

Advances in Polymer Nanocomposite Materials for Photocatalytic Degradation of Polynuclear Aromatic Hydrocarbons in Environmental Matrices: A Review

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Received: November 13, 2022 Accepted: February 27, 2023 Online Published: March 1, 2023

doi:10.5539/ijc.v15n1p13

URL: <https://doi.org/10.5539/ijc.v15n1p13>

Abstract

The immobilization of metal oxide nanoparticles into different anchoring media has recently gained great interest owing to their applications in water treatment. The choice of the polymers for the incorporation of the active catalyst particle is highly motivated by several advantages displayed by them. These include mechanical stability, chemical inertness and resistance to ultraviolet radiations, environmental stability, ease availability, and low prices. Additionally, the use of polymer nanocomposite materials (PNMs) as photocatalysts offers the possibility of a facile separation and reuse of the materials, eliminating thus the post-treatment separation processes and implicitly reducing the costs of the procedure. However, this review paper focused on recent advances made in PNMs for the photocatalytic decontamination of polynuclear aromatic hydrocarbons (PAHs) in environmental matrices. It further explores some trends in research and the markets. The review also shows the current advances made on the understanding of detoxification mechanisms and toxicological effects of PAHs in photocatalytic processes as a green alternative method for environmental pollution control and remediation. It further critically explores different ways to improve workflows for PNMs characterization and testing and the emerging need for the analysis of PAHs. It finally provides insights into the understanding of how to set up and optimize manufacturing methods of PNMs while avoiding costly time traps that prevent getting the correct answer in addressing PAH-related environmental pollution problems.

Keywords: photocatalytic degradation, polycyclic aromatic hydrocarbons, polymeric nanocomposite materials, characterization, aquatic environments

1. Introduction

Oceans, rivers, groundwater and lakes are still receiving pollutants from different anthropogenic sources such as the use of pesticides, tanneries, pharmaceutical wastes, textile, painting, food, and cosmetic industries as well as surface runoffs from urban and rural areas (Mahmoodi, & Mokhtari-Shourijeh, 2015; Khan et al., 2021). Worldwide, almost 844 million people still lack clean water due to these polluted effluents plus other disasters such as floods and droughts which are caused by climate change and deforestation (WHO, 2017). Besides these, high concentration levels of different inorganic and organic pollutants as well as heavy metals (Wang et al., 2015) are also adversely affecting the aquatic environments. Most of these contaminants are non-biodegradable and toxic, especially the organic pollutants which are continuously being loaded into the food web through different ways and bioaccumulate in human fatty tissues (Lima, 2018). These include pharmaceuticals and personal care products (PPCPs), dichloro-diphenyl-trichloroethane (DDT), persistent organic pollutants (POPs), furans, endocrine-disrupting compounds (EDCs), dioxins, volatile organic compounds (VOCs), and other contaminants of emerging concerns (CECs), heavy metals, just to mention a few. POPs are among these contaminants that are more dangerous due to their biological and chemical properties in the environment (Ghosal et al., 2016). These toxic compounds mostly composed by carbon atoms adversely affect both human health and environment around the world due to their persistence for a long-time exposure in the aquatic environment. POPs are hence divided into sub-groups such as polychlorinated biphenyls, polynuclear aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-*p*-dioxins, among others (Wheatley, & Sadhra, 2010; Pereira, 2014). PAHs are ubiquitous POPs comprising a group of toxic chemical compounds together with their derivatives still being used to manufacture pesticides, plastics and azo dyes (Wang et al., 2009; Singh, Mondal, & Sharma, 2013; Mondal et al.,

2014). Their structures are made of two or more condensed pentacyclic and benzene rings attached in a clustered, angular or linear arrangement. They exhibit low water solubility and hydrophobicity properties, while some of their members are toxic compounds persistent to any decomposition process (Jinadasa, Monteau, & Morais, 2020; Manousi, & Zachariadis, 2020; Maswanganyi et al., 2021). However, they create serious concerns owing to their mutagenicity, genotoxicity, hepatotoxicity, and carcinogenicity on humans as well as the whole ecosystem (Reddy et al., 2013; Karam et al., 2014; Rezvani-Eivari et al., 2016; Maswanganyi et al., 2021). It is in that way approximately 16 PAHs have been categorized as emerging pollutants in the environment by the US Environmental Protection Agency and European Union (Sekar et al., 2014). In the environment, PAHs may originate from domestic burning (gas, wood, coal), incomplete combustion of cigarettes, fossil fuels, and industrial wastes, natural sources (decay of organic matter, volcanic eruptions, forest fires, etc.), and agricultural sources (pesticides). PAHs from industrial activities can reach watercourses through leachates from dumpsites, steel-making and plant coal mines (García-Martínez et al., 2018; Walaszek et al., 2018; Mojiri et al., 2019; Maswanganyi et al., 2021). However, due to all these effects, they need to be monitored, treated or completely degraded from different environmental matrices. The most traditional methods used for environmental matrix treatment include biological, chemical and physical techniques. The physical methods are sedimentation, coagulation, reverse osmosis, ion-exchange, electrodialysis, filtration, and flocculation. Biological treatments include enzymes and aerobic or anaerobic microorganisms, while chemical techniques prefer to use advanced oxidation processes (AOPs) (Soo et al., 2016; Gondal et al., 2016). The most traditional methods currently used to treat aquatic environments are biological and physical techniques due to their easy implementation and low maintenance and no pre- and post-treatment request. However, these techniques only convert the pollutants from liquid phase to solid phase. To get good results, sophisticated techniques must be employed. Regarding the AOPs, the most operative strategy is photocatalytic process using semiconductor photocatalysts. When a solid particle catalyzes a chemical process using an electromagnetic field as an energy source having a wavelength in the range of Ultraviolet-Visible-InfraRed radiation, it is called a photocatalyst. These solid particles are normally semiconductors that absorb UV and/or visible light and are photostable, inexpensive, biologically and chemically inert. Heterogeneous photocatalytic process employing semiconductors has attained noteworthy development from the time when Fujishima & Honda (1972) reported the use of TiO_2 electrodes for photoinduced water decomposition (Kasanen et al., 2011; Hashimoto et al., 2005). However, various semiconductors such as oxides (SnO_2 , CeO_2 , Fe_2O_3 , V_2O_5 , ZrO_2 , ZnO , TiO_2 , WO_3 , etc.), ferrites and sulphides (CdS , SnS , ZnS , etc.) have been successfully used in wastewater treatment. Photocatalytic process highly depends on oxidation reaction derived by irradiating the photocatalyst at ambient conditions (room temperature and normal pressure). Normally, the light sensitivity of semiconductors depends on their electronic structure and bandgap energy with valence band partially filled with electrons and vacant conduction band. Though, the immobilization of these nano-sized photocatalysts can eliminate costly and impractical post-treatment recovery of spent photocatalysts in largescale operations. The most commonly used anchoring media are cellulosic materials, metallic agents, ceramics, glass, zeolites, carbonaceous substances, clay, and polymers. The main factors responsible for the selection of suitable polymers for these catalysts are mechanical stability, low density, ease of availability, chemical inertness, and high durability. Common methods for immobilization of photocatalysts are cold plasma discharge, dip coating, electrophoretic deposition radio frequency magnetron sputtering, photoetching, polymer-assisted hydrothermal decomposition, spray pyrolysis, and solvent casting (Srikanth et al., 2017). Owing to their large surface area and high catalytic activity, nanoparticles (NPs) have been explored broadly in the field of photocatalytic degradation of PAHs (Dong et al., 2015). However, this review aimed at exploring different advances made in PNMs for photocatalytic decomposition of PAHs in environmental samples. It also explores their trends on the markets and in research and the current advances made on the understanding detoxification mechanisms and toxicological effects of PAHs in photocatalytic processes as a green alternative technique for environmental pollution control and remediation. It critically explores different ways to improve workflows for PNMs characterization and testing, and the emerging need for the analysis of PAHs. Finally, it provides insights into the understanding of how to set up and optimize manufacturing methods of PNMs while avoiding costly time traps that prevent getting the correct answer in addressing PAH-related environmental pollution problems.

1.1 Extraction Methods of PAHs from Environmental Samples

Due to their low concentrations in environmental samples, a preconcentration process is generally required for their determination. The most common extraction methods of PAHs from environmental samples are Soxhlet extraction and liquid-liquid extraction (Munyengabe et al., 2017), sorptive-based micro-extraction techniques [solid-phase micro-extraction, micro-extraction in packed sorbent and stir bar sorptive extraction] and solvent-based microextraction [single drop micro-extraction, membrane-mediated liquid-phase micro-extraction, dispersive liquid-liquid micro-extraction] have been developed for quantification of PAHs in food, environmental and biological samples (Jinadasa, Monteau, & Morais, 2020). Currently, there is a wide variety of sample preparation methods, including miniaturized extraction techniques (e.g.: magnetic solid-phase extraction, dispersive solid-phase extraction, fabric phase

sorptive extraction, stir bar sorptive extraction, etc.) and micro-extraction techniques (liquid-phase and solid-phase microextractions) (Manousi, & Zachariadis, 2020).

1.2 Nanocomposite Photocatalysts from Natural Polymers

In recent decades, the application of polymers for the treatment of environmental samples has become authentic. On their basis, ecological materials with various properties have been created such as films, sorbents, membranes, filters for nano- and ultra-filtration, and functional composite materials. Some biopolymer materials with nano-dispersed TiO₂ are used to improve the functional properties of nanocomposites and increase the photocatalytic activity of TiO₂. One of the prospective biopolymers for solving such tasks is chitosan (CS), which is the product of chitin deacetylation (Zhu et al., 2011). CS matrices present a high sorption capacity and are effective sorbents of such compounds as PAHs, dyes, heavy metal ions, etc. CS has a high ability to chemical modification due to the presence of reactive hydroxyl and amino groups. This allows one to select the different characteristics of polymeric sorbent according to the tasks (Tatarinov et al., 2021). CS is the most studied natural polymer to prepare different nanocomposites. The ZnO/SnO₂ quantum dot (3-5 nm in diameter) heterojunction immobilized on cross-linked CS films (ZnO/SnO₂/CS films) were successfully synthesized (Zhu et al., 2011; Wang, Wang, & Xiao, 2021). However, CS-based nanocomposites are more often used as absorbents. Kaolin is another commonly used natural material to form nanocomposites (Wang, Wang, & Xiao, 2021). Kaolin and chitosan are exploited by their solid matrix, polycationic and biodegradable properties in preparing nanocomposites. The photocatalytic properties come from semiconductor components and light irradiation. In other applications, pH adjustment, ultrasonic resources and H₂O₂ are required for applying or preparing nanocomposites (Wang, Wang, & Xiao, 2021). Other used polymer materials include polyethersulfone, polysulfone, cellulose acetate and nitrates, polypropylene, polytetrafluoroethylene, polyimide, polyvinylidene fluoride, polyvinyl alcohol and polyacrylonitrile are the most extensively used organic membrane materials. Polymer nanocomposites have many advantages: (1) they exhibit excellent flammability properties and increased biodegradability of biodegradable polymers, (2) their barrier properties are improved compared with the neat polymer, (3) their mechanical and thermal properties are potentially superior, and (4) they are lighter than conventional composites because high degrees of stiffness and strength are realized with far less high-density material.

2. Preparation and Characterization of Polymer Nanocomposite Materials

PNMs are divided into inorganic-inorganic or organic-organic nanocomposites as well as their hybrid materials (inorganic in the organic or organic in inorganic matrix). Different preparation methods of polymer nanocomposites and their characterization techniques are illustrated in the following sections. The best method is determined by the relation and route to the polymer-nanoparticle pair. The distribution and dispersion of nanoparticles in the polymer matrix is the key to obtaining new materials with the synergism of properties of the compound. This synergism depends on how strong the intermolecular interaction between the nanoparticles and polymer matrix is. However, to generate PNs, the following important information on the components need to be considered to understand the behaviour of the new materials. These include polymer semi-crystallinity, polymer mass and chemical structure, chemical solubility and thermal stability, chemical structure, and nanoparticle surface area and dispersion (Tavares, da Silva, da Silva, & de Menezes, 2017).

2.1 Synthesis of Polymer Nanocomposite Materials

The most known methods for synthesizing PNM are solution mixing or dispersion, *in-situ* polymerization, direct compounding, melt extrusion or melt blending and intercalation method (Tavares, da Silva, da Silva, & de Menezes, 2017; Jawaid, & Khan, 2018; Das et al., 2020). Other several techniques are self-assembly, electrospinning, emulsion polymerization, phase separation, and template synthesis (Olatunji et al., 2018; Jawaid, & Khan, 2018; Sekar et al., 2018). Each method has its particularity. But the essence of all PNs, irrespective of the process, is the final morphology, which depends on PN interactions that will promote good distribution and dispersion of the nanoparticles in the polymer matrix. The final morphology also depends on the process of obtaining the PN. However, the most widely used method is *in-situ* polymerization, which is normally suitable for polymers that cannot be produced safely or economically by solution methods because the solvents used to dissolve them are highly toxic. This method promotes good distribution and dispersion of the nanoparticles in the polymer matrix (Kickelbick, 2007; Tavares, da Silva, da Silva, & de Menezes, 2017). Some important aspects of this method should be pointed out. The first is related to the cost of the process, which can require some changes compared to the normal polymer synthesis. Care is also necessary to choose the most appropriate catalyst. The apparatus used can be the same for polymerization without nanoparticles. The best improvements made in the development of PNM are in the combination of inorganic materials with polymer matrices.

2.2 Characterization Techniques for the Polymeric Photocatalytic Nanocomposites

Characterization plays a big role in chemistry where the structure and properties of the material have to be identified and compared with the literature. However, like other solid materials, the surface morphology, density and core-shell

structure of the prepared nanocomposites can be determined using field-emission scanning electron microscope coupled to an electron dispersive spectroscopy detector and a high-resolution transmission electron microscopy (TEM) (Di Mauro et al., 2017; Alizadeh, Delnavaz, & Shakeri, 2018; Rebekah et al., 2020; Patiño-Ruiz et al., 2020; Solano et al., 2021). The physical and chemical characteristics, thermal stability and crystallinity of the PNMs can be explored using thermogravimetric analyzer and an X-ray powder diffraction (XRD) (Bhaumik, Setshedi, Maity, & Onyango, 2013; Alizadeh, Delnavaz, & Shakeri, 2018). Their pore volume, pore diameter and surface area can also be identified using Brunauer-Emmett-Teller (BET) (Patiño-Ruiz et al., 2020) while functional groups are normally identified by Fourier-transform infrared spectroscopy (FTIR) (Rebekah et al., 2020; Patiño-Ruiz et al., 2020; Solano et al., 2021). They can also be characterized using atomic force microscope and small-angle X-ray scattering (Gestranius et al., 2020), Rheometric technique, Raman spectroscopy (Solano et al., 2021), thermomechanical, dynamic modulus analysis (DMA), differential scanning calorimeter (DSC) (Ray, & Okamoto, 2003), and X-ray photoelectron spectroscopy (Abinaya et al., 2019). A low-field Nuclear Magnetic Resonance relaxometry, a characterization tool that can efficiently evaluate nanoparticles' distribution and dispersion in the polymer matrix, according to the preparation method has also been used (Tavares, da Silva, da Silva, & de Menezes, 2017).

3. Application of PNMs for the Photocatalytic Decomposition of PAHs in Environmental Samples

AOPs, such as ultrasonication and photocatalytic degradation (Szreniawa-Sztajnert et al., 2013; Levchuk et al., 2014; Petronella et al., 2017) are evolving as promising methods for efficient sequestration of less biodegradable and chemically stable organic pollutants (Aljuboury et al., 2016; Bokare and Choi, 2014; Shahidi et al., 2015). AOPs involve the production of hydroxyl radicals which attack organic compounds and convert them into less toxic products like H₂O, CO₂ and other inorganic compounds (Neyens, & Baeyens, 2003; Oturan, & Aaron, 2014). Photocatalytic degradation of these organic pollutants has recently drawn much research attention (Romão, & Mul, 2016; Qi et al., 2016). In most photocatalytic degradation processes, TiO₂ powder with its strong oxidizing tendency acts as a photocatalyst (Barreca et al., 2015; León et al., 2015). PAHs are environmental pollutants having detrimental effects on living beings up to the genetic level (Boström et al., 2002). These compounds easily get absorbed in the gastrointestinal tract of mammals and are distributed in different body parts due to their high lipid solubility (Cerniglia, 1984). Further, they get oxidized in the presence of the cytochrome P450-mediated mixed-function oxidase system, resulting in the formation of epoxides or phenols. Further degradation of these compounds results in the formation of sulphates, glucuronides or glutathione conjugates. Moreover, epoxides may also get metabolized into dihydrodiols, which leads to the formation of either diol-epoxides or conjugation to form soluble detoxification products after their oxidation. Naphthalene is a common micropollutant in potable water. It covalently binds to molecules in kidney, liver and lung tissues (Wang et al., 2015; Wincent et al., 2015). It is also an inhibitor of mitochondrial respiration. Acute naphthalene poisoning in humans can lead to nephrotoxicity and haemolytic anaemia. In addition, it also causes dermal and ophthalmological changes on prolonged exposure (Falahaatpisheh et al., 2001). Phenanthrene is a mild allergen and a photosensitizer of human skin. It is also mutagenic to bacterial systems under specific conditions. It induces sister chromatid exchanges and inhibits gap junctional intercellular communication (Weis et al. 1998). Most of the hydrocarbons also affect aquatic organisms adversely on metabolic activities (Akhbarizadeh et al., 2016; Booij et al., 2016). Thus, the degradation of various petrochemical wastes is imperative for the conservation of human as well as environmental health. In the present review, authors tried to gather the information available for the degradation of photocatalysts and the possible mechanisms involved. However, the information on the application of PNMs for the photocatalytic degradation of PAHs in environmental samples is still lacking. The only available literature on their application is for heavy metal removal (Singh, Rai, & Agarwal, 2014), computer housings, building materials, car interiors, and flame retardancy (Ray, 2014; de Oliveira, & Beatrice, 2018), degradation of dyes, pharmaceuticals, fabrication and design of new materials for biomedical applications (Abinaya et al., 2019; de Oliveira, & Beatrice, 2018), packaging industry, and in food packaging to improve shelf-life and food quality (de Oliveira, & Beatrice, 2018), among others.

4. Detecting Different Fragments Resulting from the Degradation of PAHs

The determination of derivatives or fragments obtained after any degradation is normally performed using methods that are also used to determine the concentrations of PAHs, parent phenols and other hydroxylated- or alkylated-PAHs (Morueco, 2018). Like other POPs, emerging contaminants of concerns, PAHs and their derivatives are normally analyzed using a gas chromatography-mass spectrometry (GC-MS) (Munyengabe, 2016; Diao et al., 2019; Rani, & Shanker, 2019c; Patiño-Ruiz et al., 2020), high-performance liquid chromatography (HPLC) (Das, Mukherjee, & Sen, 2008), liquid chromatography-quadrupole time-of-flight mass spectrometry (Ye et al., 2019), HPLC with a fluorescence detector (Vela et al., 2012), GC-MS/tandem mass spectrometry (GC-MS/MS) (Sun et al., 2020), solid-phase luminescence (SPL) (Tatarinov et al., 2021), and liquid chromatography-tandem mass spectrometry (Shang et al., 2019).

5. Trends in Research and the Markets of PNMs

PNs were first introduced in the market as clay/nylon-6 nanocomposites in 1991 for producing engine and timing belt covers. The main driving factor for the use of PN enabled parts is their excellent physio-chemical and mechanical properties. These properties offer a reduction in the weight of the vehicle, reduction in the emission of CO₂, increased efficiency of the engine leading to low fuel consumption and safety, and comfort owing to the high performance of the vehicle. Due to excellent nanoparticle dispersion tendencies, polymer-based nanocomposites also exhibit a significantly enhanced packaging characteristic. Furthermore, the feasibility of the inclusion of biologically-active additives has shown the great potential of rendering enhanced functional properties to the end product. Hence, PN exhibiting bio-functional propensities have revealed a broad potential for application as packaging materials in the functional food packaging industry. This is due to accruable improvements in properties such as enhancements in modulus and strength, reduced gas permeability, and increment in resistance to water (Idumah, Hassan, & Ihuoma, 2019). The application of PN in packaging materials in agricultural, industrial and food products is a superior alternative to traditional packaging materials such as paper, metals and glass due to their flexibility, functionalization and minimal cost (Wróblewska-Krepsztul et al., 2018). However, usage of these materials has been hindered due to their inferior mechanical and barrier behaviours, which are susceptible to improvement through the inclusion of functionalized reinforcing nano- or macro-fillers. Furthermore, most reinforced materials exhibit inferior matrix-filler interfacial interactions, which are enhanced with reducing filler dimensions. Recently, emerging innovations in nanostructured PNMs and electrical sensors, their current applications and future outlook as food, industrial and agricultural packaging materials are also herewith elucidated (Idumah et al., 2019). The global polymer nanocomposite market (GPNM) in this review paper is segmented based on type, application, and geography. It analyses the current market trends of polymer nanocomposite-based products in different geographies and suggests future growth opportunities by analyzing government policies and regulations, thereby further increasing consumer acceptance in that particular region. Their type includes nano-clay, carbon nanotube, ceramic, metal oxides and others, where carbon nanotube accounted for the largest market in 2015 and is ready to maintain this trend for the forecasted period. Their geographical trend involves the following countries such as Latin America, the Middle East and African (LAMEA) region and North America, Europe, Asia-pacific, where the LAMEA has registered the highest compound annual growth rate (CAGR) 125% during 2016-2022. By their application, PNMs are intensively applied in automotive, construction, packaging, electronics, electric, aerospace, energy, defense, and others, where the packaging application segment accounted for around two-seventh of the GPNM revenue in 2015 (Shukla, 2016) and it was expected to reach \$66.876 million by 2022.

6. Mechanisms and Toxicological Effects of PAHs of Their Degradation in Photocatalytic Processes

Most of the PAHs are harmful to human health even in small amounts and also present bio-accumulative properties. It is well-known that when the maximum concentration of a substance of the PAH group in the environmental matrix is exceeded, the risk of developing cancer significantly increases (Kim, Jahan, Kabir, & Brown, 2013). Therefore, a prospective direction of modern research is the development of techniques for the oxidation of PAHs (Tatarinov, Sokolnikova, & Myslitskaya, 2021). PAHs can expose short- and long-term effects on human health depending on the concentration of PAHs during exposure, the route of exposure, for example via ingestion, skin contact, or inhalation, length time of exposure, and the toxicity of the PAHs (ACGIH, 2005).

7. PNMs for Photocatalytic Detoxification of PAHs in Environmental Matrices

PAHs are mainly available in soil, air, water, sludge, food, and sediment in different concentration levels due to the substrates they are in contact with (Wu, Sun, & Li, 2019). Thus, their screening and removal processes from these environmental matrices are automatically different. They can be removed from aquatic environments using conventional methods as well as new emerging technologies. The existing treatment techniques include chemical oxidation, photocatalytic degradation, adsorption (using adsorbents such as polymers, nanocomposites, geo-sorbents, silica, zeolites, graphene-based materials, and mesoporous biomass derivatives), bioremediation, and extraction (Juhasz, & Naidu, 2000; Nguyen et al., 2020; Adeola, & Forbes, 2021). Enhanced remediation using electrokinetic remediation, integrated approaches, advanced phytoremediation, green nano-remediation, and biocatalysts hold great potential and are still at the developmental stage (Adeola, & Forbes, 2021). Many research have been done on the photocatalytic degradation of PAHs in environmental samples (Lin, & Valsaraj, 2003; Zhang, Li, Gong, & Li, 2008; El-Saeid et al., 2015; Gupta, & Gupta, 2015; Liu et al., 2016; Marqués et al., 2016; Zhao et al., 2016; Liu et al., 2017; Yang et al., 2017; Zhao et al., 2017; Fu et al., 2018; Gbadamosi, 2019; Martinez-Vargas et al., 2019; Rani, & Shanker, 2019b; Nguyen et al., 2020; Xiaoping, Qiaoshan, & Jinhong, 2020; Sohara et al., 2021). However, most of the work done was concerning the degradation of anthraquinone, anthracene and phenanthrene using only photocatalysts under UV light due to their damaging effects on the environment, model and prevalence for scientific investigations (Diao et al., 2019; Martinez-Vargas et al., 2019; Rani, & Shanker, 2019a; Chauhan et al., 2021). Ag₃PO₄, ZnO-, MHCFS- and TiO₂-based and others have received important attention for photo-degradation of PAHs (Nguyen et al., 2020). For example, the

photo-degradation of phenanthrene leads to the formation of 9,10-phenanthrenequinone, which is more harmful to humans than phenanthrene itself (Wang et al., 2009; Chauhan et al., 2021). However, conventional chemical and physical removal methods simply transfer the PAHs into another form without decomposing them into harmful compounds (Rani, & Shanker, 2019b). The combination of metals or amalgamation of bimetallic oxides as an efficient photocatalyst demonstrated its propitiousness for their degradation from water resources (Chauhan et al., 2021). Most of these methods may present disadvantages and advantages (Qiao et al., 2014; Alegbeleye, Opeolu, & Jackson, 2017; Zango et al., 2020). The most concerned and applied are adsorption, photocatalytic degradation and chemical oxidation, among others. Recently, there has been an increasing interest in developing sorbents by incorporating inorganic (metal and metal oxides) into organic polymers aiming at fusing their properties in one material. In the hybrid nanocomposites, the polymer matrix can be natural or synthetic and the nanofiller or photocatalyst is usually a metal or metal oxide. The nanofillers facilitate the polymer strengthening or the condition of a supplementary interaction mechanism with the metal ions. The addition of low contents of these photocatalysts into the polymers can lead to improvements in their barrier, thermal, flammability and mechanical properties without affecting their processability. They received important attention due to the ease of production, flexibility and lightweight (de Oliveira, & Beatrice, 2018). The most applied polymer nanocomposite materials for degradation of PAHs in environmental matrices are chitosan beads modified with TiO₂ and iron oxide (FeO) nanoparticles (Chitosan-FeO/TiO₂) (Patiño-Ruiz, et al., 2020) and magnetic metal oxides-chitosan nanocomposites (ZnFe₂O₄-Chitosan) under natural sunlight (Rani, & Shanker, 2019c). Thiourea-magnetite-TiO₂ modified-chitosan beads (Chitosan-T-FeO-TiO₂) (Solano et al., 2021), graphene oxide silver phosphate (GO/Ag₃PO₄) and magnetic/graphene/chitosan nanocomposite (MG-Chitosan) (Rebekah et al., 2020) as shown in Table 1. Other polymer nanocomposite materials found in the literature are poly-aminated Fe₃O₄@chitosan core-shell magnetic nanoparticles (Fu et al., 2020), cross-linked magnetic ethylenediaminetetraacetic acid (EDTA)/TiO₂/chitosan (Alizadeh, Delnavaz, & Shakeri, 2018), and organic montmorillonite sodium alginate (Dai et al., 2020). These studies indicated that the immobilization of FeO nanoparticles within the chitosan structure enhanced the stability features of these nanoparticles against oxidative and acidic conditions. Chitosan-FeO/TiO₂ showed the highest pore size and BET surface area that are attributed to the presence of nanoparticles, which increased the surface area and promoted the formation of porosity (Patiño-Ruiz et al., 2020).

Table 1. Available Polymer nanocomposite materials, their obtained parameters and performances

Parameters and references	Polymeric nanocomposite materials				
	GO/Ag ₃ PO ₄	ZnFe ₂ O ₄ -Chitosan	Chitosan-T-FeO/TiO ₂	MGO-Chitosan	Chitosan-FeO/TiO ₂
Pore volume (cm ³ /g)	-	-	0.000147	-	4.60×10 ⁻²
Pore size (nm)	-	-	10.20	-	6.80
BET surface area (m ² /g)	-	80.11	1.58	-	27.10
Optimum pH	-	Neutral pH	6.50	2.00	8.02
Adsorption type	-	Langmuir model	Freundlich model	Freundlich model	Langmuir and Freundlich models
Adsorption capacity (mg/g)	-	1.50	133.69	169.49	33.10
Degradation efficiency (%)	49.7-100	92-95	-	-	90.00
Reusability performance of the catalyst (%)	5 times: 44.6-95.2	1 st cycle: 95; 10 th cycle: 91	-	-	-
Order model and kinetics	Pseudo-first-order	First-order	Pseudo-second order	Pseudo-second order	Pseudo-second order
Material	-	Mesoporous	Mesoporous	Nano-porous	Mesoporous
Pollutant	Phenanthrene, pyrene and naphthalene	Naphthalene	Naphthalene	2-Naphthol	Anthracene and phenanthrene
Aquatic environment	Simulated wastewater	Synthetic wastewater	Industrial effluents	Aqueous solution	Seawater
References	Yang et al., 2017	Rani, & Shanker, 2019c	Solano et al., 2021	Rebekah et al., 2020	Patiño-Ruiz et al., 2020

This available literature revealed that a small number of PNMs have been used to photodegrade PAHs in synthetic wastewater, aqueous solution, industrial effluents and seawater samples. From table 1, phenanthrene, anthracene, naphthalene and 2-naphthol as low molecular weight PAHs were photodegraded using these polymer nanocomposites under natural light. Only one research was conducted to evaluate the photo-degradation of pyrene as high molecular

weight PAH which is among the most toxic PAHs to the environment due to their low solubility in water (Sherafatmand, 2016). However, Kot-Wasik et al. (2004) and Wang et al. (2019) highly recommended the application of photocatalytic degradation on high molecular weight PAHs as a suitable method because of its economical, high efficiency and friendly to the environment. The oxidation products of PAHs produced by a photooxidation process are more soluble in water than the parent PAHs (Kot-Wasik et al., 2004). Table 1 also indicates that only graphene oxide- and chitosan-based polymer nanocomposite materials have been employed to photodegrade these kinds of PAHs in water samples. This was because they only need sunlight for action, and they are stable, recyclable, reusable and inexpensive materials. Chitosan is normally produced by deacetylation of chitin and is one of the most abundant biopolymers in nature, with its unique properties such as biocompatibility, solubility in a wide range of organic solvents, biodegradability, film-forming ability, non-toxicity, hydrophilicity, crystallinity, adsorbing nature, and chelation metal ions by hydroxyl and amino functional groups (Muzzarelli et al., 2012; Thakur, & Thakur, 2014; Muxika et al., 2017; Alizadeh, Delnavaz, & Shakeri, 2018). Most of the polymer nanocomposite materials found in the literature (Table 1) were based on the iron oxide or magnetite incorporation which generates reactive oxygen species via AOPs (Hassani et al., 2018; Gonçalves et al., 2019; Solano et al., 2020). Another finding was no study was conducted on the photodegradation of PAHs in sediment and soil which are their main sink in the environment.

8. Conclusion and Perspectives

This review paper focuses on advances made in PNMs for the photocatalytic decomposition of PAHs in environmental samples. It further explored some trends in research and the markets. The review also presented the current progress made on the understanding of detoxification mechanisms and toxicological effects of PAHs in photocatalytic processes as a green alternative technique for environmental pollution control and remediation. It critically explored different ways to improve workflows for PNMs characterization and testing, and the emerging need for the analysis of PAHs. It finally provided insights into the understanding of how to set up and optimize manufacturing methods of PNMs while avoiding costly time traps that prevent getting the correct answer in addressing PAH-related environmental pollution problems. The paper gives an origin, a brief account of the chemistry and photocatalytic transformation of PAHs, highlighting their bioaccumulation in environmental matrices. The paper finally recommends the application of PNMs for the treatment of PAHs-contaminated sediment, soils and water especially the high molecular weight PAH ones as they showed to have good degradation efficiency, high adsorption capacity and are reusable several times.

Acknowledgments

The authors would like to thank South African National Foundation (NRF) [grant No.: SRUG190420431876] for the financial support received by the postdoctoral fellow. The authors also declare that there is no conflict of interest regarding the publication of this review paper.

References

- Abinaya, M., Rajakumaran, R., Chen, S. M., Karthik, R., & Muthuraj, V. (2019). *In-situ* synthesis, characterization, and catalytic performance of polypyrrole polymer-incorporated Ag₂MoO₄ nanocomposite for detection and degradation of environmental pollutants and pharmaceutical drugs. *ACS Applied Materials & Interfaces*, 11(41), 38321-38335. <https://doi.org/10.1021/acsami.9b13682>
- Adeola, A. O., & Forbes, P. B. (2021). Advances in water treatment technologies for removal of polycyclic aromatic hydrocarbons: Existing concepts, emerging trends, and prospects. *Water Environment Research*, 93(3), 343-359. <https://doi.org/10.1002/wer.1420>
- Akhbarizadeh, R., Moore, F., Keshavarzi, B., & Moeinpour, A. (2016). Aliphatic and polycyclic aromatic hydrocarbons risk assessment in coastal water and sediments of Khark Island, SW Iran. *Marine Pollution Bulletin*, 108(1-2), 33-45. <https://doi.org/10.1016/j.marpolbul.2016.05.004>
- Alegbeleye, O. O., Opeolu, B. O., & Jackson, V. A. (2017). Polycyclic aromatic hydrocarbons: a critical review of environmental occurrence and bioremediation. *Environmental Management*, 60(4), 758-783. <https://doi.org/10.1007/s00267-017-0896-2>
- Alizadeh, B., Delnavaz, M., & Shakeri, A. (2018). Removal of Cd (II) and phenol using novel cross-linked magnetic EDTA/chitosan/TiO₂ nanocomposite. *Carbohydrate Polymers*, 181, 675-683. <https://doi.org/10.1016/j.carbpol.2017.11.095>
- Aljuboury, D. A. D. A., Palaniandy, P., Abdul Aziz, H. B., Feroz, S., & Abu Amr, S. S. (2016). Evaluating photo-degradation of COD and TOC in petroleum refinery wastewater by using TiO₂/ZnO photo-catalyst. *Water Science and Technology*, 74(6), 1312-1325. <https://doi.org/10.2166/wst.2016.293>
- American Conference of Governmental Industrial Hygienists (ACGIH). (2005). Available online at:

- <https://www.acgih.org/polycyclic-aromatic-hydrocarbons-pahs/>. Accessed on 17th January 2023.
- Barreca, D., Carraro, G., Gasparotto, A., Maccato, C., Warwick, M. E., Kaunisto, K., & Mathur, S. (2015). Fe₂O₃-TiO₂ nano-heterostructure photoanodes for highly efficient solar water oxidation. *Advanced Materials Interfaces*, 2(17), 1500313. <https://doi.org/10.1002/admi.201500313>
- Bokare, A. D., & Choi, W. (2014). Review of iron-free Fenton-like systems for activating H₂O₂ in advanced oxidation processes. *Journal of Hazardous Materials*, 275, 121-135. <https://doi.org/10.1016/j.jhazmat.2014.04.054>
- Booij, K., Robinson, C. D., Burgess, R. M., Mayer, P., Roberts, C. A., Ahrens, L., & Whitehouse, P. (2016). Passive sampling in regulatory chemical monitoring of nonpolar organic compounds in the aquatic environment. *Environmental Science & Technology*, 50(1), 3-17. <https://doi.org/10.1021/acs.est.5b04050>
- Boström, C. E., Gerde, P., Hanberg, A., Jernström, B., Johansson, C., Kyrklund, T., & Westerholm, R. (2002). Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air. *Environmental Health Perspectives*, 110(suppl 3), 451-488. <https://doi.org/10.1289/ehp.110-1241197>
- Cerniglia, C. E. (1984). Microbial metabolism of polycyclic aromatic hydrocarbons. *Advances in applied microbiology*, 30, 31-71. [https://doi.org/10.1016/S0065-2164\(08\)70052-2](https://doi.org/10.1016/S0065-2164(08)70052-2)
- Chauhan, H. A., Rafatullah, M., Ahmed Ali, K., Siddiqui, M. R., Khan, M. A., & Alshareef, S. A. (2021). Metal-based nanocomposite materials for efficient photocatalytic degradation of phenanthrene from aqueous solutions. *Polymers*, 13(14), 2374. <https://doi.org/10.3390/polym13142374>
- de Oliveira, A. D., & Beatrice, C. A. G. (2018). Polymer nanocomposites with different types of nanofiller. *Nanocomposites-Recent Evolutions*, 103-104. <https://doi.org/10.5772/intechopen.81329>
- Diao, Z. H., Pu, S. Y., Qian, W., Liang, S., Kong, L. J., Xia, D. H., & Yang, J. W. (2019). Photocatalytic removal of phenanthrene and algae by a novel Ca-Ag₃PO₄ composite under visible light: Reactivity and coexisting effect. *Chemosphere*, 221, 511-518. <https://doi.org/10.1016/j.chemosphere.2019.01.044>
- Dong, D., Li, P., Li, X., Xu, C., Gong, D., Zhang, Y., & Li, P. (2010). Photocatalytic degradation of phenanthrene and pyrene on soil surfaces in the presence of nanometer rutile TiO₂ under UV-irradiation. *Chemical Engineering Journal*, 158(3), 378-383. <https://doi.org/10.1016/j.chemosphere.2019.01.078>
- El-Saeid, M. H., Al-Turki, A. M., Nadeem, M. E., Hassanin, A. S., & Al-Wabel, M. I. (2015). Photolysis degradation of polyaromatic hydrocarbons (PAHs) on surface sandy soil. *Environmental Science and Pollution Research*, 22(13), 9603-9616. <https://doi.org/10.1007/s11356-015-4082-x>
- Falahatpisheh, M. H., Donnelly, K. C., & Ramos, K. S. (2001). Antagonistic interactions among nephrotoxic polycyclic aromatic hydrocarbons. *Journal of Toxicology and Environmental Health Part A*, 62(7), 543-560. <https://doi.org/10.1080/152873901300007833>
- Fu, J., Kyzas, G. Z., Cai, Z., Deliyanni, E. A., Liu, W., & Zhao, D. (2018). Photocatalytic degradation of phenanthrene by graphite oxide-TiO₂-Sr(OH)₂/SrCO₃ nanocomposite under solar irradiation: Effects of water quality parameters and predictive modelling. *Chemical Engineering Journal*, 335, 290-300. <https://doi.org/10.1016/j.cej.2017.10.163>
- Fujishima, A., & Honda, K. (1972). Electrochemical photolysis of water at a semiconductor electrode. *nature*, 238(5358), 37-38. <https://doi.org/10.1038/238037a0>
- García-Martínez, M. J., Ortega, M. F., Bolonio, D., Llamas, J. F., & Canoira, L. (2018). Leaching of polycyclic aromatic hydrocarbons (PAHs) from coal dumps reclaimed with apple trees: a mechanistic insight. *Environmental Geochemistry and Health*, 40(6), 2695-2706. <https://doi.org/10.1007/s10653-018-0133-9>
- Gbadamosi, T. G. (2019). *Development of a novel photocatalytic reactor for the treatment of polycyclic aromatic hydrocarbons* (Doctoral dissertation).
- Gestranis, M., Otsuka, I., Halila, S., Hermida-Merino, D., Solano, E., Borsali, R., & Tammelin, T. (2020). High-resolution patterned biobased thin films via self-assembled carbohydrate block copolymers and nanocellulose. *Advanced Materials Interfaces*, 7(7), 1901737. <https://doi.org/10.1002/admi.201901737>
- Ghosal, D., Ghosh, S., Dutta, T. K., & Ahn, Y. (2016). The current state of knowledge in microbial degradation of polycyclic aromatic hydrocarbons (PAHs): a review. *Frontiers in Microbiology*, 7, 1369. <https://doi.org/10.3389/fmicb.2016.01369>
- Gonçalves, R. G. L., Lopes, P. A., Resende, J. A., Pinto, F. G., Tronto, J., Guerreiro, M. C., & Neto, J. L. (2019). Performance of magnetite/layered double hydroxide composite for dye removal via adsorption, Fenton and photo-Fenton processes. *Applied Clay Science*, 179, 105152. <https://doi.org/10.1016/j.clay.2019.105152>

- Gondal, M. A., Suliman, M. A., Dastageer, M. A., Chuah, G. K., Basheer, C., Yang, D., & Suwaiyan, A. (2016). Visible light photocatalytic degradation of herbicide (Atrazine) using surface plasmon resonance induced in mesoporous Ag-WO₃/SBA-15 composite. *Journal of Molecular Catalysis A: Chemical*, *425*, 208-216.
- Gupta, H., & Gupta, B. (2015). Photocatalytic degradation of polycyclic aromatic hydrocarbon benzo[a]pyrene by iron oxides and identification of degradation products. *Chemosphere*, *138*, 924-931. <https://doi.org/10.1016/j.chemosphere.2014.12.028>
- Hashimoto, K., Irie, H., & Fujishima, A. (2005). TiO₂ photocatalysis: a historical overview and future prospects. *Japanese Journal of Applied Physics*, *44*(12R), 8269. <https://doi.org/10.1016/j.jap.2005.11.029>
- Hassani, A., Karaca, M., Karaca, S., Khataee, A., Açıışlı, Ö., & Yılmaz, B. (2018). Preparation of magnetite nanoparticles by high-energy planetary ball mill and its application for ciprofloxacin degradation through heterogeneous Fenton process. *Journal of Environmental Management*, *211*, 53-62. <https://doi.org/10.1016/j.jenvman.2018.01.014>
- Idumah, C. I., Hassan, A., & Ihuoma, D. E. (2019). Recently emerging trends in polymer nanocomposites packaging materials. *Polymer-Plastics Technology and Materials*, *58*(10), 1054-1109. <https://doi.org/10.1080/03602559.2018.1542718>
- Idumah, C. I., Zurina, M., Ogbu, J., Ndem, J. U., & Igba, E. C. (2019). A review on innovations in polymeric nanocomposite packaging materials and electrical sensors for food and agriculture. *Composite Interfaces*. <https://doi.org/10.1080/09276440.2019.1600972>
- Jawaid, M., & Khan, M. M. (2018). *Polymer-based Nanocomposites for Energy and Environmental Applications*. Woodhead Publishing.
- Jiménez, A., Vargas, M., & Chiralt, A. (2016). Antimicrobial nanocomposites for food packaging applications: novel approaches. *Novel Approaches of Nanotechnology in Food*, 347-386. <https://doi.org/10.1016/B978-0-12-804308-0.00011-X>
- Jinadasa, B. K. K., Monteau, F., & Morais, S. (2020). Critical review of micro-extraction techniques used in the determination of polycyclic aromatic hydrocarbons in biological, environmental and food samples. *Food Additives & Contaminants: Part A*, *37*(6), 1004-1026. <https://doi.org/10.1080/19440049.2020.1733103>
- Juhasz, A. L., & Naidu, R. (2000). Bioremediation of high molecular weight polycyclic aromatic hydrocarbons: a review of the microbial degradation of benzo[a]pyrene. *International Biodeterioration & Biodegradation*, *45*(1-2), 57-88. [https://doi.org/10.1016/S09648305\(00\)00052-4](https://doi.org/10.1016/S09648305(00)00052-4)
- Karam, F. F., Hussein, F. H., Baqir, S. J., Halbus, A. F., Dillert, R., & Bahnemann, D. (2014). Photocatalytic degradation of anthracene in closed system reactor. *International Journal of Photoenergy*, *2014*.
- Kasanen, J., Salstela, J., Suvanto, M., & Pakkanen, T. T. (2011). Photocatalytic degradation of methylene blue in water solution by multilayer TiO₂ coating on HDPE. *Applied Surface Science*, *258*(5), 1738-1743. <https://doi.org/10.1016/j.apsusc.2011.10.028>
- Khan, F., Zahid, M., Hanif, M. A., Tabasum, A., Mushtaq, F., Noreen, S., & Mansha, A. (2021). Photocatalytic polymeric composites for wastewater treatment. In *Aquananotechnology* (pp. 457-480). Elsevier. <https://doi.org/10.1016/B978-0-12-821141-0.00005-7>
- Kickelbick, G. (2007). *Hybrid materials: synthesis, characterization, and applications*. John Wiley & Sons.
- Kim, K. H., Jahan, S. A., Kabir, E., & Brown, R. J. (2013). A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects. *Environment International*, *60*, 71-80. <https://doi.org/10.1016/j.envint.2013.07.019>
- Kot-Wasik, A., Dąbrowska, D., & Namieśnik, J. (2004). Photodegradation and biodegradation study of benzo(a)pyrene in different liquid media. *Journal of Photochemistry and Photobiology A: Chemistry*, *168*(1-2), 109-115. <https://doi.org/10.1016/j.jphotochem.2004.05.023>
- León, D. E., Zúñiga-Benítez, H., Peñuela, G. A., & Mansilla, H. D. (2017). Photocatalytic removal of the antibiotic cefotaxime on TiO₂ and ZnO suspensions under simulated sunlight radiation. *Water, Air, & Soil Pollution*, *228*, 1-12. <https://doi.org/10.1007/s11270-017-3557-4>
- Levchuk, I., Bhatnagar, A., & Sillanpää, M. (2014). Overview of technologies for removal of methyl tert-butyl ether (MTBE) from water. *Science of the Total Environment*, *476*, 415-433. <https://doi.org/10.1016/j.scitotenv.2014.01.037>

- Lima, E. C. (2018). Removal of emerging contaminants from the environment by adsorption. *Ecotoxicology and Environmental Safety*, 150, 1-17. <https://doi.org/10.1016/j.ecoenv.2017.12.026>
- Lin, H. F., & Valsaraj, K. T. (2003). A titania thin film annular photocatalytic reactor for the degradation of polycyclic aromatic hydrocarbons in dilute water streams. *Journal of Hazardous Materials*, 99(2), 203-219. [https://doi.org/10.1016/S0304-3894\(03\)00060-8](https://doi.org/10.1016/S0304-3894(03)00060-8)
- Liu, B., Chen, B., Zhang, B. Y., Jing, L., Zhang, H., & Lee, K. (2016). Photocatalytic degradation of polycyclic aromatic hydrocarbons in offshore produced water: effects of water matrix. *Journal of Environmental Engineering*, 142(11), 04016054. [https://doi.org/10.1061/\(ASCE\)EE.1943-7870.0001135](https://doi.org/10.1061/(ASCE)EE.1943-7870.0001135)
- Liu, B., Chen, B., Zhang, B., Zheng, J., & Jing, L. (2017). Toxicity and biodegradability study on the enhanced photocatalytic oxidation of polycyclic aromatic hydrocarbons in offshore produced water. In *Canadian Society of Civil Engineering Annual General Conference, Vancouver, Canada*. https://www.csce.ca/elf/apps/CONFERENCEVIEWER/conferences/2017/pdfs/ENV/FinalPaper_862.pdf
- Mahmoodi, N. M., & Mokhtari-Shourijeh, Z. (2015). Preparation of PVA-chitosan blend nanofiber and its dye removal ability from coloured wastewater. *Fibers and Polymers*, 16(9), 1861-1869. <https://doi.org/10.1007/s12221-015-5371-1>
- Manousi, N., & Zachariadis, G. A. (2020). Recent advances in the extraction of polycyclic aromatic hydrocarbons from environmental samples. *Molecules*, 25(9), 2182. <https://doi.org/10.3390/molecules25092182>
- Marquès, M., Mari, M., Audí-Miró, C., Sierra, J., Soler, A., Nadal, M., & Domingo, J. L. (2016). Photodegradation of polycyclic aromatic hydrocarbons in soils under a climate change base scenario. *Chemosphere*, 148, 495-503. <https://doi.org/10.1016/j.chemosphere.2016.01.069>
- Maswanganyi, S., Gusain, R., Kumar, N., Fosso-Kankeu, E., Waanders, F. B., & Ray, S. S. (2021). Bismuth molybdate nanoplates supported on reduced graphene oxide: an effective nanocomposite for the removal of naphthalene via adsorption-photodegradation. *ACS Omega*, 6(26), 16783-16794. <https://doi.org/10.1021/acsomega.1c01296>
- Mojiri, A., Zhou, J. L., Ohashi, A., Ozaki, N., & Kindaichi, T. (2019). Comprehensive review of polycyclic aromatic hydrocarbons in water sources, their effects and treatments. *Science of the Total Environment*, 696, 133971. <https://doi.org/10.1016/j.scitotenv.2019.133971>
- Mondal, K., Bhattacharyya, S., & Sharma, A. (2014). Photocatalytic degradation of naphthalene by electrospun mesoporous carbon-doped anatase TiO₂ nanofiber mats. *Industrial & Engineering Chemistry Research*, 53(49), 18900-18909. <https://doi.org/10.1021/ie5025744>
- Munyengabe, A. (2016). *Determination of polycyclic aromatic hydrocarbons in the water, soils and surface sediments of the Msunduzi River, KwaZulu-Natal, South Africa* (Masters dissertation). <http://hdl.handle.net/10413/13963>
- Muxika, A., Etxabide, A., Uranga, J., Guerrero, P., & De La Caba, K. (2017). Chitosan as a bioactive polymer: Processing, properties and applications. *International Journal of Biological Macromolecules*, 105, 1358-1368. <https://doi.org/10.1016/j.ijbiomac.2017.07.087>
- Muzzarelli, R. A., Greco, F., Busilacchi, A., Sollazzo, V., & Gigante, A. (2012). Chitosan, hyaluronan and chondroitin sulphate in tissue engineering for cartilage regeneration: a review. *Carbohydrate Polymers*, 89(3), 723-739. <https://doi.org/10.1016/j.carbpol.2012.04.057>
- Neyens, E., & Baeyens, J. (2003). A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials*, 98(1-3), 33-50. [https://doi.org/10.1016/S0304-3894\(02\)00282-0](https://doi.org/10.1016/S0304-3894(02)00282-0)
- Nguyen, T. P., Tran, Q. B., Ly, Q. V., Le, D. T., Tran, M. B., Ho, T. T. T., & Van Le, Q. (2020). Enhanced visible photocatalytic degradation of diclofenac over N-doped TiO₂ assisted with H₂O₂: A kinetic and pathway study. *Arabian Journal of Chemistry*, 13(11), 8361-8371. <https://doi.org/10.1016/j.arabjc.2020.05.023>
- Olatunji, M. A., Khandaker, M. U., Ladan, M., & Bradley, D. A. (2018). Polypyrrole-based nanocomposite adsorbents and its application in the removal of radioactive materials. In *Polymer-based Nanocomposites for Energy and Environmental Applications* (pp. 465-489). Woodhead Publishing. <https://doi.org/10.1016/B978-0-08-102262-7.00017-9>
- Oturan, M. A., & Aaron, J. J. (2014). Advanced oxidation processes in water/wastewater treatment: principles and applications. A review. *Critical Reviews in Environmental Science and Technology*, 44(23), 2577-2641. <https://doi.org/10.1080/10643389.2013.829765>
- Patiño-Ruiz, D. A., De Ávila, G., Alarcón-Suesca, C., González-Delgado, A. D., & Herrera, A. (2020). Ionic cross-linking fabrication of chitosan-based beads modified with FeO and TiO₂ nanoparticles: Adsorption

- mechanism toward naphthalene removal in seawater from Cartagena Bay area. *ACS Omega*, 5(41), 26463-26475. <https://doi.org/10.1021/acsomega.0c02984>
- Pereira, L. (2014). Persistent organic chemicals of emerging environmental concern. In *Environmental Deterioration and Human Health* (pp. 163-213). Springer, Dordrecht. https://doi.org/10.1007/978-94-007-7890-0_8
- Petronella, F., Truppi, A., Ingrosso, C., Placido, T., Striccoli, M., Curri, M. L., & Comparelli, R. (2017). Nanocomposite materials for photocatalytic degradation of pollutants. *Catalysis Today*, 281, 85-100. <https://doi.org/10.1016/j.cattod.2016.05.048>
- Qi, K., Selvaraj, R., Al Fahdi, T., Al-Kindy, S., Kim, Y., Wang, G. C., & Sillanpää, M. (2016). Enhanced photocatalytic activity of anatase-TiO₂ nanoparticles by fullerene modification: A theoretical and experimental study. *Applied Surface Science*, 387, 750-758. <https://doi.org/10.1016/j.apsusc.2016.06.134>
- Qiao, M., Qi, W., Liu, H., & Qu, J. (2014). Oxygenated, nitrated, methyl and parent polycyclic aromatic hydrocarbons in rivers of Haihe River System, China: Occurrence, possible formation, and source and fate in a water-shortage area. *Science of the Total Environment*, 481, 178-185. <https://doi.org/10.1016/j.scitotenv.2014.02.050>
- Rani, M., & Shanker, U. (2019a). Degradation of tricyclic polyaromatic hydrocarbons in water, soil and river sediment with a novel TiO₂ based heterogeneous nanocomposite. *Journal of Environmental Management*, 248, 109340. <https://doi.org/10.1016/j.jenvman.2019.109340>
- Rani, M., & Shanker, U. (2019b). Mineralization of carcinogenic anthracene and phenanthrene by sunlight active bimetallic oxides nanocomposites. *Journal of Colloid and Interface Science*, 555, 676-688. <https://doi.org/10.1016/j.jcis.2019.08.016>
- Rani, M., & Shanker, U. (2019c). Sunlight mediated improved photocatalytic degradation of carcinogenic benz[a]anthracene and benzo[a]pyrene by zinc oxide encapsulated hexacyanoferrate nanocomposite. *Journal of Photochemistry and Photobiology A: Chemistry*, 381, 111861. <https://doi.org/10.1016/j.jphotochem.2019.111861>
- Ray, S. S., & Okamoto, M. (2003). Polymer/layered silicate nanocomposites: a review from preparation to processing. *Progress in Polymer Science*, 28(11), 1539-1641. <https://doi.org/10.1016/j.progpolymsci.2003.08.002>
- Rebekah, A., Bharath, G., Naushad, M., Viswanathan, C., & Ponpandian, N. (2020). Magnetic graphene/chitosan nanocomposite: A promising nano-adsorbent for the removal of 2-naphthol from aqueous solution and their kinetic studies. *International Journal of Biological Macromolecules*, 159, 530-538. <https://doi.org/10.1016/j.ijbiomac.2020.05.113>
- Reddy, K. R., Xie, T., & Dastgheibi, S. (2014). PAHs removal from urban stormwater runoff by different filter materials. *Journal of Hazardous, Toxic, and Radioactive Waste*, 18(2), 04014008. [https://doi.org/10.1061/\(ASCE\)HZ.2153-5515.0000222](https://doi.org/10.1061/(ASCE)HZ.2153-5515.0000222)
- Rezvani-Eivari, M., Amiri, A., Baghayeri, M., & Ghaemi, F. (2016). Magnetized graphene layers synthesized on the carbon nanofibers as a novel adsorbent for the extraction of polycyclic aromatic hydrocarbons from environmental water samples. *Journal of Chromatography A*, 1465, 1-8. <https://doi.org/10.1016/j.chroma.2016.08.034>
- Romão, J., & Mul, G. (2016). Substrate specificity in photocatalytic degradation of mixtures of organic contaminants in water. *ACS catalysis*, 6(2), 1254-1262. <https://doi.org/10.1021/acscatal.5b02015>
- Sekar, A. D., Muthukumar, H., Chandrasekaran, N. I., & Matheswaran, M. (2018). Photocatalytic degradation of naphthalene using calcined FeZnO/PVA nanofibers. *Chemosphere*, 205, 610-617. <https://doi.org/10.1016/j.chemosphere.2018.04.131>
- Shahidi, D., Roy, R., & Azzouz, A. (2015). Advances in catalytic oxidation of organic pollutants-prospects for thorough mineralization by natural clay catalysts. *Applied Catalysis B: Environmental*, 174, 277-292. <https://doi.org/10.1016/j.apcatb.2015.02.042>
- Sherafatmand, M. (2016). *Biodegradation of polycyclic aromatic hydrocarbons (PAHs) using microbial fuel cells (MFCs) in the contaminated sediment and wastewater*. (Doctoral dissertation, National University of Singapore). <http://scholarbank.nus.edu.sg/handle/10635/124218>
- Shukla, S. (2016). Polymer nanocomposites market by type (Carbon Nanotubes, Nano-clays, Metal oxide, Ceramics), application (Construction, automotive, electrical & electronics, Packaging)-global opportunity analysis and industry Forecast, 2014-2022. *Advance Materials*, 1194.
- Singh, N. B., Rai, S., & Agarwal, S. (2014). Polymer nanocomposites and Cr (VI) removal from water. *Nanosciences Technology*, 1, 1-10.

- Singh, P., Mondal, K., & Sharma, A. (2013). Reusable electro-spun mesoporous ZnO nanofiber mats for photocatalytic degradation of polycyclic aromatic hydrocarbon dyes in wastewater. *Journal of Colloid and Interface Science*, 394, 208-215. <https://doi.org/10.1016/j.jcis.2012.12.006>
- Sohara, K., Yamauchi, K., Sun, X., Misawa, K., & Sekine, Y. (2021). Photocatalytic degradation of polycyclic aromatic hydrocarbons in fine particulate matter (PM_{2.5}) collected on TiO₂-supporting quartz fibre filters. *Catalysts*, 11(3), 400. <https://www.mdpi.com/2073-4344/11/3/400#>
- Solano, R. A., De León, L. D., De Ávila, G., & Herrera, A. P. (2021). Polycyclic aromatic hydrocarbons (PAHs) adsorption from aqueous solution using chitosan beads modified with thiourea, TiO₂ and Fe₃O₄ nanoparticles. *Environmental Technology & Innovation*, 21, 101378. <https://doi.org/10.1016/j.eti.2021.101378>
- Soo, C. W., Juan, J. C., Lai, C. W., Abd Hamid, S. B., & Yusop, R. M. (2016). Fe-doped mesoporous anatase-brookite titania in the solar-light-induced photodegradation of Reactive Black 5 dye. *Journal of the Taiwan Institute of Chemical Engineers*, 68, 153-161. <https://doi.org/10.1016/j.jtice.2016.08.025>
- Srikanth, B., Goutham, R., Narayan, R. B., Ramprasad, A., Gopinath, K. P., & Sankaranarayanan, A. R. (2017). Recent advancements in supporting materials for immobilized photocatalytic applications in wastewater treatment. *Journal of Environmental Management*, 200, 60-78. <https://doi.org/10.1016/j.jenvman.2017.05.063>
- Sun, L., Ye, Z., Ling, Y., Cai, S., Xu, J., Fan, C., & Li, Y. (2020). Relationship between polycyclic aromatic hydrocarbons and rheumatoid arthritis in US general population, NHANES 2003-2012. *Science of The Total Environment*, 704, 135294. <https://doi.org/10.1016/j.scitotenv.2019.135294>
- Szreniawa-Sztajnert, A., Zabiegała, B., & Namieśnik, J. (2013). Developments in ultrasound-assisted microextraction techniques for isolation and preconcentration of organic analytes from aqueous samples. *TrAC Trends in Analytical Chemistry*, 49, 45-54. <https://doi.org/10.1016/j.trac.2013.02.015>
- Tatarinov, D. A., Sokolnikova, S. R., & Myslitskaya, N. A. (2021). Applying chitosan-TiO₂ nanocomposites for photocatalytic degradation of anthracene and pyrene. *Journal of Biomedical Photonics & Engineering*, 7(1), 010301. <https://doi.org/10.18287/JBPE21.07.010301>
- Tavares, M. I. B., da Silva, E. O., da Silva, P. R. C., & de Menezes, L. R. (2017). Polymer nanocomposites. *Nanostructured Materials-fabrication to Applications*. Seehra M. Editor, 135-151. <https://doi.org/10.5772/intechopen.68142>
- Thakur, V. K., & Thakur, M. K. (2014). Recent advances in graft copolymerization and applications of chitosan: a review. *ACS Sustainable Chemistry & Engineering*, 2(12), 2637-2652. <https://doi.org/10.1021/sc500634p>
- Walaszek, M., Bois, P., Laurent, J., Lenormand, E., & Wanko, A. (2018). Micropollutants removal and storage efficiencies in urban stormwater constructed wetland. *Science of the Total Environment*, 645, 854-864. <https://doi.org/10.1016/j.scitotenv.2018.07.156>
- Wang, E. Z., Wang, Y., & Xiao, D. (2021). Polymer Nanocomposites for Photocatalytic Degradation and Photoinduced Utilizations of Azo-Dyes. *Polymers*, 13(8), 1215. <https://doi.org/10.3390/polym13081215>
- Wang, H., Yuan, X., Wu, Y., Chen, X., Leng, L., Wang, H., & Zeng, G. (2015). Facile synthesis of polypyrrole decorated reduced graphene oxide-Fe₃O₄ magnetic composites and its application for the Cr (VI) removal. *Chemical Engineering Journal*, 262, 597-606. <https://doi.org/10.1016/j.cej.2014.10.020>
- Wang, X. W., Zhong, N. N., Hu, D. M., Liu, Z. Z., & Zhang, Z. H. (2009). Polycyclic aromatic hydrocarbon (PAHs) pollutants in groundwater from coal gangue stack area: characteristics and origin. *Water Science and Technology*, 59(5), 1043-1051. <https://doi.org/10.2166/wst.2009.050>
- Weis, L. M., Rummel, A. M., Masten, S. J., Trosko, J. E., & Upham, B. L. (1998). Bay or baylike regions of polycyclic aromatic hydrocarbons were potent inhibitors of Gap junctional intercellular communication. *Environmental Health Perspectives*, 106(1), 17-22.
- Wheatley, A., & Sadhra, S. (2010). Carcinogenic risk assessment for emissions from clinical waste incineration and road traffic. *International Journal of Environmental Health Research*, 20(5), 313-327. <https://doi.org/10.1080/09603121003663487>
- Wincent, E., Jonsson, M. E., Bottai, M., Lundstedt, S., & Dreij, K. (2015). Aryl hydrocarbon receptor activation and developmental toxicity in zebrafish in response to soil extracts containing unsubstituted and oxygenated PAHs. *Environmental science & technology*, 49(6), 3869-3877. <https://doi.org/10.1021/es505588s>
- World Health Organization (WHO). (2017). 2.1 billion people lack safe drinking water at home, more than twice as many lack safe sanitation. Available online at:

<https://www.who.int/news/item/12-07-2017-2-1-billion-people-lack-safe-drinking-water-at-home-more-than-twice-as-many-lack-safe-sanitation>. Accessed on 6th September 2021.

- Wróblewska-Krepsztul, J., Rydzkowski, T., Borowski, G., Szczypiński, M., Klepka, T., & Thakur, V. K. (2018). Recent progress in biodegradable polymers and nanocomposite-based packaging materials for a sustainable environment. *International Journal of Polymer Analysis and Characterization*, 23(4), 383-395. <https://doi.org/10.1080/1023666X.2018.1455382>
- Wu, H., Sun, B., & Li, J. (2019). Polycyclic aromatic hydrocarbons in sediments/soils of the rapidly urbanized lower reaches of the River Chaoju, China. *International Journal of Environmental Research and Public Health*, 16(13), 2302. <https://www.mdpi.com/1660-4601/16/13/2302#>
- Xiaoping, C., Qiaoshan, C., & Jinhong, B. (2020). Progress in photocatalytic degradation of polycyclic aromatic hydrocarbons in soil. *Progress in Chemistry*, 38. <https://doi.org/10.7536/PC200743>
- Yang, X., Cai, H., Bao, M., Yu, J., Lu, J., & Li, Y. (2017). Highly Efficient Photocatalytic Remediation of Simulated Polycyclic Aromatic Hydrocarbons (PAHs) Contaminated Wastewater under Visible Light Irradiation by Graphene Oxide Enwrapped Ag₃PO₄ Composite. *Chinese Journal of Chemistry*, 35(10), 1549-1558. <https://doi.org/10.1002/cjoc.201700202>
- Ye, T., Qi, W., An, X., Liu, H., & Qu, J. (2019). Faceted TiO₂ photocatalytic degradation of anthraquinone in aquatic solution under solar irradiation. *Science of The Total Environment*, 688, 592-599. <https://doi.org/10.1016/j.scitotenv.2019.06.319>
- Zango, Z. U., Jumbri, K., Sambudi, N. S., Ramli, A., Abu Bakar, N. H. H., Saad, B., & Sulieman, A. (2020). A critical review on metal-organic frameworks and their composites as advanced materials for adsorption and photocatalytic degradation of emerging organic pollutants from wastewater. *Polymers*, 12(11), 2648. <https://doi.org/10.3390/polym12112648>
- Zhang, L., Li, P., Gong, Z., & Li, X. (2008). Photocatalytic degradation of polycyclic aromatic hydrocarbons on soil surfaces using TiO₂ under UV light. *Journal of Hazardous Materials*, 158(2-3), 478-484. <https://doi.org/10.1016/j.jhazmat.2008.01.119>
- Zhao, S., Jia, H., Nulaji, G., Gao, H., Wang, F., & Wang, C. (2017). Photolysis of polycyclic aromatic hydrocarbons (PAHs) on Fe³⁺-montmorillonite surface under visible light: degradation kinetics, mechanism, and toxicity assessments. *Chemosphere*, 184, 1346-1354. <https://doi.org/10.1016/j.chemosphere.2017.06.106>
- Zhao, X., Cai, Z., Wang, T., O'Reilly, S. E., Liu, W., & Zhao, D. (2016). A new type of cobalt deposited titanate nanotubes for enhanced photocatalytic degradation of phenanthrene. *Applied Catalysis B: Environmental*, 187, 134-143. <https://doi.org/10.1016/j.apcatb.2016.01.010>
- Zhu, H. Y., Xiao, L., Jiang, R., Zeng, G. M., & Liu, L. (2011). Efficient decolorization of azo dye solution by a visible-light-induced photocatalytic process using SnO₂/ZnO heterojunction immobilized in chitosan matrix. *Chemical Engineering Journal*, 172(2-3), 746-753. <https://doi.org/10.1016/j.cej.2011.06.053>

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