using TiO_2 coating (coating thickness: ca. 3 μm) inside of a fused silica circular capillary (i.d. 530 μm, o.d. 660 μm) and UVLED (wavelength 365 nm, intensity 640−3200 mW cm^{-2}, beam diameter 10 mm) was studied by Tsuchiya (2012) for the degradation of new coccine (NC), sunset yellow (SY), and methyl red (MR) as azo dyes; Rhodamine 6G (Rh6G) and erythrosine (Ery) as xanthenes dyes; and methylene blue (MB) as a thiazine dye, by monitoring the fluorescent spectra.[86] The reaction mechanisms of the photocatalytic degradation processes of the dyes were analyzed, and the results suggested that methylene blue is not suitable for evaluation of photocatalytic activity of the photocatalyst, as it involves various complicated reaction pathways and, additionally, the evaluation result is easily affected by the adsorption property of MB molecules.

5.3. Degradation of VOC in Air. The emission of odorous pollutants from wastewater treatment plants, landfills, livestock facilities, exhaust emissions from automobiles, and wastewater from paper production plants presents serious environmental and health concerns. Many of the emitted compounds are highly toxic and harmful to the environment. Dimethyl sulfide (DMS) and nitrogen monoxide are representative compounds for studies of environmental remediation. VOCs, including formaldehyde trichloroethylene (TCE) and 2-propanol, are generally detected in indoor environments. A traditional technology for purifying indoor VOCs is adsorption; however, this only transfers VOCs to another phase rather than oxidizing them into innocuous compounds, such as water vapor and carbon dioxide. Due to the advantage of LEDs over traditional ultraviolet light sources, LEDs have recently been employed for the removal of gases from air. It has been reported that various organic air pollutants, such as formaldehyde, glucose, isopropyl methyl phosphonofluride, dimethyl sulfide, 2-propanol, aceton vapors, tolune, and trichloroethylene, were degraded using different LEDs.[45,91−99]

Dimethyl sulfide is a representative of odorous compounds emitted during various natural processes as well as paper pulping and wastewater treatment processes.[91] DMS has a very low odor threshold value of 0.6−40 ppb and is an irritant to the eyes, skin, and respiratory system. The photocatalytic degradation of DMS under LED irradiation at different wavelengths has been studied by Wang et al., who investigated the feasibility, kinetics, and reaction pathways of the photocatalytic degradation of dimethyl sulfide (DMS) in a LED based continuous reactor and compared four types of LEDs, with peak wavelengths at 365, 375, 385, and 402 nm, for their photocatalytic performance. It was observed that the LED with a wavelength of 365 nm had the highest removal efficiency (up to 90% at 2.5 mW cm^{-2}), and the order of the rate constants k for the four types of LED was determined to be 365 nm > 375 nm > 385 nm > 402 nm, and the values for 385 and 402 nm LEDs were significantly smaller than those 365 and 375 nm LEDs. During the photocatalytic reaction, dimethyl sulfoxide, dimethyl sulfone, dimethyl disulfide, methanethiol, methanesulfonic acid, and sulfate were identified as the reaction products by gas chromatography−mass spectrometry (GC-MS) and ion chromatography.[91] Wang et al. reported a model study of a UVLED based photocatalytic removal of dimethyl sulfide by integrating computational fluid dynamics (CFD) modeling of the gas flow in the reactor with LED-array radiation field calculation and Langmuir−Hinshelwood reaction kinetics.[92]

Another use of TiO_2 and nitrogen doped TiO_2 coating on the inner surface of an annular reactor was reported by Jo et al. (2011) to compare the photocatalytic decomposition efficiency

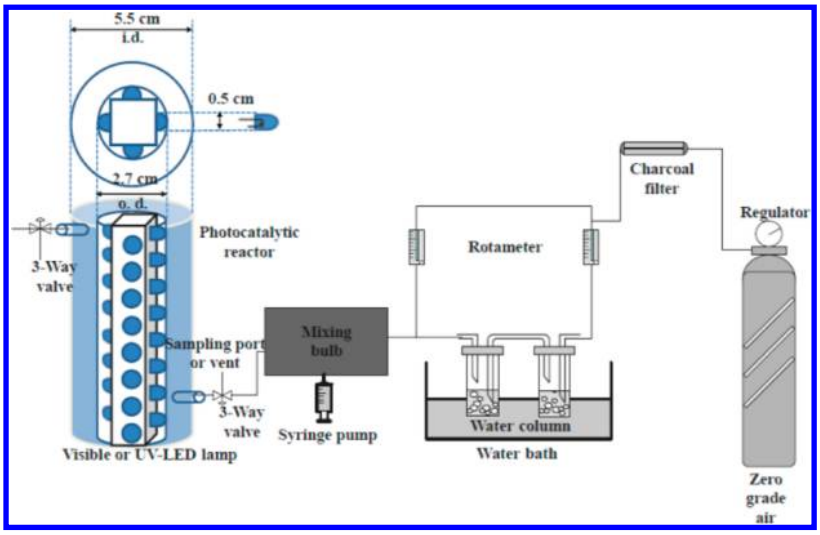

Figure 6. Schematic diagram of experimental setup for decomposition of DMS.[93]

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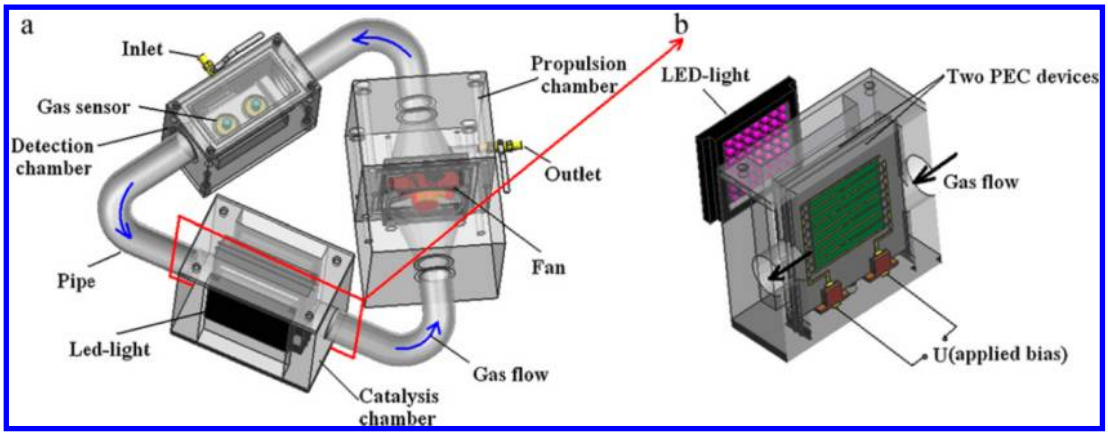

Figure 7. Schematic of the PEC reactor and sectional view of catalysis chamber.[94]

of DMS. The photocatalytic composition studies were conducted using a conventional 8 W UV/TiO_2 and UVLED/TiO_2 system and a conventional 8 W visible lamp/N-doped TiO_2 (NET) and six different visible-LED/NET systems (visible LED: violet, blue, white, green, yellow, red). A schematic diagram of experimental setup is given in Figure 6. It was observed that the photocatalytic decomposition efficiency was higher for the 8 W black-light lamp/TiO_2 system than for the UV-LED/TiO_2 system, while the ratio of photocatalytic decomposition efficiency to the electric power consumption was reversed. Another visible light irradiation set up using four of six visible-LED/NET systems (blue, violet, white, and green-LED/NET systems) exhibited higher decomposition: power consumption ratios than a conventional UV-lamp/TiO_2 system. It was also found that three parameters (flow rate, input concentration, and hydraulic diameter) should also be considered for better DMS removal efficiencies when applying LED lamps to photocatalytic technology. They also confirmed that LEDs can still be energy-efficiently utilized as alternative light sources for the photodegradation of DMS under various operational conditions.[93]

The photoelectrocatalytic (PEC) flat-plate type reactor using blue LEDs (470 nm) was also reported for the degradation of acetone vapor using a TiO_2/WO_2 nanocomposite.[94] TiO_2/WO_3 flat-plate type devices were fabricated by a screen printing technique and were used in a catalytic chamber. Figure 7 shows the schematic of the PEC reactor system and catalytic chamber. Two PEC devices were placed in the catalytic chamber during the test. Ultraviolet (365 nm) and blue (475 nm) LEDs were selected as the light source because of their narrow wavelength width of 10 nm. The light intensity at the surface of the device was 5 mW/cm^2 and supplied potential bias to the PEC device with a voltage control range of 0−5 V. The total volume of the reactor system was 825 mL, and the area of the photocatalyst film on the PEC device was 50 mm × 50 mm. In this study, the PEC degradation rate under UV-light (365 nm) irradiation by applying only 0.2 V bias was about 12.28×10^{-3} min^{-1}, which was 2.42 times that of the of photocatalytic degradation rate of acetone. Under blue-light (475 nm) irradiation, the composite still exhibited a good degradation efficiency, and the rate constant was about 2.6×10^{-3} min^{-1}. This also indicated that the blue LED can also be useful for photocatalytic degradation in gaseous phase.

5.4. Bacteria Inactivation. The contamination of water by harmful microorganisms is a serious concern as it directly affects public health and causes millions of deaths and cases of disease and disability each year.[100] Especially, intestinal parasitic infections and diarrheal diseases caused by bacteria have become pervasive problems afflicting people throughout the world.[101,102] In order to address this significant problem, extensive research is underway to develop advanced methods for the elimination of hazardous organisms from the environment. The organism inactivation efficiency is strongly dependent on the spectral distribution of the light source of photons. In terms of the emitting wavelength, the electromagnetic spectrum of UV irradiation can be classified as UVA, UVB, and UVC. If a lamp is applied within the UVC range, the disinfection effect is very fast, even in the absence of a photocatalyst. Photocatalytic processes using semiconductors as photocatalysts under appropriate illumination is attracting extensive attention within a number of environmental applications. Compared to conventional technologies, semiconductor-based heterogeneous photocatalysis has many advantages, including mild operating conditions, avoiding the use of hazardous chemicals, and complete oxidation of organic pollutants.[103,104]

Considering the merits of LEDs, various researchers have focused on the use of UV or visible LEDs for the inactivation of microorganism. These include fish pathogens, such as Photobacterium damselae subsp. piscicida BCRC17065,[104] *Escherichia coli* K-12,[105−108] *Bacillus subtilis* spores,[109] coliform and enterococci,[110] and *Pseudomonas aeruginosa*, *Staphylococcus aureus*, and *Candida albicans* in water as well as bacteria of concern in certain atmospheres, such as *Staphylococcus aureus*.[111]

The destruction of fish pathogens using TiO_2/Fe_3O_4 in seawater and freshwater may be achieved using irradiation with blue LEDs (475 nm) being less harm to human eyes than UV light and, hence, more appropriate in certain circumstances. The photocatalytic activity efficiency and bactericidal effects of TiO_2/Fe_2O_3 photocatalysts with different molar ratios of TiO_2 and Fe_2O_3 was studied in waters of various salinity. A higher photocatalytic activity was determined in solutions of higher TiO_2/Fe_3O_4 molar ratios, and photocatalytic activity was decreased with increasing salinity.[104]

Chen et al. studied the photocatalytic inactivation of *Escherichia coli* by natural sphalerite suspension under different spectra, wavelengths, and intensities of visible light (VL) emitted by a light-emitting-diode lamp. The spectrum effect of VL on disinfection efficiency was studied by using white LED, fluorescent tube (FT), and xenon lamp (XE) as irradiation sources. The result demonstrated that the discrete peak

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spectrum of FT is more effective for the inactivation of bacteria than the continuous spectrum of LED and XE. The photocatalytic disinfection of bacteria was compared under different single spectrum (blue, green, yellow, and red) LEDs. The results also show that the most effective wavelength ranges of visible light for photocatalytic disinfection with natural sphalerite are 440−490 and 570−620 nm. Furthermore, a positive relationship was determined between the disinfection efficiency and the visible light intensity. The experiment shows that NS can completely inactivate 107 cfu mL^{-1} *E. coli* K-12 within 8 h irradiation by white LED, with an intensity of 200 mW cm^{-2} at pH 8, and no bacterial colony was detected at 96 h after a regrowth test for inactivated bacteria.[105]

The effects of emitted wavelengths with two photolytic batch reactors, both utilizing LEDs, for the sterilization of E-coli (K-12) in water was reported by Vilhunen et al. Two batch reactors using different UV LEDs were prepared with ten similar LEDs in each reactor, including TO-39 LEDs, manufactured by Seoul Optodevice Co., Ltd., Korea. The reactors had a viewing angle of 120° (low flat) and differed from each other according to their emitting wavelengths of 269 and 276 nm. Ultrapure water, nutrient water, and water with nutrients and humic acids were each evaluated as test media. The efficiency results of reactors showed that they were almost the same, even though the one which emitted the higher wavelength had twice the optical power of the other. Therefore, the strong influence of specific wavelength was evident, and radiation emitted at 269 nm was determined to be the most powerful for the sterilization of water. In the 5-min experiment, the bacterial reduction of three to four log colony-forming units (CFU) per cubic centimeter was achieved, in all cases. They concluded that LEDs were considered to have low optical power, even though UV LEDs were efficient in the destruction of *E. coli*.[106]

6. FUTURE PROSPECT AND CHALLENGES

The feasibility studies of LEDs for the degradation of various pollutants present in air and water confirm the practical applicability of LEDs for photocatalytic applications. At present, most photocatalysis work utilizing LEDs is rarely carried out, and current applications use low power LED arrays for the degradation of low level concentrations of pollutants in air and water. Till today only a few pollutants degraded under LEDs are reported, due to the less power consumption of LEDs over traditional ultraviolet mercury sources. Still, there is a need to study the photocatalytic different pollutants present in the air and water at various concentrations. Although at present there are LEDs with limited wavelengths in ultraviolet and visible ranges available, but if the semiconductor technology focuses on this and provides new LED of different wavelengths, then they may be more applicable in photocatalysis. The wavelength of the LEDs will also be one of the important parameters for the enhancement photocatalytic degradation of pollutant and based on the pollutant type particular wavelength LED may be useful for effective degradation. At present a number of studies were done using the standard P25 Degussa and some modified TiO_2 but soon according to the wavelength of irradiation of LEDs catalyst design may help to enhance the efficiency of photocatalytic degradation. A number of photocatalysts and their composition may provide a solution for environmental cleanup under irradiation LED. Till today a number of visible photocatalysts are synthesized and evaluated for their photocatalytic performance under sunlight or artificial visible light. The same photocatalysts may be very helpful for photocatalytic degradation of pollutants under irradiation different visible LED. At present the cost of UVLED is higher than visible LED so the use of visible LED may reduce the cost of photocatalytic reactor. Still, there are a number pollutants that need to be tested under LED light irradiation for their degradation.

The LEDs are being established as potential sources of light for photocatalytic systems because they are energy efficient, ecofriendly, safe, and robust. However, the challenges in the utilization of these sources are that still they need to be tested for decomposition of different pollutants present in air and water and also the need to have high power in order to degrade pollutant of higher concentration. The development in the semiconductor industry toward the manufacturing of LEDs with high power and WPE and safe removal of metal from the used LEDs may be highly beneficial to environmental photocatalytic applications.

7. CONCLUSION

A number of environmental pollutants such as organic compounds, dyes, and indoor and outdoor hazardous gases have been degraded under the irradiation of ultraviolet and visible LED light irradiation, and still it is required to study a great of number of pollutants in order to understand the complete potential of the LEDs for environment abatement. The results have demonstrated that LEDs represent a practical and competitive alternative light source for photocatalysis applications. Till today, mainly standard photocatalyst P25 Degussa with modification and a few synthesized photocatalysts were used to carry out the photocatalytic degradation of pollutants under irradiation of LEDs; however, there is a need to develop new tuned bandgap photocatalysts, which can absorb the particular wavelength of the LED and provide higher photocatalytic efficiency. From the literature, it is clear that due to the small size and no need of cooling provided an opening to develop different types and designs of photocatalytic reactor setups using mobilized or immobilized photocatalysts. Presently, the degradation of pollutants has been achieved at low level concentrations using low power and a small number of LEDs. However, it may be increased if the number of LEDs can be increased with a higher number of LEDs having higher power. The development in also some efforts is under progress to utilize visible LED for the photocatalytic application which may reduce the cost of experimental setup in addition to low power consumption and may be most suitable for drinking water purifications systems.

■ ASSOCIATED CONTENT

Supporting Information

List of semiconductor composition used in LED to produce different wavelengths of light and the summary of photocatalytic degradation of organic compound, dyes, and volatile organic compounds degraded under ultraviolet and visible LEDs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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