Nanomaterials significance; contaminants degradation for environmental applications

Sadaf Bashir Khan¹  and Shern Long Lee¹

¹ Institute for Advanced Study, Shenzhen University, Shenzhen, Guangdong, 518060, People’s Republic of China
² Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Optoelectronic Engineering, Shenzhen University, Shenzhen, Guangdong 5180603, People’s Republic of China

E-mail: sllee@szu.edu.cn

Keywords: Air pollution, organic dyes; photocatalysis wastewater, contamination, nanoparticles (NPs), nanomaterials, 2, 4-dichlorophenol, chlorophenol compounds

Abstract
Nanotechnology provides an innovative platform that is inexpensive, reasonable, having least chances of secondary contamination, economical, and an effective method to concurrently eradicate numerous impurities from contaminated wastewater. Presently, different researches have been conducted exhibiting versatile multifunctional nanoparticles (NPs) that concurrently confiscate several impurities existing in the water. Nanotechnology helps in eliminating impurities from water through the rapid, low-cost method. Pollutants such as 2,4-dichlorophenol (death-causing contaminant as it quickly gets absorbed via the skin), or industrial dyes including methyl violet (MV) or methyl orange (MO) causing water contamination were also concisely explained. In this mini-review, nanomaterials were critically investigated, and the practicability and effectiveness of the elimination of contaminations were debated. The analysis shows that a few of these processes can be commercialized in treating diverse toxins via multifunctional nanotechnology innovations. Hence, nanotechnology shows a promising and environmental friendly method to resolve the restrictions of current and conventional contaminated water treatment. We can progress the technology, without influencing and affecting the natural earth environment conditions.

1. Introduction
Nanomaterials contribute a significant role in the reduction of environmental contamination, industrial, factories, and agricultural wastes treatment. Environmental pollution can easily decline via green progression and production, emissions control, desulfurization/denitrification, and agriculture upgrading. The management of industrial and agricultural wastes encompasses the transformation of wastes products into goods, remediation groundwater via photocatalysis and nanomembranes. Nanomaterials modify physical properties due to their high specific surface area to volume ratio. The nanomaterials having nanoscale dimensions were used as adsorbents, catalysts, membranes, or additives to upsurge activity and competency due to their high specific surface areas. Hence, nanomaterials are more effective at handling environmental trashes [1].

There are different kinds of observable, non-observable pollution influencing one in daily life. Industrial pollution, water pollution, greenhouse gases (GHG) [2, 3]. Ozone (O) dangers are common factors enhancing environmental pollution, generating atmospheric toxins polluting water resources (rivers, lakes, and oceans) land and air [4]. Industrial waste contaminates both water and soil [5]. One cannot see different kinds of toxins until they move in the surrounding atmosphere extending in the far-flung and widespread region. Factory pollution is observable, retaining stinking cloudy smoke emissions. The factory air pollutants comprise greenhouse gases due to fossil fuel burning. Factories also detoxify water and land via acidifying rain, chemical, or dumping toxic waste. Carbon dioxide (CO2) is the most destructive greenhouse gas released in the air via the burning of fossil fuels. Sulfur dioxide also generates from burning fossil fuels, a significant source of causing acid...
rain. However, a particular benefit of sulfur dioxide present in the air is to keep the atmosphere fresh to balance the warming instigated by CO$_2$ [6]. Ozone is an alternative crucial air poison. Ozone is structurally comprised of three oxygen atoms (O$_3$) than required for breathing (O$_2$). The third oxygen atom makes corrosive oxygen, which is harmful to the lungs. However, O is beneficial in the upper atmosphere as it helps in blocking ultraviolet emission from the Sun. Its presence in the lower atmosphere is detrimental to living beings. Factories or vehicles effluence generates ground ozone complications, known as ‘smog,’ causing noteworthy health problems. Factories, predominantly using enormous industrial air conditioners, also discharge destructive vapors, contributing to O depletion in the higher atmosphere where it is desirable [7].

Additionally, concentrated animal feeding operation (CAFO), is also a source of environmental pollution infecting air, land, and water. CAFO industries are technologically advanced used to harvest meat or dairy products in large amounts generating vapors (methane, ammonia) lowering air quality, which is detrimental to health. The animal leftover often ends up in the water, sullying streams, lakes, and ponds with harmful bacteria (E. coli) [8–10]. The industrial sector contaminates water directly via discarding pollutants into streams or lakes. However, few countries pay special attention to the dumping of hazardous waste. According to National geographic information, 70% of all industrial effluence is cast-off directly into the water table, poisoning drinking water too. In China, textile-dye wastewater via clothing industrial unit is generating water pollution. However, filtration plants are continually being developed to clean the industrial unit waste before it flows into the water supply [11].

The environmental pollution in the surrounding atmosphere causes numerous severe health problems, comprising life-threatening ailments. A pollutant usually occurs either in a gaseous, liquefied, or solid-state. The pollution either exists due to indoor activities (CH$_3$OH, CO, or tobacco smoke) and open-air effluence (C$_6$H$_5$Cl, NO$_2$, ozone, and HCl) sources. Toxins generally pass in the human system via skin, eyes, ears, nose, or mouth causing acute abrupt illness to long-term chronic diseases if exposed for long term. Air contamination consists of tiny particles (dust and debris > 2.5 micrometers in diameter) that can be easily breathed in. Once a contaminant is breathed in it causes instant harm to human organs, i.e. damage lungs or flow in the bloodstream. The plasma is a central component in transferring nutrients, clearing wastes, regulating body temperature, and immune system. Persistent exposure to respiratory toxins may cause chronic bronchitis, tissue damage, worsened asthma, or blood cancer (Leukemia due to benzene exposure generates from oil and gas production) [12]. Exposure to carbon monoxide, nitrogen oxides, SO$_2$, Pb, or ozone causes irregular heart pulses, abnormal inflammatory responses, arterial shrinking, or heart disease [13]. Continuous exposure to air pollution generates different health issues in humans, according to the National Institute of Health, i.e., stroke, Alzheimer’s sickness, Parkinson’s ailment, and brain syndromes. It also affects the birth rate and congenital heart defects or vehicle air pollutants associated with brain and spine abnormalities [3, 14, 15]. Figure 1. represents few factors instigating environmental pollution focusing on anthropogenic sources disturbing the natural ecosystem.

Hence, over the last several decades, several natural potentially polluted events occur such as deforestation, farmland wildfires, forest exudates, volcanic eruptions, oil spills and human-made anthropogenic incidents such as hazardous waste, oil extraction, carbonaceous materials, lubricants usage, unintentional oil filter sand discharges during transportation have been one of the major causes of climate change [16]. As organic materials i.e. coal, gasoline, timber, and vegetation are subjected to thermal decomposition (pyrolysis), causing polycyclic aromatic hydrocarbons (PAHs) to generate, while significant quantities of PAHs discharged by fossil fuels are due to inadequate combustion. PAHs are organic compounds with cluster structures that typically consist of two or even more fused benzenic chains. In environments such as marine ecosystem, sedimentary rocks, surface water, groundwater, or in the air they are electrochemically stable and shows a resistance to decompose [17, 18]. Due to its higher potential for mutagenicity, carcinogenic effects, oxidative damage, and contamination of the 16 dangerous PAHs identified by the Environmental Protection Agency (EPA), China’s seven blacklisted PAHs are rated as environmental contaminants [19]. The existence of PAHs within the soil is attributed to its hydrophobic nature as proved by mass transfer kinetics limited bacterial development on PAHs [20]. PAHs survive maximally in sediments in the marine setting than it does in the water column [21]. It is a major environmental source of pollution, already recorded in vegetation (fruits, vegetables, and grains) or marine organisms. Currently, the current physicochemical and biological techniques are developing to remove PAHs using chemical treatments such as solidification, dispersing, dechlorination, and solvothermal techniques and physical processes such as skimming regulated combustion, absorption, UV deterioration, or fixation [20].

However, in case of industrial pollution, among numerous harmful dyes and compounds emitted from various industrial unit, most harmful one is the one that extracts from various kinds of dyes and compounds from wastewater. Forms of dyes are primarily used in producing textiles, pharmaceuticals, paper, coloring, and printing industrial sectors. Including picric acids and nitrophenols, the azodiadines, were extremely poisonous, non-biodegradable, mutagenic, and carcinogenic agents [22]. In the manufacturing industry, through the usage of pigments such as crystal violet (CV), CBB, or congo red (CR), the color may be also modified from pale blue to
purple. The inhaled ultrafine particles created on e-cigarettes and other recently developed items have caused serious health concerns. Many methods have been used to cope with contamination problems, including the elimination of toxins through filtration, adsorption, oxidation, or by biological agents. On the other side, pathogens that we historically did not know becomes the key component that triggers several terrible infections and diseases connected with skin and respiratory infections [23]. Many researchers are interested in the production of therapeutic agents due to metals among microbes and their ability to battle against microbial diseases. Recently, metallic nanomaterials have been the subject of a great deal of concern in the area of biomedical science owing to their potentially biomedical advantages.

Besides this, pathogenic microorganisms are also becoming a key problem of infectious agents among all demographic groups varying from adolescents to the elderly. The tolerance of pathogenic bacteria increases the probability of illnesses with pathogenic diseases in the gastrointestinal tract. The fact scientists have been creating antibacterial medicines that are immune to infection has pushed doctors to discover new and creative methods to suppress them. In the current status, NPs are being regarded favorably for treatment of various diseases, and even for the treatment of AIDs or HIV [24].

2. Motivation and objective of study proposed

It is a need in today's time to control toxins, contaminations, and take steps to decline pollutants for a living being. The present review focus on the recent progression and innovative ideas to control, regulate, and clean the toxins and contaminants generated from different pollution sources at a safer level for the benefit of living habitats. In this review article, the discussion starts with an overview of various pollutants classes, and particular focus is given on 2,4 DCP (Molecular formula: C₆H₄Cl₂O) having a melting point of 45 °C showing poor biodegradability (0%, four weeks) with water solubility 4.5 g l⁻¹ (20 °C) having adverse effects on humans [25, 26]. In the past, the immediate death of workers was reported if exposed to 2,4 DCP, i.e., worker (male) died instantly when exposed to broiling steam having 2,4-DCP (EPA, 2000). Earlier, it was reported that a worker suffers epileptic seizures in 20 min and expired after splashed (only 10% of the body) with pure molten 2,4-DCP. It shows that 2,4-DCP exposure instantly gets absorbed via skin which is deadly and harmful [27].

In nature, freshwater is a valued resource that can easily be contaminated. It is highly problematic to reinstate the quality of freshwater once it gets 'polluted. The water in streams, reservoirs, lakes or alongside the water that drifts continually in watercourses/ channels, can easily be contaminated because it is used for water supplies,
agriculture, industry, or recreation. The majority of diseases spread due to drinking contaminated water. Chlorophenol compounds (CPCs) are poisonous, carcinogens, and extensively used as pesticides, wood preservatives, drugs, fungicides, insecticides, or in anticorrosive rust production organically polluting waters and soil continuously [28, 29]. CPCs are non-biodegradable due to their physicochemical characteristics depending on chlorine substitutes. The chlorinated hydrocarbons biodegradation through microorganisms becomes problematic and difficult with growing chlorine substitutes on CPC [29, 30]. As a consequence, it leads towards the accumulation of CPC, cause danger to human health via food chains. Furthermore, it can also initiate disorders in cellular bilayer phospholipids structure, generating cancer-causing, and mutagenic disease in humans [31]. It is considered toxic, harmful waste, and hazardous in US Clean Water Act as well as EU Directive 2455/2001/ECI[32].

3. Developed methodology

A variety of methods, often classified into three groups, make possible the removal of dye from wastewater i.e. i) physical shielding, which involves adsorption and ion diffusion; chemical processes such as electrical deterioration, chemical oxidation, photocatalytic degradation or ozonation; and (iii) natural degradation [33]. The physical adsorption system is a time-consuming process. Likewise, natural degradation methods are disadvantaged due to their poor degradation efficacy for certain dyes and expensive treatment procedures [34]. Photocatalysis seems to be a feasible substitution throughout the currently accessible strategies for the removal of pollutants [35]. Diverse semiconductors were used throughout the years as photocatalysts. The popular photocatalysts TiO₂ has indeed been widely known and has already been classified as a remarkable photocatalyst due to its strong flexibility and its exceptional corrosion resistance. The use of manganese oxide, namely birneit is widely investigated due to its significant use in different fields, such as electrical condensers, aquatic oxygen therapy, catalytic oxidation of natural dies, and gas equipment. Thanks to the excellent possessions of electron transport and multiple adsorption and oxidation capabilities of MnO₂, having bandwidths of 2.20–2.63 eV have fascinated significant interest for photocatalysis [36].

4. Metallic nanoparticles synthesis

Metallic nanoparticles were also considered to be able to be an effective antioxidant agent against pathogenic bacteria besides resolving water contamination issues. Despite the existence of numerous metallic nanoparticles such as lead, bronze, zinc, copper, titanium, and magnesium, investigations have been carried against such bacterial infections. Metals oxide possessing specific structural configurations make them conductive, insulator, or semiconductive. Nanomaterials were prepared via co-precipitation, thermal decomposition, microemulsion, hydrothermal or sonochemical processes. These nanomaterials can be used in lithium-based batteries, solar panels sensors, or as pigments and dyes beside medications. Although NPs are not as hazardous as arsenic and mercury, they are dose-dependent and become toxic at higher concentrations. The degradation of picric acid Pd@TiO₂ nanoparticles for anticancer activity [37]. Different methods have been used to synthesis metallic nanomaterials using top down or bottom up approaches as depicted in schematic figure 2.

5. Water contamination and its removal techniques

Owing to massive urbanization and industrialization globally, contaminated water is pervasive. Hazardous waste management is now a serious ecological problem that affects sea animals, water environments, and public health emitted from numerous industries such as textiles, manufacturing, leathers, food manufacturing and pharmaceutical goods, pharmacy, paper, maquillage, and rubber [38]. Cationic crystal dye (CV) was used in medical diagnostics due to its easy interaction with many other materials. Furthermore, inhaling excess CV or CR pigments may induce gastrointestinal system allergic reactions, vomiting, diarrhea, nausea, distorted vision, phlegm cell damage, or genetic mutation [38, 39]. Photoelectrocatalytic dye degradation is an increasing strategy that attracts considerable interest in handling chemical dye-containing wastewater. Manufacturers processing significant quantities of toxins utilizing techniques like adsorbent, ultrafiltration, flocculation, filtration, solvent extraction, reverse osmosis, or biodegradation for wastewater treatment [39]. In contrast, some decaying microbes, including certain fish scales, eggshells, oyster shells, or biomaterials, have been used in numerous experiments to degrade impurities due to their cost-effective, environmental friendly nature and the ability for accelerated degradation of dangerous dyes [40].

Photocatalysis is a groundbreaking technique developed in light of the failure of the conventional water treatment techniques. The three key features comprising heterogeneous photocatalytic (mostly oxygen)
reactions are selective i.e. selective wavelength photons, catalyst (especially the solid catalyst), and a strong oxidant. The participation of NPs must comply with all relevant requirements about the use of the metal nanomaterials, such as CuO, Ag, and others for biomedicine [41]. The use of non-metallic nanoparticles nevertheless encourages a safer, non-toxic approach to the degeneration of photocatalytic dyes. Researchers thus focus on the use of nanosized hydroxyapatite (HAp) in synthetic dyes deterioration. A significant inorganic material in all vertebrates is hydroxyapatite. It comprises around 70 percent of the chemical formula of apatite calcium phosphate, \( \text{Ca}_{10} \left( \text{PO}_4 \right)_6 (\text{OH})_2 \), \( \text{HAp} \). HAp’s biocompatibility, degradability, and ion exchange characteristics allow them ideal products for the implementation of cartilage, such as automated bone marrow transplants, orthopedic therapy, and regenerative medicine systems [42]. In science and nanotechnology uses, HAp’s similarity to bone minerals renders it a biocompatible ceramic. The reduced crystallite size nanostructured HAp represents the biological HAp configuration. HAp may be processed using different processes, including hydrothermal processing, the chemical reaction of sol-gel, and the technique of wet chemical precipitation [43]. The usage of HAp for wastewater treatment and its potential to extract fluorides, heavy metal ions as well as dyes from aqueous solutions have been documented by several researchers. Selvam Sathiavimal has documented the preparation and characterization of HAp from fish (Gibelion Catla) bones and its sustainable and environmental use as photocatalytic activity for deterioration of CV or CR dyes through natural daylight irradiation, taking into account the efficient application of Hap demonstrating 77% degradation of CV and 87% of CR within 75 min of exposure [38].

Pinaud et al [44] have recently established the strong photocatalytic activity of nanocomposite MnO2/TiO2 to degrade methylene blue under visible light radiation. Effective photocatalysts for water oxidation were also found to be chemically shaped i.e. manganese-calcium oxides, but their structures at the atomic level are not clear. The load concentration and oxidation of manganese are affected by Ca\(^{2+}\) ions [45] Lucht et al have shown that birnite frameworks with Sr, Ca, B and Al are capable of separating water. A sufficient lighting variance is needed for anhydrous Ca Birnesite. Rapid nanotechnological reforms are expected to illustrate the marketing trend for the usage of nanostructures in polluted water treatment [46]. Nanocomposites, utilizing single metal nanoparticles, are formed and vary considerably due to different physical, structural and optoelectronic properties [47]. These nanocomposites were considered to provide an outstanding remarkable dye degradation efficiency and energy conservation capacity for metal oxides and are thus labeled energy materials. Different studies reported the synthesis of mixed oxide catalysts used for different nanostructured materials. The method involves sol-gel, hydrothermal flammable spray, deposition of the chemical gas phase, or combustion. The microstructures and attributes of the product are therefore distinct and highly reliant on synthesis processes and conditions. The sol-gel mechanism, solvothermal growth, or ultrasonication approach also appears to be a better way to synthesize nanoparticles. The ultrasonication provides a simple and easy solution and is a valuable tool for the development of standardized materials which cannot be processed utilizing conventional methods [48]. Thus cleaning contaminated water could be carried out using different approaches mentioned in schematic figure 3.

Polluted water, including systems built around groundwater, profoundly impacts community life. Water supplies have indeed been polluted by poisonous chemicals as a consequence of the growing industrial revolution. In the long term, the difficulties in accessing clean drinking water is a massive concern, for even a significant period. Toxins that reach the water supplies have become so complex that it is challenging as an unbroken subject to deal with it in one cohesive direction. Pigments were considered as dyes frequently used in

![Figure 2](image_url). Demonstrates various techniques to synthesize metallic nanoparticles.
several applications, including fabrics, pharmaceutical drugs, nutrition, makeup, plastic, painting, ink, photography, wood, or automobile industries parts. A detrimental effect is due to the use of colored water infiltration systems because of their chemical and particle composition. In the aqueous phase, pigments throughout various proportions specifically refer to various categories, like oxidative, acidic, basic, dispersed, aldehyde, diazo, anthraquinone-based, or metal-complex pigments. The origins of such pigments consist of various components classified as toxic substances, like benzidine or naphthalene. Furthermore, once these dyes were broken down by microorganisms, the byproducts could still be lethal. Few pigments are naturally xenobiotics, however, in the wastewater stream withstand traditional removal techniques. There have been various strategies for the degradation of impurities in drinkable water that have already been introduced. After all, it’s indeed essential to multiply the efficacy of treatment according to the considerations. Figure 4 represents the model explaining various factors which may impact the pollutant degradation from contaminated water.

In view of that, nanoparticles have attracted interest in different disciplines in recent years, such as bioengineering, photocatalysis, detectors, robotics or in optoelectronics [49]. The synthesis of metallic nanoparticles with controlled structural composition and practical benefits is the objective of researchers. Environmental friendly nanoparticles synthesis is now implemented to eliminate the occurrence of contamination and encourage sustainable development. In specific, throughout environmental sustainability, multiple concepts are often used to minimize the use of harmful and pathogenic contaminants or chemicals to synthesize sustainable and non-toxic nanomaterials. Natural resources such as plantations comprising leaves, wood, vegetables, flowers, seedlings, or microbes, such as bacteria, seaweeds, etc. can function as metallic and non-metallic nanostructures. Therefore, by removing the use of harmful chemical substances, natural resources have offered an eco-sustainable and environmentally friendly route to synthesize possible nanomaterials [50]. Amongst various metal oxide nanoparticles, zinc oxide and TiO₂ particles are the most commonly shown in beauty products, moisturizer creams and cleansers, and commercial applications. ZnO has significant antibacterial activity, in biological processes as well as the ecosystem, it’s a much more stable nanomaterial due to its durability and long-term effectiveness against microbes [51]. Laser beam deposition (PLD), evaporation, molecular beam epitaxy (MBE), or sputtering are part of the physical technique for nanomaterials processing, whereas chemical synthesis is conducted utilizing spray pyrolysis, co-precipitation, hydroxylation, hydrolysis, advanced oxidation process (AOP), or sol-gel approaches [52].

The use of nanoparticles to remove dyes from contaminated water has risen to prominence over the last couple of years as they have a greater surface area, large adsorption properties, less diffusion resistance, and faster equilibrium rates. More primarily, several other research teams all around the world have investigated the effect of nanomaterials in wastewater treatment. The physical, chemical and biological properties of nanomaterials are preferable, helping to identify uses in numerous industries. Besides nanomaterials exhibit antimicrobial properties that promote their effects in the treatment of wastewater. Photocatalysis is a mechanism in the removal of dye effluents, in which electrons moved to conduction from the valence band when exposed to radiation, leading to the production of electron-hole pairs. The produced hydroxyl radical serves as a strong oxidizing agent and fully deteriorates the dye into anti harmful bi-products (CO₂, H₂O, etc.) [53]. The Advanced

![Figure 3. Demonstrating various methods of treating water contamination.](image-url)
oxidation process (AOP) due to its efficient performance and stability, has been employed for handling these organic and inorganic pollutants without generating secondary left-over difficulties. In AOP, hydroxyl radicals (·OH) were generated for the oxidation process. The nanoscale zero-valent iron (ZVI) or metallic NPs (Pd/Fe, Cu/Fe, Ni/Fe) remain potential reductants besides ecologically biocompatible for the reduction of harmful waste. Recently, Fangbai Li [54] and his colleagues fabricate Fe/Cu/Pd catalytic agents to analyze their catalytic activity. They use 4-nitrophenol (PNP) as an ideal composite and transform it into an aminophenol (useful chemical) via reduction reactions in the presence of NaBH₄ [55]. The experimental result demonstrates that PNP reduction via NaBH₄ was 25-fold advanced than that without NaBH₄. Figures 5(i) & (ii) reflects the schematic of the proposed 4-nitrophenol (PNP) reduction mechanism, BH₄⁻ product is non-toxic B(OH)₃ does not affect the environment. In aerobic surroundings (BH₄⁻ ) has established huge consideration for transforming nitrophenol to aminophenol [56]. BH₄⁻ ions serve as electron centers continuously producing electrons on the catalyst surface generating active hydrogen species (H⁺). Besides this, different researchers also investigates different textile dye wastes [2,4-dichlorophenol (DCP), tetrabromobisphenol (TBBPA), nitrobenzene (NB), and methylene Blue (MB)]. The reduction kinetics displays that the reduction of the pollutants is remarkably
heightened. It displays considerably enhanced reactivity of Fe/Cu@Pd in NaBH₄ presence in comparison to metallic constituent part (nZVI and Fe/Cu). It was experimentally proved that PNP could be competently reduced attained from various water sources, i.e., lake, pure water, and groundwater, having different flow rates. This innovative method offers the lessening of carbon-based impurities in aerobic surroundings, outspreading the nZVI-based method to wide-ranging applications in water cleaning. It also confirms the advantage of Fe/Cu@Pd for proficiently decreasing the electron-deficient compounds in the occurrence of NaBH₄[19].

The dechlorination of 2,4-DCP via polyvinylpyrrolidone (PVP) coated Cu/Fe bimetallic NPs has also been experimentally performed. The experimental analysis shows that the fraction of PVP to Cu/Fe should be 0.35, Cu percentage in Cu/Fe NPs was 41%. PVP helps in dispersing and stabilizing uniformly distributed Cu/Fe NPs. PVP also enhances the reactivity for removing 2,4-DCP via Cu/Fe NPs. A low pH and advanced temperatures, boost the dechlorination rate. These PVP-Cu/Fe NPs are easily usable due to their magnetic characteristics, which permit quick magnetic separation of the catalysts[57]. Earlier, oxidative degradation of 2,4-DCP via ethylenediaminetetraacetic acid (EDTA)bimetallic Cu–Fe coordination was also investigated, which shows 100% degradation in 1 (pH range of 3 ~ 7) [29] as 2,4-DCP is abundantly present in the groundwater contaminating it. Humic acid (HA) is also used for the dechlorination of chlorinated hydrocarbons via Pd/Fe bimetallic NPs. Different influencing aspects i.e., NO₃ absorption or Pd concentration also impact the lessening of 2,4-DCP [58]. The experimental consequences propose that a low concentration of HA has a marked effect on 2,4-DCP dechlorination [58].

Many reductive substituents have been employed for the photocatalytic reduction and remediation of polluted water using advanced technologies and small power consumption. The extensively cast-off semiconductor photocatalyst titanium dioxide (TiO₂) was restricted in practical applications due to its narrow UV-light response [59]. Wang et al report the water splitting of metal-free photocatalyst a metal-free polymeric graphitic carbon nitride (g-C₃N₄)[60]. Afterward, wide-ranging investigations have been carried out on environmental purification [61]. Though, the photocatalytic activity is restrained because of the fast recombination of photo-generated electrons. However, the photocatalytic efficacy was improved via two procedures ion doping [61, 62] or treating with noble metals [63]. These methods simultaneously extend light absorbance as well as accelerate the charge separation process [64, 65]. Heterojunction approach [66, 67] and Z-scheme [68, 69] coordination also supports in attaining the high charge separation. As long as the global environment is concerned, the development of dangerous chemicals, in particular heavy metals and dyes, is a disturbing aspect, attracting the attention of many scholars to address this global crisis. The increasing pollution of dyes in the aquatic ecosystem is listed as one of the most serious environmental issues. Dyes stay persistent and do not suffer normal deterioration in the climate, which consequently affects and causes the environment pollutant due to manufacturing operations i.e. paints, fabrics or in bioindustries, p-nitrophenol (4-NP) a pollutant penetrates the aquatic systems having adverse consequences. Besides this, the primary dyeing material used in numerous industries, such as wood, fiber, or MB which also causes eye illness.

Calcium magnesium oxide nano flakes were used to remove organic toxins from waste synthesized via co-precipitation technique supported by ultrasonication. Their physical and chemical analysis was implemented to establish the physicochemical, structural, and functional properties and the composition of nano flakes. HR-TEM test proves the diameter of nano flakes from 10 to 30 nanometers with an average size of 25 nanometers. The photocatalytic function of flake and p-nitrophenol (4-NP) was also determined by the rate of removal of these compounds under UV radiation. Synthesized nanoflakes will decompose 4-nitrophenol and methylene blue in a short time suggesting the usage of CaMgO nanoflakes to handle wastewater [70].

In recent times, Bismuth tungstate (Bi₂WO₆) has generated consideration owing to visible irradiation compelled characteristics and fast oxidizability [71, 72]. The conduction and valence band edge in Bi₂WO₆ is at about −0.12 and 2.59 eV, and the g-C₃N₄ band gap is −0.78 eV and 1.89 eV [73, 74]. The experiments proved that photo-generated electrons in the Bi₂WO₆ conduction band might quench with g-C₃N₄ holes present in the valence band, developing the Z-scheme coordination as shown in figure 6(a). Xiao et al synthesize a composite photocatalyst (g-C₃N₄@Ag–Bi₂WO₆) displaying Z-scheme [75]. The Ag takes part as an electron mediator, showing enhanced photocatalytic activity during Rhodamine B degradation. Similarly, Ma et al [30] synthesis a Z-scheme g-C₃N₄@RGO-Bi₂WO₆ which shows an outstanding reduction of 2,4,6-trichlorophenol (TCP) [76]. Though, the use of noble metals (electron mediators) restricted this approach practically at a commercial scale due to high cost. As a consequence, researchers investigate and concentrate on developing mediator-free Z-scheme [77–79].

Sintering and heating technique was used to synthesize composite based binary photocatalysts comprising of a graphitic carbon nitride and bismuth tungstate (g-C₃N₄/Bi₂WO₆). The binary photocatalysts displayed heightened photocatalytic performances due to active decline in charge recombination and comprehensive spectrum absorption range under UV–vis light irradiation [80]. The schematic representation of the photogenerated charge carrier’s separation and transference in g-C₃N₄/Bi₂WO₆ under UV–vis irradiation is shown in figure 6(a). The as-prepared g-C₃N₄/Bi₂WO₆ (samples mass ratios at 3:7) degraded 2,4-DCP entirely within 2 h (h). The operational and retrieval activity of g-C₃N₄/Bi₂WO₆ showing that the binary photocatalyst retains its
high photocatalytic activity even after five successive sequences, specifying the catalyst stability. The 2,4-DCP reaction pathways, intermediates, and finishing bi-products were investigated, which shows that intermediates comprise o-CP and p-CP, producing phenol (P) as a final product. The potential dechlorination pathway based on detection results was proposed in figure 6(b).

Without illumination (dark conditions), isopropanol and 2,4-DCP adsorbed on surface of a binary catalytic agent. During illumination (UV–vis light), the dechlorination of 2,4-DCP into o-CP and p-CP takes place due to the binary composite catalyst which excites and produces electrons in the interim electrons conglomerate with protons and 2,4-DCP. Additionally, the produced o-CP and p-CP react with accumulated electrons and protons, developing the final last product, phenol (figure 6(b)). Thus, these binary photocatalysts help in reducing electron-hole pairs recombination rate and enhancing photon efficacy. In the heterostructure system, the band arrangement shows a fundamental role in defining the movement of photo-generated carriers [73]. The conduction band (CB) and valence band (VB) potentials of g-C3N4 are negative than that of Bi2WO6. In these circumstances, the charge carriers transference paths may follow two patterns: Firstly, in the heterojunction type, the generated electrons due to light exposure in g-C3N4 CB transfer to Bi2WO6 CB, whereas holes in VB of Bi2WO6 transport to VB of g-C3N4. Secondly, via Z scheme in which the generated electrons due to light exposure in the Bi2WO6 CB transferal to g-C3N4 VB, leaving photo-generated electrons in CB of g-C3N4 and holes in the VB of Bi2WO6.

CeO2/g-C3N4 complexes can be synthesized via a wet-chemical solution method, which displays improved visible-light activity for 2,4-DCP. It is due to an improved charge carrier’s separation and transfer among the two constituent coordination. A graphic mechanism for 2,4-DCP degradation via CeO2/g-C3N4 amalgams is suggested in figure 7. The C3N4 valence band is positioned at 1.4 eV and the CB is at −0.79 eV versus normal hydrogen electrode (NHE) [81]. According to UV–vis diffuse reflectance spectra, bandgap of CeO is nearly at 2.82 eV. The VB of CeO at 2.03 eV (measured via XPS spectra), and the conduction band is at −0.79 eV. The work functions (Φ) of CeO2/g-C3N4 were 4.69 eV and 4.34 eV [82–84]. The heterojunction is formed between binary composites CeO2/g-C3N4 generating charge carriers (electron–hole pairs) under visible-light. The band alignments of CeO2/g-C3N4 are well-coordinated, which facilitates and enhances the electron–hole pair’s separation.

Additionally, the CeO2/g-C3N4 interface in composite offers a stage for charge carrier’s passage between CeO and CN. The visible-light irradiation excited CB electrons of g-C3N4, which transfer to CeO2 CB, because of the higher work function of g-C3N4 w.r.t CeO2. At the same time, the photo-induced holes of CeO2 in VB transfer to the g-C3N4 VB. The competent electron–hole pairs transmission among the two constituents may considerably diminish charge carriers recombination possibility. The photocatalytic cycle comprises 3h, after which the photocatalyst was used for a second time to degrade the fresh 2,4-DCP solution. Experimental results prove that CeO/CN composite shows consistency and remains unchanged even after four times repetition demonstrating stability [85].

Accordingly, different methods have been employed to degrade 2,4-DCP such as via functional bacteria in anaerobic microbial system (dechlorination effectiveness: 98.5 ± 1.5,12h) [86] sepiolite–based bimetallic Fe/Ni NPs (3h efficiency >95%) [87] Heterogeneous Fenton oxidation and reductive dechlorination (1.5 h) [88,89], dechlorination via Pd/Fe NPs(absence of ultrasonic irradiation 65%, presence of ultrasonic irradiation 91%)
within 2 h [90]. The illumination source also influences the dechlorination as CdTe/CdS/N-rGO homologous heterojunctions composites structure exhibits 70% degradation of 2,4-DCP under visible light radiation for 6h, 90% under ultraviolet light (100 W lamp), and it shows 65% under the infrared light [91]. Ag/Ag3PO4/BiPO4 nanocomposites show 90% photocatalytic degradations in 1.5h [92], a porous g-C3N4 (pg-C3N4)/8-quinolinolato iron(III) (Q3Fe)/H2O2 [93], TiO2/g-C3N4 nanocomposites [94] system were used to purify the organic pollutant and enhance the contaminant removal efficiency.

Besides the physical and chemical techniques, the biological method of treating chlorophenols also gathered attention. Different microorganisms consume the chlorophenols as carbon or energy source [95, 96, 97] few of them includes Pseudomonas pickettii, Alcalilgenes eutrophus, Desulfomonile tiedjei, or Phanerochaete chrysosporium. The activated sludge systems or bioaugmentation are used to biotreat the pollutants to improve the elimination of contaminants comprising of phenols, chloroaniline, chlorobenzoate, resin acid, or chlorinated phenols [95]. In bioaugmentation, the appropriate selection of bioaugmentation microorganisms and applicable bioaugmentation approach is significant to degrade the pollutant. Yi Qian combines the conventional activated sludge system with bioaugmentation for the deduction of 2,4-DCP efficiently, besides chlorophenols i.e., 4-monochlorophenol or 2,4,5-trichlorophenol [95]. The aerobic granular treatment of 2,4-dichlorophenol and COD shows 96% and 95% degradation within 270 min; the sequencing batch reactor (SBR) nearly takes 80 d for stabilizing the granules [96]. Similarly, S.G Wang shows the formation of the pellets within 39 d showing 94% 2,4 DCP degradation which is a potential candidate for treating industrial waste water [99]. Similarly, 2,4-DCP abolished up to 52% and 78% in up-flow anaerobic sludge blanket (UASB). The aerobic suspended growth ASG reactor shows 2,4-DCP (86%) and COD (95%) eliminations within 26 h [100]. The recent development in degrading the organic pollutant 2,4 DCP, MB, MV and MO using different nanomaterial system is mentioned in table 1. Different factors influence the % removal efficiency of these toxin, such as catalyst concentration, pH, illumination source, temperature, amount of contaminant presence, time consumption, technique, or temperature. However, still, it is a need to design such kind of nanomaterial system which is economical, durable, showing persistent consistency, and degrade the organic pollutant in less time consumption.

6. In-depth analysis

Humans influence nature slowly, but its after-effects are permanent such as greenhouse warming. The air and noise pollution via vehicles or industries increases day by day slowly and continuously as everyone could feel the noise, smell the odorous goings-on, and observe the black smoke influencing the surrounding local community representing a worsening atmosphere. All of us need to live in an unpolluted environment having pure air, clean water, and fresh surrounding air including standard living material. Unluckily, all these practical demands may be challenging to accomplish for every individual at the same time due to industrialized progression. Human modification of earth is essential emerging and increasing. The majority of the land surface, water, and air have been transformed and polluted by human action and industrial development. The CO2 concentration has increased by nearly 30% since the start of the industrial revolution in the atmosphere. The available water is used
Table 1. Representing the 2,4 DCP, MO, MB and CR dyes with previously reported literature removal via different nanomaterial systems.

| Nanomaterial System                  | Toxin    | Removal Efficiency | Time (h) | Reference |
|-------------------------------------|----------|--------------------|----------|-----------|
| H₂O₂/TiO₂                           | 2, 4 DCP | 52.27%             | 6        | [101]     |
|                                     | COD      | 73.35%             |          |           |
| SiO₂-coated nZVI                    | 2, 4 DCP | 100%               | 12       | [102]     |
| S- TiO₂                             | 2, 4 DCP | 100%               | 36       |           |
| Sulphite, dithionite sulfide        | 2, 4 DCP | 97%                | 8        | [103]     |
|                                    |          | 99.4%              | 40 min   | [104]     |
|                                    |          | 10.73%             |          |           |
| TiO₂/Ru-IrO₂                        | 2, 4 DCP | 94.3%              | 1        | [105]     |
| MWCNT/TiO₂                          |          | 100%               | 3 – 5:30 | [106]     |
| Fe/Ps                               | 2, 4 DCP | 100%               | 1h       | [107]     |
| Pd/Fe nanoparticles                 | 2, 4 DCP | 99.2%              | 5h       | [90]      |
| Pd/GO/Ti                            | 2, 4 DCP | 92.2%              | 5h       | [108]     |
| SiO₂-coated nZVI                    |          | 45%                | 28       | [109]     |
| Pseudomonas putida DLL-E4, Pseudomonas reactants, and Pseudomonas fluorescens | 2,4-dichlorophenoxyacetic acid | 99.5% | 24 | [110] |
|                                    |          | 2,4-dichlorophenol (2,4-DCP) | 98.4 |         |
|                                    |          | 2,4,6-trichlorophenol (2,4,6- TCP) | 94.0% |         |
| Pd/Al₂O₃                            | 2,4-DCP  | 91.6%              | 5h       | [111]     |
| m-alginate/Cf₂O₃/CdS composite      | CR       | 65%                | 2h       | [112]     |
| CZ-400                              | CR       | 95%                | 3h       | [113]     |
| Bi₀.₀₉Gd₀.₀₅Sm₀.₀₅FeO₃              | CR       | 85.9%              | 3h       | [114]     |
| Chitosan/nano-Cds                    | CR       | 71%                | 2h       | [115]     |
| BiFeO₃-graphene                     | CR       | 70%                | 2h       | [116]     |
| BiFeO₃/TiO₂(1 : 1)                  | CR       | 82%                | 1h 20 min| [117]     |
| TiO₂-SWNT-P-21                      | CR       | 86.3%              | 1h       |           |
| ZnO/UV-A                            | CR       | 95%                | 40       | [118]     |
| Bi₀.₀₉Gd₀.₀₅Sm₀.₀₅FeO₃              | CR       | 91.6%              | 5h       | [119]     |
| m-alginate/Cf₂O₃/CdS composite      | CR       | 99.61%             | 3h       | [120]     |
| TiO₂                                | MO       | 90%                | 3h       | [121]     |
| CuO/RGO                             | MO       | 70%                | 5h       | [122]     |
| Zn₂SnO₄                             | MO       | 42%                | 1h       | [123]     |
| ZnO                                 | MO       | 92%                | 3h       | [124]     |
| Fc₂O₃@SiO₂@TiO₂@Ho                  | MO       | 78.4%              | 2h       | [125]     |
| V₂O₅                                | MO       | 99.98%             | 3h       | [126]     |
| m-alginate/Cf₂O₃/CdS                | CR       | 91.6%              | 5h       | [127]     |
| CZ-400                              | CR       | 65%                | 2h       | [128]     |
| Bi₀.₀₉Gd₀.₀₅Sm₀.₀₅FeO₃              | CR       | 95%                | 3h       | [129]     |
| Chitosan/nano-Cds                    | CR       | 85.9%              | 3h       | [130]     |
| BiFeO₃-graphene                     | CR       | 71%                | 2h       | [131]     |
| BiFeO₃/TiO₂(1 : 1)                  | CR       | 70%                | 2h       | [132]     |
| TiO₂-SWNT-P-21                      | CR       | 82%                | 1h 20 min| [133]     |
| Bi₀.₀₉Gd₀.₀₅Sm₀.₀₅FeO₃              | CR       | 95%                | 40       | [134]     |
| m-alginate/Cf₂O₃/CdS composite      | CR       | 91.6%              | 5h       | [135]     |
| V₂O₅                                | MB       | 70%                | 2h       | [136]     |
| V₂O₅/CNT/TiO₂                       | MB       | >29% then BiVO₄    | 3h       | [137]     |
| ZnS/CdS                             | MB       | 73%                | 6h       | [128]     |
| ZnFe₂O₄                             | MB       | 95%                | 3h       | [129]     |
| ZnS                                 | MB       | 88%                | 1h 30 min| [130]     |
| TiO₂ nanofilms                      | MB & MV  | 97% & 98%          | 4h       | [131]     |
| TiO₂ nanofilms                      | MB, MV, MO| 67.21              | 4h       | [1]       |
| AgNPs                               | CV, CBB  | 87% & 74%          | 3h       | [22]      |

by civilization due to which one-quarter of the bird and animal species have been driven to extinction. Investigators have executed comprehensively, promising, and well-defined efforts in the arena of photocatalysis and decontaminating pollutants. The semiconductive NPs as photocatalysts are narrow because they respond
only to UV-excitation. Until now, a lot of scope and effort is required for the synthesis of UV-Visible light-induced nanomaterials that show enhanced catalytic activities; in less time, consumption, as well as its fabrication, should take place at a large scale to come across the requirements.

Nanostructures having surface area ranging (<100 nm) display different distinctive properties that have never been observed in bulk. The significance of nanomaterials in every domain has been directly linked to high surface sites for physicochemical properties, that are unavailable in bulk. In the treatment of wastewater, there have been four main categories of functional nanoparticles, namely dendrimers, nanocomposites comprising metals, zeolites, or carbonate nanoparticles. Nanostructures comprising metals are effective as biocides and killing several microbes adhering both for gram-positive and negative groups. Besides, they help with the elimination of toxic metals including arsenic or halogen besides degradation of dissolved dyes as well as other toxic elements. Zeolites operate to eliminate contaminants from water as an ion-exchange medium. In an aqueous medium, carbonaceous materials could perhaps operate as sorbents for organic solutes. Through the use of bioactive nanoparticle-integrated membrane surface to eliminate hazardous chlorinated compounds is advancement in this respect to perform the catalytic activity in a short time, having various bioactive immobilized enzymes. Besides this, core/shell nanomaterials were indeed highly efficient materials with enhanced characteristics and attained progressive attention. By modifying core/shell physicochemical characteristics or amount, the characteristics of core/shell nanoparticles are quite diversified and adapted to various applications. The core/shell are dual-phase nanomaterials composed of various elements with the main core structure and an external shell. These particulates can reveal interesting characteristics increasing from the combination of core and shell, its configuration, and material design. These nanocomposites, have been used in multiple fields, based upon certain remarkable physical-chemical characteristics including therapeutics, metallurgy, photocatalyst or optoelectronics devices [132]. Figure 8 demonstrates the advantages of nanomaterials importance in today's life. Nanomaterials rely mostly on purpose to adjust the material properties at incredibly tiny dimensions to accomplish particular attributes, thereby enhancing the materials characteristics.

7. Conclusion

Nanotechnology offers a cost-effective way to both purify water and minimize overall costs by simultaneously eliminating harmful and unwanted impurities. Various investigations have been performed displaying multipurpose NPs that simultaneously eliminate numerous impurities in water. Nanotechnology was critically
studied in this review, and the feasibility and effectiveness of eliminating contaminations were discussed. The aim of the research was to completely eliminate infectious microorganisms, inorganic compounds, and environmental contaminants. The future advanced effort is a prerequisite to initiate metal oxide response in the visible light. However, few researchers fabricate the binary metal oxide composite photocatalysts, but the output is quite low. The recognizing and degradation concerns of the hazardous and toxic chemicals should be determined and resolved. The incorporation of the nanomaterials for the removal of decontamination and toxins bring unexpected benefits due to intrinsic nanoscale dimensions, to induce info at atomic resolutions, enhance low signal levels, accelerate response times, and continuously regulate changes. Developing nanostructured instruments for the eco-friendly environment needs the engineering progressions in identifying and distinguishing mechanisms and configurations, for the future emerging requirements.

Henceforth, information on the diverse artificial techniques used for the synthesis of photocatalytic constituents should be considered necessary. Besides this, the exploration of new photocatalysts having preferred characteristics to persuade the oxidation reaction of organic substrates or the reduction of the pollutants under visible light irradiation should be invigorated. The population rise, associated with the quick resource consumption and constant industrial growth and agrarian advancement has led to surplus wastewater with compositional modifications texture, toxicity, and noxiousness due to different kinds of contaminants existing in wastewater. Currently, the challenges faced via wastewater management are primarily linked with the wastewater structural intricacy as it makes difficulties in treatment progresses via requiring different equipment and advanced technologies, thus causing prolong handling periods and higher working expenses.

Acknowledgments

The authors thank the NSFC (21972095), Shenzhen University, Guangdong Government (2018A030313467), Shenzhen city (the overseas talent set-up funding, JCYJ2018-0305124732178); Exploring 3D supramolecular assemblies, JCYJ (20190808151815169); and China Postdoctoral Science Foundation (65th Batch-2019M653033).

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Author Contributions

Dr Shern Long Lee and Dr Sadaf Bashir Khan comprehended and planned the review; Dr Sadaf Bashir Khan wrote the review paper.

Conflicts of Interest

The authors declare no conflict of interest.

ORCID iDs

Sadaf Bashir Khan https://orcid.org/0000-0001-9024-8824

References

[1] Khan S B, Hou M, Shuang S and Zhang Z 2017 Morphological influence of TiO₂ nanostructures (nanozigzag, nanohelics and nanorod) on photocatalytic degradation of organic dyes Appl. Surf. Sci. 400 184–93
[2] Chen G, Wei Y, Xuan F, Zhong J, Zhang Z and Wang Z 2014 Greenhouse Gases (GHG) Emissions from Gas Field Water in Southern Gas Field, Sichuan Basin, China, Water Air & Soil Pollution 225 1902
[3] Xie J F 2002 A review of studies on mechanism of greenhouse gas (GHG) emission and its affecting factors in arable soils Agricultural Meteorology 23 47–52
[4] Andreae M O and Ramanathan V 2013 Climate change. Climate’s dark forcings Science 340 280–1
[5] Andersen S O, Halberstadt M L and Borgford-Parnell N 2013 Stratospheric ozone, global warming, and the principle of unintended consequences—An ongoing science and policy success story
[6] Baldocchi D, Falge E, Gu L, Olson R, Hollinger D, Running S, Anthoni P, Bernhofer C, Davis K and Jarvis A 2001 FLUXNET: A new tool to study the temporal and spatial variability of ecosystem-scale carbon dioxide, water vapor, and energy flux densities Bull. Am. Meteorol. Soc. 82 2415–34
[7] Devi L G and Kavitha R 2013 A review on non metal ion doped titania for the photocatalytic degradation of organic pollutants under UV/solar light: Role of photogenenated charge carrier dynamics in enhancing the activity Appl. Catalysis B 140 559–87
[8] Bradford S A, Segal E, Zheng W, Wang Q and Hutchins S R 2008 Reuse of concentrated animal feeding operation wastewater on agricultural lands J. Environ. Qual. 37 397
[9] Rule A M, Chapin A R, McCarthey S A, Gibson K E, K.J.S. and Buckley T J 2005 Assessment of an aerosol treatment to improve air quality in a swine concentrated animal feeding operation (CAFO) Environmental Science & Technology 39 9649
[10] Imhoff D 2010 The Tragedy of Industrial Animal Factories CAFO (Concentrated Animal Feeding Operation) ISBN: 978-1-60109-058-4 513
[11] Sajid M M, Shad N A, Khan S B, Zhang Z and Amin N 2019 Facile synthesis of ZnS vanadate Zn3(VO4)2 for highly efficient visible light assisted photocatalytic activity J. Alloys Compd. 775 281–9
[12] Munawer U, Raghavendra V B, Nagaraj S, Krishna K L, Ghosh A R, Melappa G and Pugazhendhi A 2020 Biofabrication of gold nanoparticles mediated by the endophytic Cladosporium species: Photodegradation, in vitro antitumor activity and in vivo antitumor studies Int. J. Pharm. 588 119729
[13] Hsiu-Min C, Yu-Hsuan L, Rong-Jane C, Hui-Wen C, Bour-Jr W and Ying-Jan W 2013 The immunotoxic effects of dual exposure to PA and TCDDD Chem. Biol. Interact. 206 166–74
[14] Sanchaisiruya K, Fuchareon S, Fuchareon G, Ratanasiri T, Sanchaisiruya P, Changtraku Y, Ukosanakakun U, Usawaphak W and Schelp F P 2005 A reliable screening protocol for thalassemia and hemoglobinopathies in pregnancy: an alternative approach to electronic blood cell counting American Journal of Clinical Pathology 123 113
[15] Dalton P, Caraway E A, Gibb H and Fulcher K 2011 A multi-year field olfactometry study near a concentrated animal feeding operation J. Air Waste Manage. Assoc. 61 1398–408
[16] Mohanrasu P N, K, Rao R G R, Dinesh G H, Prakash G S, Pugazhendhi A, Jeyakanthan J, Govarthanan M, Kumar P and Arun A 2020 Effect of C/N substrates for enhanced extracellular polymeric substances (EPS) production and poly cyclic aromatic hydrocarbons (PAHs) degradation Environ. Pollut. 275 116035
[17] Quantini C, Joner E J, Portal M J and Berthelin J 2005 PAH dissipation in a contaminated river sediment under anoxic and anoxic conditions Environ. Pollut. 134 315–22
[18] Wehner M and Totsche K U 2009 Difference in PAH release processes from tar-oil contaminated soil materials with similar contamination history Geochemistry 69 109–24
[19] Fetzer J C 2007 The chemistry and analysis of large PAHs Polycyclic Aromatic. Compl. 27 143–62
[20] Wick L Y, Colangelo T and Harms H 2001 Kinetics of mass transfer-limited bacterial growth on solid PAHs Environmental Science & Technology 35 535–61
[21] Kim K-H, Jahim S A, Kahire M and Brown R J 2013 A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects Environ. Int. 60 71–80
[22] Seerangaraj V, Sathiavimal S, Shankar SN, Mandapagadda J G T, Balashanmugam P, Al-Misned F A, Shammugavel M, Senthil Kumar P and Pugazhendhi A 2021 Cytotoxic effects of silver nanoparticles on Pteris vermiculata: Photocatalytic degradation properties against crystal violet and coomassie brilliant blue J. Environ. Chem. Eng. 9 105088
[23] Munagapati V S, Yarramuthi V and Kim D-S 2017 Methyl orange removal from aqueous solution using goethite, chitosan beads and goethite impregnated with chitosan beads J. Mol. Liq. 240 329–39
[24] Shanmuganathan R, LewisOscar F, Shankmugam S, Thajjuddin N, Alharbi S A, Alharbi N S, Brindhadevi K and Pugazhendhi A 2020 Core/shell nanoparticles: Synthesis, investigation of antimicrobial potential and photocatalytic degradation of Rhodamine B J. Photochem. Photobiol., B 202 111729
[25] Xing L, Sun J, Liu H and Yu H 2012 Combined toxicity of three chlorophenols 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol to Daphnia magna J. Environ. Monit. 14 1677–83
[26] Program T 1989 NTP toxicology and carcinogenesis studies of 2,4-Dichlorophenol (CAS No. 120–83–2) in F344/N rats and B6C3F1 mice (feed studies) National Toxicology Program Technical Report 353 1
[27] Holcombe Gw Faup, Phipps Gl L, Phipps Gi Faup and Findt T J 1982 Effects of phenol, 2,4-dimethylphenol, 2,4-dichlorophenol, and pentachlorophenol on embryo, larval, and early-juvenile fathead minnows (Pimephales promelas) Archives of Environmental Contamination and Toxicology 11 73–78
[28] Kone T, Hanna K and Usmann M 2011 Interactions of synthetic Fe(II)-Fe(III) green rusts with pentachlorophenol under various experimental conditions Colloids & Surfaces A Physicochemical & Engineering Aspects 385 152–8
[29] Liu X, Fan H and Ma L M 2015 Simultaneously degradation of 2,4-dichlorophenol and EDTA in aqueous solution by the bimetallic Ca3–CeO2/n system Environmental Science & Pollution Research 22 1186–98
[30] Methatham T, Lu M C and Ratanatamskul C 2011 Removal of 2,4-dichlorophenol as herbicide’s by-product by Fenton’s reagent combined with an electrochemical system Desalination & Water Treatment 32 42–8
[31] Song G, Nie T and Wang H 2008 Theoretical study of the reaction of 2,4-Dichlorophenol with 1 O 2 J. Mol. Struct. THEOCHEM 861 27–32
[32] Jamil T S, Mansor E S, Abdallah H and Shaban A M 2018 Innovative high flux/low pressure blend thin film composite membranes for water softening React. Funct. Polym. 131 384–99
[33] Nagpal M and Kakkar R 2019 Use of metal oxides for the adsorptive removal of toxic organic pollutants Sep. Purif. Technol. 211 522–39
[34] Radek H, Simandl D and Santen P 2011 Combined toxicity of 2,4-Dichlorophenol to Pimephales promelas Archives of Environmental Contamination and Toxicology 61 1001–8
[35] Adekunle A S, Oyekunle J A O, Durosissi M M, Lwuwafemi O S, Olayanju D S, Akinola A S, Obisesan O R, Akinaye O F and Ajayosha T A 2020 Potential of cobalt and cobalt oxide nanoparticles as nanocatalyst towards dyes degradation in wastewater Nano-Structures & Nano-Objects 21 100403
[36] Bel Hadjltaief H, Ben Amour S, Da Costa P, Ben Zina M and Elena M 2018 Galvez, Photocatalytic decolorization of cationic and anionic dyes over ZnO nanoparticle immobilized on natural Tunisian clay Appl. Clay Sci. 152 148–57
[37] Harirahar D, Thangumaniyandi P, Selvakumar P, Devan U, Pugazhendhi A, Vasantharaja R and Nehru L C 2019 Green approach synthesis of Pd@TiO2 nanoparticles: characterization, visible light active picric acid degradation and anticancer activity Process Biochem. 87 83–8
[38] Sathiavimal S, Vasantharaj S, Shamungavel M, Manikandan E, Nguyen-Trí P, Brindhadevi K and Pugazhendhi A 2020 Facile synthesis and characterization of hydroxyapatite from fish bones: Photocatalytic degradation of industrial dyes (crystal violet and Congo red) Prog. Org. Coat. 148 105890
Ameen S, Akhtar M S, Nazim M and Shin H-S 2013 Rapid photocatalytic degradation of crystal violet dye over ZnO flower nanomaterials Nanom. Lett. 96 228–32

Ngawabebho A F, Gazi M and Oladipo A A 2016 Adsorptive removal of multi-azo dyes from aqueous phase using a semi-IPN superabsorbent chitosan–starch hydrogel Chem. Eng. Res. Des. 112 274–88

Lewis-Oscar F, MubarakAli D, Nithya C, Priyanka R, Gopinath V, Alharbi N S and Thajuddin N 2015 One pot synthesis and anti-biofilm potential of copper nanoparticles (CuNPs) against clinical strains of Pseudomonas aeruginosa Biofueling 31 379–91

Pal A, Paul S, Choudhury A R, Bala V K, Das M and Sinha A 2017 Synthesis of hydroxyapatite from Lates calcarifer fish bone for biomedical applications Mater. Lett. 203 89–92

Chai Y and Tangaya M 2018 Simple preparation of hydroxyapatite nanosstructures derived from fish scales Mater. Lett. 222 156–9

Pinaud B A, Chen Z, Abram D N and Jaramillo T F 2011 Thin films of sodium bimnesite-type MnO2: optical properties, electronic band structure, and solar photoelectrochemistry The Journal of Physical Chemistry C 115 11830–8

Bougarrani S, Skadell K, Arndt R, El Azzouzi M and Gläser R 2018 Novel CaMnOy hybrid perovskite nanolayers: an unprecedented strategy for hybrid perovskite thin-film solar cells Int. J. Hydrogen Energy 43 36819–30

Khan S B, Wu H, Fei Z, Ning S and Zhang Z 2017 Antireduction of 4-nitrophenol by heterostructured gold-magnetite nanocatalysts J. Hazard. Mater. 318 262–8

Zhang Z, Lu X, Baig S A and Xu X 2014 Catalytic dechlorination of 2,4-dichlorophenol by NiFe-layered double hydroxide for solar-driven photoelectrochemical water oxidation Nano Lett. 14 3906–13

Yan Z, Yukun Z, Jianqiang Y, Dongjiang Y, Tsz Wai N, Po Keung W and Yu J C 2013 Enhanced photocatalytic water disinfection using N-doped graphene nanosheets as durable catalysts for enhancing bioelectricity generation J. Mater. Chem. 23 15670–76

Sun J H, Feng J L, Tian X K and Dong S Y 2010 Preparation, characterization and photocatalytic properties of superabsorbent chitosan-starch hydrogel Mater. Lett. 64 940–4

Zhang Z, Wang W, Wang L and Sun S 2012 Enhancement of visible-light photocatalysis by coupling with narrow-band-gap semiconductor: a case study on Bi2S3/Bi2WO6 ACS Appl. Mater. Interfaces 4 593–8

Bougarrani S, Skadell K, Arndt R, El Azzouzi M and Gläser R 2018 Novel CaMnOy hybrid perovskite nanolayers: an unprecedented strategy for hybrid perovskite thin-film solar cells Int. J. Hydrogen Energy 43 36819–30

Zhang Z, Lu X, Baig S A and Xu X 2014 Catalytic dechlorination of 2,4-dichlorophenol by NiFe-layered double hydroxide for solar-driven photoelectrochemical water oxidation Nano Lett. 14 3906–13

Yan Z, Yukun Z, Jianqiang Y, Dongjiang Y, Tsz Wai N, Po Keung W and Yu J C 2013 Enhanced photocatalytic water disinfection using N-doped graphene nanosheets as durable catalysts for enhancing bioelectricity generation J. Mater. Chem. 23 15670–76

Sun J H, Feng J L, Tian X K and Dong S Y 2010 Preparation, characterization and photocatalytic properties of superabsorbent chitosan-starch hydrogel Mater. Lett. 64 940–4

Zhang Z, Wang W, Wang L and Sun S 2012 Enhancement of visible-light photocatalysis by coupling with narrow-band-gap semiconductor: a case study on Bi2S3/Bi2WO6 ACS Appl. Mater. Interfaces 4 593–8
[74] Li H, Liu J, Hou W, Na D, Zhang R and Tao X 2014 Synthesis and characterization of g-C3N4 / Bi2MoO6 heterojunctions with enhanced visible light photocatalytic activity Applied Catalysis B: Environmental 160–161 89–97

[75] Wei J, Xiao X, Yang Y, Rui X, Pan C.X and Jing S 2016 Photoresponse and mechanism of g-C3N4 and Ag-Co-Modified Bi2WO6 microsphere under visible light irradiation. Acute Sustainable Chemistry & Engineering 4 3017–3023

[76] Dong M, Wu L, Gao M, Xin Y, Ma T and Sun Y 2016 Fabrication of Z-scheme g-C3N4 / RGO/ Bi2WO6 photocatalyst with enhanced visible-light photocatalytic activity. Chem. Eng. J. 290 136–46

[77] Lv J, Kai D, Zhang J, Lei G, Liang C, Liu Q, Zhu G and Chen C 2015 Facile synthesis of Z-scheme graphitic-C3N4 / Bi2MoO6 nanocomposite for enhanced visible-light photocatalytic properties. Appl. Surf. Sci. 358 377–84

[78] Che H, Liu C, Wei H, Hao H, Jin Q L, Jiao Y D, Wei D S, Li C and Dong H 2017 NGQDs active sites as effective collectors of charge carriers for improving photocatalytic performance of Z-scheme g-C3N4/Bi2WO6 heterojunctions under Vis- and NIR-light. Catalysis Science & Technology 8 622–631

[79] Tian N, Huang H, He Y, Guo Y, Zhang T and Yang Z 2015 Mediator-free direct Z-scheme photocatalytic system: BiVO4/g-C3N4 organic-inorganic hybrid photocatalyst with highly efficient visible-light-induced photocatalytic activity. Dalton. Trans. 44 4297–307

[80] Gaoyuan Long J D, Xie L, Sun R, Chen M, Zhou Y, Huang X, Han G, Li Y and Zhao W 2018 Fabrication of mediator-free g-C3N4/Bi2WO6 Z-scheme with enhanced photocatalytic reduction dechlorination performance of 2,4-DCP. Appl. Surf. Sci. 453 1010–18

[81] Dong X, Zhang X, Zhang W, Dong X, Wang G, Ma C, Zhang X, Ma H and Xue M 2015 Ultra-thin C3N4 nanosheets for rapid charge transfer in the core–shell heterojunction of α-sulfur@g-C3N4 for superior metal-free photocatalysis under visible light. RSC Adv. 5 15052–8

[82] Pawar R C and Lee C S 2014 Single-step sensitization of reduced graphene oxide sheets and CdS nanoparticles on ZnO nanorods as visible-light photocatalysts. Appl. Catalysis B 144 57–65

[83] Bi L, Xu D, Zhang L, Lin Y, Wang D and Xie T 2015 Metal Ni-loaded g-C3N4 for enhanced photocatalytic H2 evolution activity: the change in surface band bending. Physical Chemistry Chemical Physics 17 29899–105

[84] Warule S S, Chaudhari N S, Kale B B, Patil K R, Koinkar P M, More M A and Murakami R I 2012 Organization of cubic CeO2 nanoparticles on the edges of self-assembled tapered ZnO nanorods via a template free one-pot synthesis: Significant cathodoluminescence and field emission properties. J. Mater. Chem. 22 8887–903

[85] Hamayun M, Hu Z, Khan A, Cheng W, Yuan Y, Zheng Z, Fu Q and Luo W 2019 Highly efficient degradation of 2,4-dichlorophenol over CeO2/g- C3N4 composites under visible-light irradiation: detailed reaction pathway and mechanism. J. Hazard. Mater. 364 635–644

[86] Jingli Z, Jia H, Tingting Z and Zhapin C 2019 Improvement of 2,4-dichlorophenol degradation and analysis of functional bacteria in anaerobic microbial system enhanced with electric assistance Biocatalysis Reports 5 80–85

[87] Naeim Ezzatahmadi D L M, Hou K, Ayoko G A, Millar G J and Xi Y 2019 Simultaneous adsorption and degradation of 2,4-dichlorophenol on sepiolite-supported bimetallic Fe/Ni nanoparticles. J. Environ. Chem. Eng. 7 102855

[88] Renchao L, Ying C, Xingyong J, Zuliang C, Mallavarapu M and Ravendra N 2013 Fenton-like oxidation of 2,4-DCP in aqueous solution using iron-based nanoparticles as the heterogeneous catalyst. J. Colloid Interface Sci. 438 87–93

[89] Li R, Jin X, Megharaj M, Naidu R and Chen Z 2015 Heterogeneous Fenton oxidation of 2,4-dichlorophenol using iron-based nanoparticles and persulfate system. Chem. Eng. J. 264 587–94

[90] Deming Z, Min L, Deking Z, Shams Ali B and Xinhua X 2013 Reductive dechlorination of 2,4-dichlorophenol by Pd/Fe nanoparticles prepared in the presence of ultrasonic irradiation Ultras. Sonochim. 20 1864–71

[91] Liu C, Li J, Sun L, Zhou Y, Liu C, Wang H, Hoo P, Ma C and Yan Y 2018 Visible-light driven photocatalyst of CdTe/CdS homologous heterojunction on N-rich CeO2 for efficient degradation of 2,4-dichlorophenol. J. Taiwan Inst. Chem. Eng. 93 603–615

[92] Li T, Lu G, Hu X, Xie W, Qiao X and Liao S 2017 Ag3PO4/CdS homologous photocatalyst with 2,4-dichlorophenol decomposition path. Mater. Lett. 188 392–5

[93] Feng W, Zhang L, Fang J, Lu S, Wu S, Yi C and Fang Z 2017 Improved Photodegradation efficiency of 2,4-DCP through a combined Q 3 Fe(III)-decorated porous g-C3N4/0.5H2O2 system. Water Air Soil Pollut. 228 373

[94] Zada A, Qu Y, Ali S, Sun N, Lu H, Yan R, Zhang X and Jing L 2017 Improved visible-light activities for degrading pollutants on TiO2/g-C3N4 nanocomposites by decorating SPR Au nanoparticles and 2,4-dichlorophenol decomposition path. J. Hazard. Mater. 342 715–23

[95] Quan X, Shi H, Hong L, Wang J and Yi Q 2004 Removal of 2,4-dichlorophenol in a conventional activated sludge system through biosaugmentation Process Biochem. 39 1701–7

[96] Fava F, Armenante P M and Kafkewitz D 2010 Aerobic degradation and dechlorination of 2–chlorophenol, 3-chlorophenol and 4-chlorophenol by a Pseudomonas plessiti strain Lett. Appl. Microbiol. 21 307–12

[97] Kiyohara H, Hatta T, Ogawa Y, Kakuda T, Yokoyama H and Takizawa N 1992 Isolation of Pseudomonas pickettii strains that degrade 2,4,6-trichlorophenol and their dechlorination of chlorophenols Applied & Environmental Microbiology 58 1276–83

[98] Khan M Z, Khan F and Sabir S 2011 Aerobic granular treatment of 2,4-dichlorophenol Can. J. Chem. Eng. 89 914–20

[99] Wang S G, Liu X W, Zhang H Y, Gong W X, Sun X F and Gao B Y 2007 Aerobic granulation for 2,4-dichlorophenol biodegradation in a sequencing batch reactor Chemosphere 69 769–75

[100] Atanuaya E J, Purohit H J and Chakrabarti T 2000 Anaerobic and aerobic biodegradation of chlorophenols using UASB and ASG bioreactors World Journal of Microbiology & Biotechnology 16 95–8

[101] Dixit A, Tirpude A J, Munrday A K and Chakraborty M 2011 Degradation of 2,4 DCP by sequential biological–advanced oxidation process using UASB and UV / TiO2/ H2O2 Desalination 272 265–9

[102] Cao Z, Zhang M, Zhang J and Zhang H 2016 Impact of continuous and intermittent supply of electric assistance on high-strength 2,4-dichlorophenol (2,4-DCP) degradation in electro-microbial system Bioreour. Technol. 212 138–43

[103] Gar Alalm M, Samy M, Okakawa S and Ohno T 2018 Immobilization of S-TiO2 on reusable aluminum plates by polysiloxane for photocatalytic degradation of 2,4-dichlorophenol in water Journal of Water Process Engineering 26 329–333

[104] Yu X, Cabooter D and Dewil R 2018 Effects of process variables and kinetics on the degradation of 2,4-dichlorophenol using Advanced Reduction Processes (ARP). J. Hazard. Mater. 357 81–8

[105] Jing L, Wang Y, Di C, Ke X, Tao G and Xu Z 2018 Enhanced photoelectrocatalytic degradation of 2,4-dichlorophenol by TiO2 / Ru-IrO2 bifacial electrode Chem. Eng. J. 343 69–77

[106] Mohammad M and Sabbaghi S 2014 Photo-catalytic degradation of 2,4-DCP wastewater using WMCNT / TiO2 nano-composite activated by UV and solar light Environmental Nanotechnology Monitoring & Management 1 24–9

[107] Xiang L, Zhou M, Pan Y and Xu L 2017 Pre-magnetized Fe0 / persulfate for notably enhanced degradation and dechlorination of 2,4-dichlorophenol Chem. Eng. J. 307 1092–104

16
[108] Zhang J, Liu H, Wang B, Thahit M and Bai H 2015 Preparation of Pd/GO/Ti electrode and its electrochemical degradation for 2,4-dichlorophenol Mater. Des. 86 664–9

[109] Junjie Wan X F, Li Y, He J, Zhao N, Liu Z, Lin Y, Yang C and Liang W 2019 Effect of Mesoporous Silica Molecular Sieve Coating on nZVI for 2,4-DCP Degradation: Morphology and Mechanism During the Reaction 135 68–81

[110] Olaniran A O, Singh L, Kumar A, Mokoena P and Pillay B 2017 Aerobic degradation of 2,4-dichlorophenoxyacetic acid and other chlorophenols by Pseudomonas strains indigenous to contaminated soil in South Africa: Growth kinetics and degradation pathway Applied Biochemistry & Microbiology 53 209–16

[111] GoMex-Quero S, Caldelas-Lizana F and Kezne M A 2008 Effect of metal dispersion on the liquid-phase hydrodechlorination of 2,4-Dichlorophenol over Pd/Al2O3 Ind. Eng. Chem. Res. 47 6841–53

[112] Jiang R, Yao J, Zhu H, Fu Y, Guan Y, Xiao L and Zeng G 2014 Effective decolorization of Congo red in aqueous solution by adsorption and photocatalysis using novel magnetic alginate/γ-Fe2O3/CdS nanocomposite Desalin. Water Treat. 52 238–47

[113] Lan S, Liu L, Li R, Leng Z and Gan S 2014 Hierarchical hollow structure ZnO: synthesis, characterization, and highly efficient adsorption/photo-catalysis toward Congo red Ind. Eng. Chem. Res. 53 3113–9

[114] Irfan S, Shen Y, Rizwan S, Wang H C, Khan S B and Nan C W 2017 Band-gap engineering and enhanced photocatalytic activity of Sm and Mn doped BiFeO3 nanoparticles J. Am. Ceram. Soc. 100 31–40

[115] Zhu H, Jiang B, Xiao L, Chang Y, Guan Y, Li X and Zeng G 2009 Photocatalytic decolorization and degradation of Congo Red on innovative crosslinked chitosan/nano-CdS composite catalyst under visible light irradiation J. Hazard. Mater. 169 933–40

[116] Li Z, Shen Y, Guan Y, Hu Y, Lin Y and Nan C-W 2014 Band-gap engineering and enhanced interface coupling of graphene–BiFeO3 nanocomposites as efficient photocatalysts under visible light J. Mater. Chem. A 2 1967–73

[117] Li S, Lin Y-H, Zhang B-P, Li J-F and Nan C-W 2009 BiFeO3/TiO2 core–shell structured nanocomposites as visible-active photocatalysts and their optical response mechanism J. Appl. Phys. 105 054310

[118] Jafry H R, Liga M V, Li Q and Barron A R 2011 Single walled carbon nanotubes (SWNTs) as templates for the growth of TiO2–the effect of silicon in coverage and the positive and negative synergies for the photocatalytic degradation of Congo red dye New J. Chem. 35 409–6

[119] Vanga P R, Mangalaraja R and Ashok M 2016 Effect of co-doping on the optical, magnetic and photocatalytic properties of the Gd modified BiFeO3 J. Mater. Sci.: Mater. Electron. 27 5699–706

[120] Sajid M M, Shad N A, Javed Y, Khan S B, Zhang Z, Amin N and Zhai H 2020 Preparation and characterization of Vanadium pentoxide (V2O5) for photocatalytic degradation of monoazo and diazo dyes Surfaces and Interfaces 19 100502

[121] Wang D, Xiao L, Luo Q, Li X, An J and Duan Y 2011 Highly efficient visible light TiO2 photocatalyst prepared by sol–gel method at temperatures lower than 300 °C J. Hazard. Mater. 192 150–9

[122] Cai J, Liu W and Li Z 2015 One-pot self-assembly of Cu2O/RGO composite aerogel for aqueous photocatalysis Appl. Surf. Sci. 358 146–51

[123] Masjedi-Arani M and Salavati-Niasari M 2016 A single sonochemical method for the synthesis and characterization of Zn3SiO4 nanostructures UltraSon. Sonochem. 29 226–35

[124] Mohammad A, Kapoor K and Mobin S M 2016 Improved photocatalytic degradation of organic dyes by ZnO-nanoflowers ChemistrySelect 1 3483–90

[125] Mortazavi-Derazkola S, Salavati-Niasari M, AmirI O and Abbasi A 2017 Fabrication and characterization of Fe3O4@SiO2@TiO2@Ho nanostructures as a novel and highly efficient photocatalyst for degradation of organic pollution Journal of Energy Chemistry 26 17–23

[126] Chen M-L and Oh W-C 2010 The Improved Photocatalytic Properties of Methylene Blue for V2O3/CNT/TiO2 Composite under Visible Light Int. J. Photoenergy 2010 264831

[127] Sajid M M, Shad N A, Javed Y, Khan S B, Zhang Z and Amin N 2020 Study of the interfacial charge transfer in bismuth vanadate/reduce graphene oxide (BiVO4/rGO) composite and evaluation of its photocatalytic activity Res. Chem. Internat. 46 1201–15

[128] Soltani N, Saito E, Hussein M Z, Erfani M, Abedini A, Bahmanrokh G, Navasery M and Vaziri P 2012 Visible light-induced degradation of methylene blue in the presence of photocatalytic ZnS and CdS nanoparticles Int. J. Mol. Sci. 13 12242–12258

[129] Xia S, Zhang L, Pan G, Qian P and Ni Z 2015 Photocatalytic degradation of methylene blue with a nanocomposite system: synthesis, photocatalysis and degradation pathways Phys. Chem. Chem. Phys. 17 5545–51

[130] Hao R, Lu Z, Liu X, Ge H, Zhang Z, Zou P, He H and Wang Y 2016 Visible light-driven photocatalytic degradation performance for methylene blue with different multi-morphological features of ZnS RSC Adv. 6 46299–307

[131] Khan S B, Zhang Z and Lee S L 2020 Single component: Bilayer TiO2 as a durable antireflective coating J. Alloys Compd. 834 155137

[132] Khan S B, Wu H, Ma L, Hou M and Zhang Z 2017 HfO2 nanorod array as high-performance and high-temperature antireflective coating Adv. Mater. Interfaces 4 1600892