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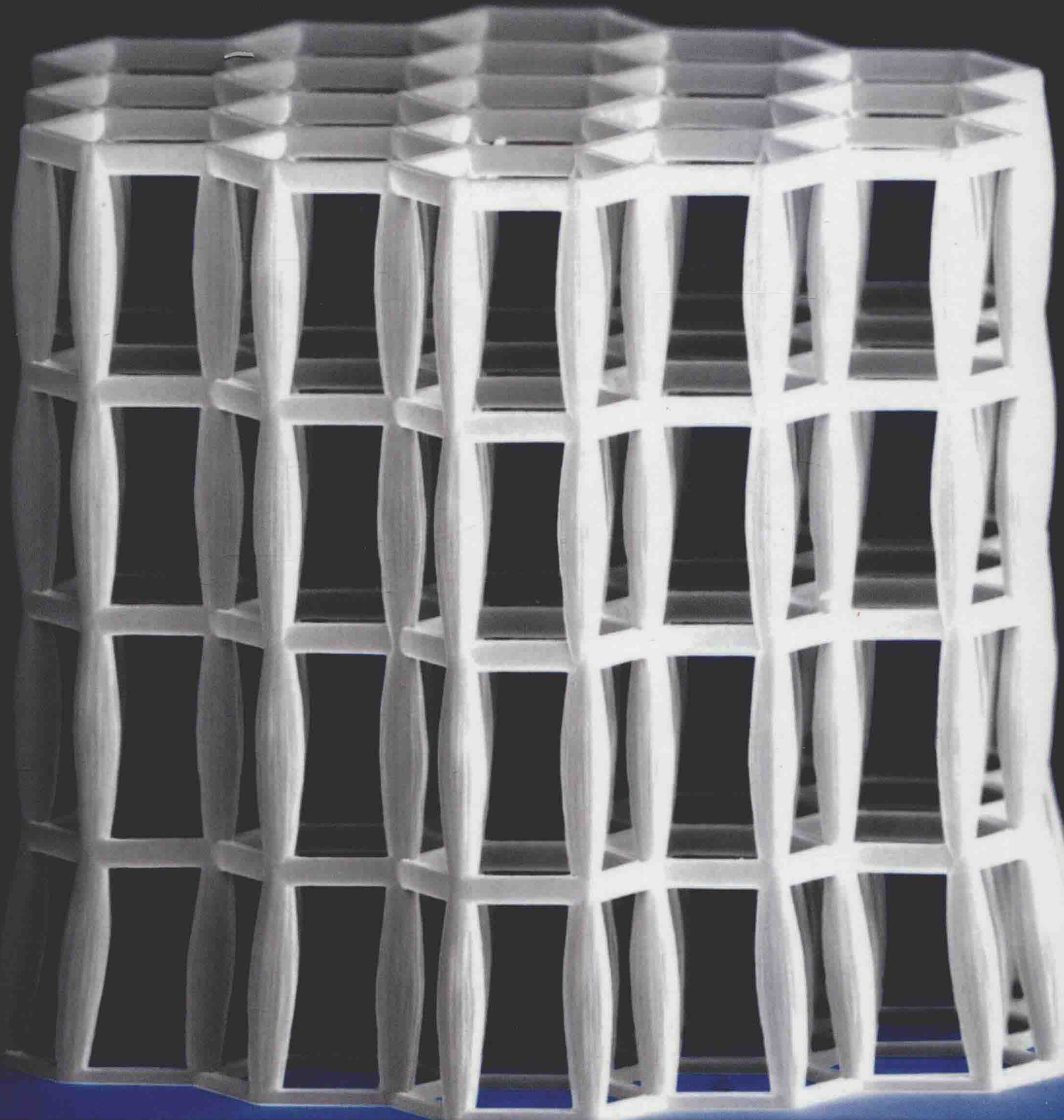
Recent Developments in Nanomaterials

Andrew Green

Volume II



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Preface

When a chemical substance or material is manufactured and utilized in any application at a very small scale, we call it nanomaterial. They can be 10,000 times smaller than the diameter of human hair. Nanomaterials exhibit characteristics such as conductivity, chemical reactivity and increased strength in comparison to the material without nanoscale feature.

Applications of Nanomaterials are already in use such as batteries, anti bacterial clothing, coating etc. By the end of 2015 it is being expected that the market will grow to hundreds of billions. It is also being expected that the sectors like health, industry, innovation, environment, energy, transport, information society, employment and occupational safety and health, security and space will be flooded by nano innovations.

Nanomaterials are also believed to have the potential that will improve the quality and also they can contribute in industrial competitiveness. However, everything comes with pros and cons and these nanomaterials can pose risks to human life, but with existing risk assessment measures; it can be tackled. It is true that nanomaterials are not dangerous but there is always a chance of scientific uncertainty.

I wish to thank all the authors for their contributions for this book and it is my pleasure to acknowledge the assistance of the publication team throughout the editing process of this book and its preparation in final format. Finally I would like to acknowledge my family who has supported me at every step.

Editor

Contents

Removal of Hazardous Pollutants from Wastewaters: Applications of TiO_2-SiO_2 Mixed Oxide Materials

Shivatharsiny Rasalingam, Rui Peng, and Ranjit T. Koodali

Department of Chemistry, University of South Dakota, Vermillion, SD 57069, USA

Correspondence should be addressed to Ranjit T. Koodali; ranjit.koodali@usd.edu

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The direct release of untreated wastewaters from various industries and households results in the release of toxic pollutants to the aquatic environment. Advanced oxidation processes (AOP) have gained wide attention owing to the prospect of complete mineralization of nonbiodegradable organic substances to environmentally innocuous products by chemical oxidation. In particular, heterogeneous photocatalysis has been demonstrated to have tremendous promise in water purification and treatment of several pollutant materials that include naturally occurring toxins, pesticides, and other deleterious contaminants. In this work, we have reviewed the different removal techniques that have been employed for water purification. In particular, the application of TiO_2-SiO_2 binary mixed oxide materials for wastewater treatment is explained herein, and it is evident from the literature survey that these mixed oxide materials have enhanced abilities to remove a wide variety of pollutants.

1. Introduction

The energy demand is expected to be greater than 25 TW by the year 2050. This increase is expected to pose undue burden on natural resources and create challenges for sustaining our environment and quality of human life. In addition to energy, the demand for clean water is also expected to rise rapidly due to increasing global population. In addition, with the expeditious pace of industrialization, the disposal of industrial effluents poses threats to the environment and is becoming the biggest concern for the sustainable development of human society. Wastewater reclamation and recycling are essential goals to protect the global ecosystem and improve the quality of the environment. Several methods have been utilized for the removal of pollutants from contaminated water sources [1–9]. Among them, advanced oxidation processes (AOP) have emerged to be promising, efficient, economic, and reliable for the removal of pollutants from aquatic environments [4, 9, 10]. Among the various AOP methods, heterogeneous photocatalysis, using titanium dioxide (TiO_2) based photocatalysts, has emerged as a viable process for degrading a wide variety of pollutants [11–13].

Although TiO_2 has several important properties, such as ease of synthesis, excellent photostability, nontoxicity, and valence bands that are located at high positive potentials, there are several drawbacks that impair the performance of TiO_2 in photocatalytic processes. The absorbance of TiO_2 is limited to the UV region, and, thus, only a small fraction of the solar spectrum is utilized. The fast recombination of the photoinduced electron-hole pairs impedes the efficiency of the overall photocatalysis reaction. In addition, the relatively low surface area of TiO_2 limits the number of adsorptive sites of the target pollutant molecule. To overcome these aforementioned challenges, researchers have developed TiO_2 based mixed oxide materials that can provide large number of adsorptive sites by dispersion of TiO_2 species into a porous support with large surface area. Silica has been widely employed as a robust and stable mesoporous support for immobilizing photoactive TiO_2 species. The TiO_2-SiO_2 mixed oxide photocatalysts have shown significantly enhanced activities compared to pure TiO_2 for a number of photocatalytic reactions for environmental remediation. The improved photocatalytic performance over TiO_2-SiO_2 mixed oxide materials can be accredited to the presence of highly dispersed TiO_2 species in the SiO_2 support, the better adsorption of the pollutant, and the presence of Ti-O-Si bonds that favor the activation of the organic pollutant [14].

In this review, we will first discuss the different types of aqueous pollutants followed by a discussion of selected removal techniques and their basic principles. Then, a brief overview of the synthesis methods of titania-silica (TiO_2-SiO_2) mixed oxides is presented. This is followed by an extensive description of available characterization techniques of periodic and aperiodic titania-silica catalysts. Following this, the heterogeneous photocatalytic degradation of several pollutants, in particular, organic materials in aqueous phase, is discussed. Finally, the factors that influence the degradation reactions are critically reviewed.

1.1. Aquatic Pollution. Clean water is the most important and indispensable resource that maintains the demands for the daily activities of every aspect of human society, such as drinking, cleansing, industrial manufacture, and farm irrigation. However, the squandering of clean water at discretion and careless handling of wastewater to aquatic systems from households and industries severely contaminate the quality of natural aquatic environments. In general, the sources that result in water pollution can be classified as point and non-point sources [15]. The former one contains pollutants that are discharged from industries, septic materials, animal feedlots, mines and oil industries, and so forth into water sources [16]. The latter one includes runoffs from agriculture, sediment, animal wastes, and so forth [17]. Nonpoint sources, due to their irregularity, are more difficult to be tracked compared to point sources [18]. However, according to the Environmental Protection Agency (EPA), nonpoint sources are claimed to be the major cause of aqueous pollutants. The existence of these pollutants in water systems can cause serious environmental issues and pose threat to public hygiene and health. For instance, the contamination of groundwater by pesticides can endanger aquatic ecosystems. As the fertilizer is discharged into water sources, it can boost the multiplication of algae, which interrupts the oxygen level and upsets the ecological balance in the water system. Moreover, close contact or drinking of the contaminated water can cause skin rashes and other severe diseases like typhoid fever and stomach illness in humans. Waste inorganic and/or organic chemicals, in particular heavy metal ions, in the water may be ingested by fish and may also cause infection in humans, who catch and consume it. In the following section, the most commonly occurring hazardous pollutants along with their effects will be discussed.

1.2. Hazardous Pollutants. The most commonly observed hazardous wastes that threaten the global aquatic system can be divided into four groups according to the classification by the EPA: (i) hazardous wastes from nonspecific industrial processes, (ii) hazardous wastes from specific industrial sources, (iii) commercial chemical products, and (iv) toxic wastes. The EPA estimates that the above-mentioned pollutants have been increasingly detected during the past few decades in rivers, lakes, and oceans. In the following part, we will discuss the some important inorganic and organic wastes in water.

1.2.1. Inorganic Wastes

Anionic Wastes. Phosphates (PO_4^{3-}) and nitrates (NO_3^-) are the most prevalent pollutants in contaminated surface water [19, 20]. Phosphorus (P) and nitrogen (N) are indispensable elements used in fertilizers for agriculture. Application of extensive amounts of P and N containing fertilizers on arable lands causes extensive accumulation of the phosphate (PO_4^{3-}) and nitrate (NO_3^-) in the soil. Due to the use of manual irrigation and/or natural rainfall, phosphates and nitrates can leach into ground and surface water sources, such as rivers and lakes. In addition to the P and N containing fertilizers, the manure from livestock is also a major source of phosphate and nitrate contaminants in water systems.

The contamination of water by nitrates poses a threat to the health of humans and other animals. Nitrate is found to be extremely toxic at high concentrations in water. It has been postulated to be the origin of methemoglobinemia in infants and it can cause toxic effects on livestock. Although phosphorus is not as toxic as nitrate in water, it can stimulate the growth of algae in water along with nitrate pollutants. Their excessive discharge to the surface water sources can lead to severe eutrophication in surface water sources. Eutrophication is the most widespread water contamination in global aquatic systems and it brings about numerous negative aftermaths to the environment and ecosystem. The most commonly observed consequence of eutrophication is that it causes the multiplication of algae and aquatic weeds, which give bad odor and taste of water in the aquatic systems, and prevents the use of such polluted systems as sources for clean water for industry, agriculture, and humans. In addition, eutrophication can induce the growth of phytoplankton and zooplankton in various aquatic environments. Besides, eutrophication is considered to be the cause for the disappearance of coral reefs and the extinction of several fish species.

Cyanides are another important class of anionic pollutants. Cyanides, which can be generated from either anthropogenic or natural sources, commonly exist in the form of cyanide salts, such as sodium cyanide and potassium cyanide, or in gaseous phase as hydrogen cyanide. Cyanides can be discharged into aquatic system from carelessly treated industry sewage, coal gasification, electroplating operations, and incomplete combustion of fuels. Cyanides cause severe threat to human life as the cyanide anion (CN^-) is recognized to be highly toxic. The ingestion and/or inhalation of cyanide anion (CN^-) by humans can lead to low vitamin B_{12} levels in the human body and can be lethal.

Cationic Wastes. The most commonly seen inorganic cationic wastes in aquatic systems are heavy metal ions, such as lead (Pb^{2+}) [21], arsenic ($As^{3+/5+}$) [22], mercury (Hg^{2+}) [23], chromium (Cr^{6+}) [24], nickel (Ni^{2+}) [25], barium (Ba^{2+}), cadmium (Cd^{2+}) [26], cobalt (Co^{3+}) [27], selenium (Se^{2+}) [28], and vanadium (V^{5+}) [25]. These above-mentioned heavy metal ions can be introduced into aquatic system via diverse means [29]. For example, large amounts of heavy metal ions are produced from natural processes, such as weathering, volcano activities, and crustal movement. As in the modern society, the major sources of heavy metal pollutants are from human/industry activities, for instance, printed board and semiconductor manufacturing, metal finishing and plating, industrial dyeing processes, and so forth. Many heavy metal ions, for example, Fe^{3+}, Zn^{2+}, Cu^{2+}, Mn^{2+}, Co^{3+}, Ni^{2+}, and so forth, are actually essential trace elements (required in less than 100 mg per day) to maintain the daily metabolism of the human body. However, these heavy metal ions exhibit fatal toxicity and can poison humans and animals under excessive exposure and close contact. The indication of heavy metal poisoning in humans can be divided into acute and chronic symptoms. Acute symptoms include fatigue, hallucinations, headache, nausea, numbness, and abdominal pain. Chronic symptoms contain anxiety, dyslexia, lack of concentration, migraines, and so forth. Therefore, the removal of heavy metal ion pollutants from aquatic system is indispensable.

1.2.2. Organic Wastes. Organic pollutants are toxic molecular compounds and can cause significant diseases in humans, when exposed to high concentration levels. These organic compounds originate from a variety of industrial products such as detergents, petroleum hydrocarbons, plastics, organic solvents, pesticides, and dyes, and they can be found in diverse environments. In addition, these organic pollutants are a threat to wildlife and human, due to long-term deleterious effect and chemical complexity. In particular, thousands of persistent organic pollutants (POPs) are a family of chemicals consisting of a diverse group of organic substances, which are toxic, bioaccumulative, and prone to long range of transport [30–33]. It was reported elsewhere that POPs mainly differ in the level of chlorine substitutions and persist in the environment with long lives particularly in soils, sediments, and air [34]. They are released into the environment via municipal and industrial wastes, landfill effluents, agricultural practices, and so forth and undergo various reactions that validate their prevalence. There are a wide number of pollutants listed under the toxic and hazardous categories and some of the main types are detailed here.

Aliphatic organic compounds are mainly runoffs from the surface and are particularly seen in urban areas. In addition, the petroleum oils and the byproducts from the combustion of oil also are mostly aliphatic compounds. A variety of aliphatic organic compounds, that include alkenes, alkynes, dichlorodifluoromethane, 1,2-dichloroethane, 2-propanol, and tetramethylammonium ions, have been reported as toxic pollutants from aquatic environment mainly from surface runoffs. Polycyclic aromatic hydrocarbons (PAH) are another type of organic substances released to the environment from the incomplete combustion of organic substances including wood, carbon, and oil. They are neutral, nonpolar organic molecules consisting of two or more fused benzene rings and reported as a priority pollutant by the EPA [35]. The extensive use of polychlorinated biphenyls (PCBs) in numerous industrial processes, electrical transformers, capacitors, carbonless copy paper, and plastics increases their penetration into the environment.

Surfactants are among the most versatile group of organic compounds utilized in industrial, household, personal care, and health products [36]. Owing to their existence in anionic, cationic, nonionic, and amphoteric forms, they have the ability to alter the physicochemical state of the natural habitat. At high concentrations, they can form complexes in water and cause harmful effects to microorganisms. Pesticides are another type of organics found in diverse chemical structures and are used for various agricultural and nonagricultural applications such as herbicides, insecticides, fungicides, and germicides. Dyes are colored substances that have strong affinity for the substrate to which it is being applied. Dyes are applied to numerous substrates such as textiles, leather, plastic, and paper. Dyes can be classified under different categories according to their application method, chemical structure, usage, or the type of chromophore present in them [37].

Phenol and phenolic compounds byproducts formed from many industrial processes, such as the manufacturing of herbicides, plastics, polymer precursors, photographic developers, dyes, drugs, and pulp and paper industry [38]. In addition, incomplete mineralization of the phenolic compounds ends up with natural organic byproducts that include humic substances, lignins, and tannins, which are prevalent in our environment. The toxicity of phenols and phenol derivatives is mainly attributed to the ease of donation of free electrons, forming phenoxy radicals and intermediates. These phenoxy radicals can penetrate the cell and damage membranes of endoplasmic reticulum, mitochondria, and nucleus and also their components like enzymes and nucleic acids. Furthermore, exposure to phenol may damage the skin through its reaction with amino acids in the epidermis [39].

2. Removal Techniques

Continuous increase of pollutants in water bodies has necessitated the need to develop cost-effective methods for their removal. Destroying the pollutants to benign chemicals and/or removing these pollutants from contaminated water is imperative for a green environment. There are numerous treatment processes that have been applied for pollutant removal from wastewater, such as electrochemical oxidation [40], biodegradation [41, 42] membrane process [43], coagulation [44, 45], adsorption [46–49], precipitation [50], sonochemical degradation [51, 52], micellar enhanced ultrafiltration, and AOP [4, 9, 10]. Though these methods are considered as efficient methods for pollutant removal, each method has its own benefits and drawbacks. In this section, we will explain some of the most common methods that are frequently used for pollutant removal and their basic principles.

2.1. Electrochemical Oxidation. Electrochemical oxidation is an efficient and economic method, suitable when the wastewater contains nonbiodegradable organic pollutants. This method poses several advantages since it does not require auxiliary chemicals, high pressures, or high temperatures. In addition, owing to its versatility and cost-effectiveness, electrochemical techniques have gained great attention for the removal of pollutants. The process of electrochemical oxidation mechanism is mainly based on the generation of the hydroxyl radicals at the electrode surface.

Two different types of mechanisms have been elaborated for electrochemical oxidation, such as direct and indirect oxidation methods [53]. In direct electrochemical oxidation, the degradation of organic compound occurs directly over the anode material, where the hydroxyl radical ($^{\bullet}OH$) or the reactive oxygen species react with the organic compound. The pollutants are first adsorbed at the surface of the anode and are then degraded by an anodic electron transfer reaction as given by

$$M + H_2O \longrightarrow M\left({}^{\bullet}OH\right) + H^+ + e^- \tag{1}$$

In the indirect electrochemical oxidation, the organics are treated in the bulk solution by oxidants, such as $^{\bullet}OH$, Cl_2, hypochlorite (ClO^-), peroxodisulfate ($S_2O_8{}^{2-}$), and ozone (O_3), which are electrochemically generated at the electrode surface. Even though high removal efficiencies are achieved by both the direct and indirect electrochemical oxidation processes, their effectiveness strongly depends on the treatment conditions including pH, current density, types and concentration of pollutants, supporting electrolyte, flow rate, electrode preparation method, and nature of the electrode materials. Several electrode materials that include Pt, PbO_2, Ti-SnO_2, Ti/Pt, Ti/Pt–Ir, Ti/PbO_2, Ti/PdO–Co_3O_4, Ti/RhO_x–TiO_2, Ti coated oxides of Ru/Ir/Ta, IrO_2, Ti/RuO_2, SnO_2, PbO_2, and so forth, and boron doped diamond (BDD) [6, 54–73] have been listed as efficient electrodes for the degradation of organics by electrochemical oxidation. Apart from these anode materials, graphite anodes are also considered as efficient materials for anodic oxidation of several organic pollutants [6, 62]. Particularly, the high oxygen overpotential, high electrocatalytic activity, chemical stability, long lifetime, and cost-effectiveness have been credited for the high efficiency of these graphite electrodes. In a recent publication, Govindaraj et al. investigated the electrochemical oxidation of bisphenol A (BPA) from aqueous solution using graphite electrodes [6]. The effect of the supporting electrolyte (type and concentration), initial pH, and applied current density on the performance was discussed in their work. The oxidation of polyhydroxybenzenes was conducted using a single-compartment electrochemical flow cell as illustrated in Figure 1 [56]. Diamond-based material was used as the anode and stainless steel was used as the cathode.

The effectiveness of this electrode was evaluated by monitoring the concentration of BPA. Chemical oxygen demand (COD) removal of 78.3% was obtained, when 0.05 M NaCl was used as the electrolyte at an initial pH of 5 and a current density of 12 mA/cm^2. In a different study, the effect of different types of supporting electrolytes in the degradation of phenol using BDD electrode was studied by Alencar de Souza and coworkers [70]. The electrochemical performance was examined by measuring COD and the concentrations of all phenolic compounds formed during the electrolysis process. The oxidation kinetic constants using different electrolytes were found to be in the following order: $k_{Na_2SO_4} \approx k_{Na_2CO_3} > k_{H_2SO_4} > k_{H_3PO_4}$. However, the addition of chloride ion to the electrolyte solution caused a major change in the reaction kinetics, and the rate constants were found to be in the following order: $k_{H_2SO_4} > k_{Na_2SO_4} > k_{Na_2CO_3}$. The difference in the reaction kinetics was explained by the oxidation mediated by the chloride ions, which was formed at low pH values. Though the concentration of chloride ions helped to rapidly increase the reaction rate, increment in the supporting electrolyte concentration also assisted to improve the reaction kinetics. Apart from the above-mentioned studies, there are several reports describing the utilization of BDD for oxidation of several organics such as salicylic acid [68], nitrophenol [73], nitrobenzene [72], and tetracycline [66]. A brief review regarding the application of BDD for incineration of synthetic dyes towards environmental application [67] and another review article by Martínez-Huitle and Ferro providing clarity for the electrochemical oxidation of organic pollutants are available [53].

2.2. Biological Process. In the 1990s, biological processes were used for the removal of heavy metal due to the reactive ability of microorganisms with a variety of pollutants that include organic and inorganic species. It was recognized that the microorganisms influence the mobility of the metal by modifying the chemical and physical characteristics of the metals [93]. Recently, Lu et al. investigated a novel biological filter with bacterial strain of *P. putida* immobilized in Ca-alginate granules for removal of formaldehyde in the gas phase [94]. The effects of inlet concentration, empty bed residence time, and nutrient feeding rate on the performance of the system were examined in their study. It was found that the removal efficiency of the dripping biofilter system increased from 68.6% to 93.5%, when the inlet formaldehyde concentration was in the range of 0.2 to 1.34 mg/m^3. Among the various technologies, such as adsorption [95], chemisorption, photocatalytic oxidation [96], and botanical filtration [97], that have been tried for the removal of formaldehyde, the complete removal is still a challenging problem due to low kinetics, byproduct formation, and low efficiency using any of the above-mentioned methods. However, biological degradation technology with high removal efficiency has been successfully applied in industries for effluents and waste gas treatments. Even though biological processes have been used for several applications that include heavy metal ion removal and indoor air purification, its application has not been intensely investigated for numerous reasons. Thus, researchers have combined biological process with other techniques such as chemical processes [98, 99], photocatalysis [100], and AOP [74, 101, 102].

Combined biological and chemical degradation methods were carried out to evaluate the effectiveness of mature municipal landfill leachate in laboratory scale by Di Iaconi and coworkers. The biological treatment was followed by chemical oxidation for further removal of COD [98]. Higher removal efficiency was obtained due to the use of chemical treatment. In another study, a combined AOP and biological process was carried out to remove pesticides in aqueous

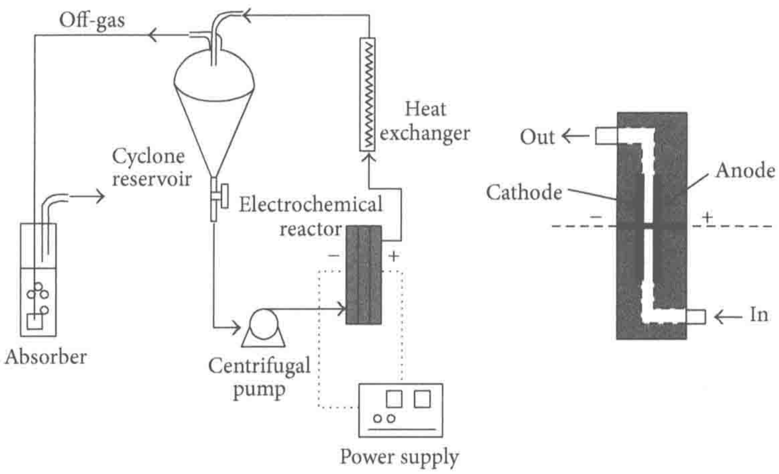

FIGURE 1: The pilot plant arrangement and illustration of electrochemical cell (reprinted with permission from [56]).

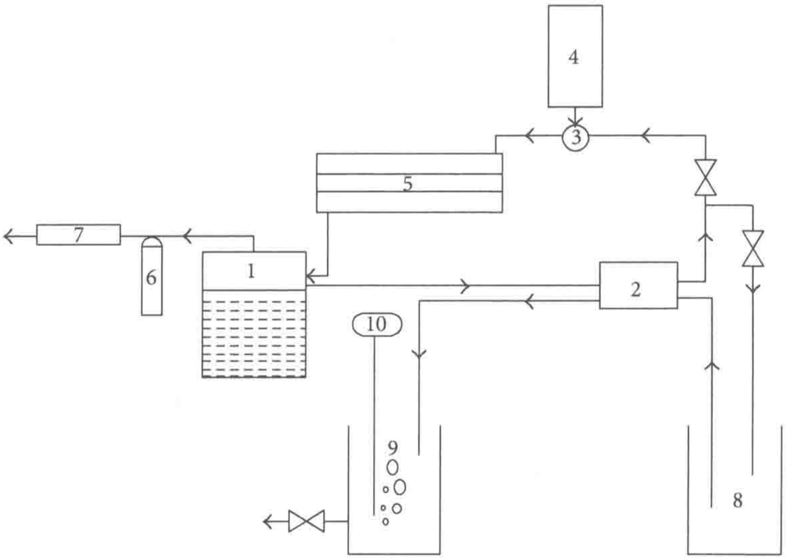

FIGURE 2: Experimental setup for combined chemical and biological degradation: (1) chemical oxidation tank, (2) peristaltic pump, (3) diffuser valve, (4) ozone generator, (5) UV emitting device, (6) excess KI trap, (7) ozone destruction device, (8) neutralizer, (9) biological treatment tank, and (10) air sparger (reprinted with permission from [74]).

solution [74]. The experimental setup for their study is illustrated in Figure 2. The chemical oxidation process was carried out in the tank labeled as 1. The UV emitting device (labeled as 5) consists of a stainless steel tube with a coaxial mercury vapor lamp. Ozone was produced from air by an ozone generator and was continuously fed into the oxidation tank. Finally, the pH of the system was adjusted to 7, and then the pollutant was fed to the biological treatment tank labeled as 9.

It was found that O_3 and O_3/UV oxidation treatment was able to achieve 90 and 100% removal of the pesticide deltamethrin, in a period of 210 min. Utilization of ozone with UV irradiation was found to enhance the degradation of pesticides. It has been well documented elsewhere that the rate of pesticide removal mainly depends on both the chemical nature of the pesticides being treated [103] and the treatment conditions [104]. In a different study, a sequential UV and biological degradation of a mixture of 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol were tested with an initial concentration of 50 mg/L [105]. Under their reaction conditions, pentachlorophenol degraded faster compared with other phenolic compounds and 4-chlorophenol degraded the slowest. A combined biological and chemical procedure was also used as an ecologically and economically favorable remediation technique for 2,4,6-trinitrotoluene (TNT) reduction in contaminated ground and surface water [106, 107]. It was observed that the anaerobic transformation process resulted in a faster reduction of TNT due to significant change in the redox potential of the solutions under both aerobic and anaerobic conditions. Biodegradation of organic pollutants by halophilic bacteria was carried out by Le Borgne and coworkers [108].

In a very recent study, wastewater from a pharmaceutical formulation facility in Israel was treated with a biological activated-sludge system followed by ozonation [101].