

Review

Environment-Friendly Removal Methods for Endocrine Disrupting Chemicals

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Abstract: In the past few decades, many emerging pollutants have been detected and monitored in different water sources because of their universal consumption and improper disposal. Among these, endocrine-disrupting chemicals (EDCs), a group of organic chemicals, have received global attention due to their estrogen effect, toxicity, persistence and bioaccumulation. For the removal of EDCs, conventional wastewater treatment methods include flocculation, precipitation, adsorption, etc. However, there are some limitations on these common methods. Herein, in order to enhance the public's understanding of environmental EDCs, the definition of EDCs and the characteristics of several typical EDCs (physical and chemical properties, sources, usage, concentrations in the environment) are reviewed and summarized in this paper. In particular, the methods of EDC removal are reviewed, including the traditional methods of EDC removal, photocatalysis, biodegradation of EDCs and the latest research results of EDC removal. It is proposed that photocatalysis and biodegradation could be used as an environmentally friendly and efficient EDC removal technology. Photocatalytic technology could be one of the water treatment methods with the most potential, with great development prospects due to its high catalytic efficiency and low energy consumption. Biodegradation is expected to replace traditional water treatment methods and is also considered to be a highly promising method for efficient removal of EDCs. Besides, we summarize several photocatalysts with high catalytic activity and some fungi, bacteria and algae with strong biodegradability.

Keywords: endocrine-disrupting chemicals; photocatalytic degradation; biodegradation

1. Introduction

The endocrine system is known as one of the three major information transmission systems of human beings and plays a key role in regulating various functions of the body and maintaining the relative stability of the internal environment [1,2]. Disorders of the endocrine system may cause disease. Many natural and synthetic compounds, endocrine-disrupting chemicals (EDCs), can alter normal endocrine function by removing or binding to endogenous hormone receptors, altering processes such as synthesis, storage, release, metabolism and transport [3,4]. These so-called EDCs are a large group of emerging contaminants found in water environments and process effluents at low concentrations [5] and are also termed “endocrine disruptors” or “environmental hormones”. According to the definition of the World Health Organization (WHO), an EDC is “an exogenous substance or mixture that can alter normal hormonal functions in humans and animals, and consequently affects the endocrine system of

living organisms". These contaminants have different classifications due to their usage or origin and effects. EDCs mainly originate from (1) pharmaceuticals; (2) personal care products; (3) pesticides such as herbicides, dicofol, dichlorodiphenyltrichloroethane (DDT) and its metabolite; (4) plastics and food preservatives; (5) hormonal agents and phytoestrogens; etc. It was reported that there are two typical EDCs in the water environment: the first class is estrogen, and the second one is endocrine-disrupting phenolic compounds [6]. Estrogen is found at low concentrations in sewage (ng/L) but has high estrogen activity, including natural steroidal estrogens such as 17β -estradiol (E2) and the synthetic contraceptive 17α -ethynylestradiol (EE2) [7,8]. As for endocrine-disrupting phenolic compounds such as nonylphenol (NP) and bisphenol A (BPA), they have the characteristics of low estrogenic activity, but their concentration in wastewater is relatively high, reaching micrograms per liter [9,10].

EDCs could enter the environment through various channels, such as consumer activities and waste disposal [11,12], and sometimes, EDCs are accidentally released or otherwise discharged into the environment. In recent decades, large amounts of endogenous and synthetic hormones have been detected in sewage, surface water, groundwater and soil [13,14]. EDCs may cause negative effects even at trace-level concentrations ($<1 \mu\text{g/L}$) [15]. Some scientists have detected different concentrations of EDCs in rivers, lakes and other natural waters and found that these EDCs have led to feminization and androgynous abnormalities in aquatic organisms in some areas [16,17]. EDCs are toxic chemicals and have complex chemical structures, which are difficult to remove from the environment. EDCs could cause harm to human beings as follows: they could (1) decrease reproductive and developmental functions, (2) reduce human immunity and induce tumors and (3) cause neurological disorders [3,18,19]. Thus, the removal of EDCs from the environment is an urgent problem to be solved.

According to previous studies, methods of EDC removal include flocculation, precipitation, adsorption, membrane treatment and other conventional wastewater treatment methods. However, there are some limitations on these approaches. Foreign studies such as that by Kim [20] have compared the effects of flocculation, filtration and adsorption. The results have indicated that traditional water treatment processes such as flocculation and precipitation cannot effectively remove EDCs, including NP and BPA, and the removal efficiency of BPA is below 10%. Gomez [21] has experimentally demonstrated that membrane treatment failed to remove environmental hormones, especially bisphenol F (BPF). Compared with the conventional wastewater treatment technologies mentioned above, photocatalytic degradation is hailed to be a promising technology that could decompose and mineralize most organic pollutants with sunlight as excitation energy. In addition, microbial-mediated bioremediation or biodegradation technology is considered to be an effective way to eliminate stubborn organic pollutants in the environment, too [22].

Herein, a slight comprehensive description is given of the several typical EDCs and their impact on the environment. Then, the methods of eliminating environmental EDCs, including adsorption, chemical advanced oxidation, biodegradation and photocatalytic degradation, are reviewed. In addition, the purpose of this paper is to analyze and introduce the core of EDC removal by biodegradation and photocatalytic degradation, that is, microorganisms and catalysts. The microorganisms for biodegradation and various catalysts applied in photocatalytic degradation are summarized and provided, respectively. Towards the end, the application of photocatalytic coupling microorganism technology in the removal of EDCs is considered.

2. Representatives of EDCs

Among the various EDCs from the environment, bisphenol A (BPA), nonylphenol (NP) and triclosan (TCS) have obtained great attention due to their toxicity and persistence in the environment. In this section, an introduction is given to the applications of these emerging pollutants in human life as well as their toxic effects on biology and the environment. Moreover, estrone (E1), a natural estrogen, is also covered briefly.

2.1. Bisphenol A

In the field of industrial production, BPA is used in the production of epoxy resin and polycarbonate (PC) plastics and is widely used in various types of food and beverage packaging, baby bottles and dental sealants in life [23]. BPA is a strong endocrine disruptor that can cause carcinogenesis [24]. BPA has been widely used despite the fact that it is hazardous. Consequently, there was an increase in BPA in global consumption by 5.5% per year from 2009 to 2012 [25]. It has been reported that human exposure to BPA in the environment can be divided into three main ways, namely, intake, inhalation and skin contact [26]. In addition, studies have shown that BPA can have adverse effects on aquatic organisms even in environments where the concentration of BPA is less than 1 mg/L. The public concern surrounding BPA mainly focuses on children because BPA could be gradually released during normal use of baby bottles [27]. At present, some countries have regulated the use of BPA. China, for example, has banned the production of baby bottles containing BPA. Canada also banned the use of polycarbonate plastic containing BPA in baby bottles in 2008. In addition, Malaysia, the United States and the European Union have issued documents restricting the use of BPA [28].

2.2. Nonylphenol

Nonylphenol (NP) is the main raw material for the synthesis of NP ethoxylates and also the main degradation product. NP and its ethoxylates, like NP1EO, are known as surfactants and are widely used in industrial, commercial and domestic household products. There are many products containing nonylphenol endocrine disruptors used in daily life, mainly including detergents, personal care products and insecticides, and products commonly used in industry, such as lubricants, defoamers, emulsifiers and paints. NP is also involved in the textile and metal processing industries [29,30]. The widespread use of these substances has caused higher concentrations of nonylphenol endocrine disruptors to enter the environment, increasing human exposure to these substances. Furthermore, the fact that these chemicals tend to accumulate has aroused greater concern. NP has been identified as one of 27 priority controlled persistent toxic pollutants by the United Nations Environmental Protection Agency. At present, environmental concentrations of NP are also specified in some countries. In order to protect aquatic organisms, the U.S. EPA has set an Ambient Water Quality Criteria for NP, which stipulated that the acute exposure value of NP in freshwater environments is 28 µg/L and the chronic exposure value is 6.6 µg/L. Additionally, in saltwater, the acute criterion is close to 7.0 µg/L, while the chronic exposure value is 1.7 µg/L [31].

2.3. Triclosan

In addition to these well-known EDCs, triclosan (TCS), a broad-spectrum antibacterial agent, is widely used in daily chemicals such as soaps, toothpastes and facial cleansers [32]. TCS is also used as a preservative. It has been found that TCS has potential estrogenic activity and slight teratogenicity. When a product containing TCS is washed out from a drain pipe, it is collected by the sewage system to reach the sewage disposal plant, and the untreated TCS finally enters the aquatic environment, posing a potential threat to the living organisms.

2.4. Estrone

Estrone (E1) is a natural estrogen that naturally occurs in humans and animals. E1 is considered to be an important contributor to estrogen activity in wastewater environments [33]. Moreover, natural estrogens also include estradiol and estriol, with estradiol being the strongest.

EDCs, such as the synthetic endocrine disruptors (BPA, NP and TCS) mentioned above, and natural estrogens, such as E1 and E2, have a common distribution in the environment. These pollutants have been detected in surface water, groundwater, sediment and even marine water samples and other environments of different countries [34–36]. Many reports indicate that EDCs can be found in the water and effluents of municipal sewage treatment plants [37].

According to the order of the ecological risk quotient and estradiol equivalent, domestic scholars have screened out four pollutants whose control should be given priority in China's urban sewage treatment plants, three of which are E1, NP and BPA. There is no doubt that natural estrogen and endocrine disruptors with strong endocrine disruption ability have attracted more and more attention in recent years. However, based on the fact that there are many species of EDCs in the environment, it is impossible to study and control all EDCs under the current conditions. The priority of control should be analyzed according to the existing status of EDCs in actual sewage and the removal effect of existing sewage treatment processes.

Table 1 briefly summarizes the properties, usage and environmental impacts of BPA, NP, TCS and E1.

Table 1. The properties, usage and environmental impacts of bisphenol A (BPA), nonylphenol (NP), triclosan (TCS) and estrone (E1).

Compounds	Bisphenol A (BPA)	Nonylphenol (NP)	Triclosan (TCS)	Estrone (E1)
Molecular formula	C ₁₅ H ₁₆ O ₂	C ₁₅ H ₂₄ O	C ₁₂ H ₇ Cl ₃ O ₂	C ₁₈ H ₂₂ O ₂
Molecular weight (g/mol)	228.29	220.35	289.54	270.4
Solubility in water (mg/L)	120–300	Insoluble	Slightly soluble in water, 10 mg/L	30
LogKow	3.32	5.76	4.76	3.43
Usage/origin	Food and beverage packaging, baby bottles, dental sealants, etc. Harmful substance;	Commercial and industrial surfactants, paints, lubricants, etc.	Spectral antimicrobials; household products such as soap and toothpaste	Estrogen drugs, biochemical studies, etc.
Properties/environmental effects	the concentration of BPA in most water systems keeps a level of nanograms per liter; bioaccumulation	Hazardous substance; negative effects on organisms	Recalcitrant micropollutant	Natural estrogen; negative effects on organisms
Examples	(1) BPA could accumulate in zooplankton through phytoplankton; (2) fetuses and infants are at higher risk of BPA exposure and accumulation due to their low metabolizable xenobiotics	NP was listed as a priority toxic substance by the European Union	TCS is a refractory compound and persistent in the environment due to the aromatic nature and high chlorine content	E1 could disturb sexual development or cause breast cancer in females
References	[38]	[39]	[40]	[41]

3. Conventional Water Treatment Technologies for EDCs

So far, one of the strategies for EDCs in the environment is to control their source, that is, to stop commercial production or to reduce the usage of chemicals that contain endocrine disruption effects. Besides, based on the current sewage treatment technology, other measures are to use a variety of physical and chemical methods to degrade or eliminate environmental EDCs.

Currently, the methods for removing environmental EDCs include flocculation, precipitation, adsorption, chemical oxidation and other conventional water treatment technologies. Therefore, wastewater treatment plants (WWTPs) undertake the task of removing EDCs. However, some studies have shown that WWTPs cannot effectively remove EDCs from wastewater by monitoring micropollutants in WWTPs. A study by Benotti et al. [42] has found that the removal of insecticides such as atrazine in water treatment was less effective, and the removal rate was less than 50%. A report by Ternes et al. [43] indicated that chemical coagulation was an inefficient method of drug removal; for example, the removal rate of diclofenac was less than 25%.

3.1. Adsorption Technology

Adsorption technology is often used in wastewater treatment processes. Adsorption is a mass transfer process in which hydrophobic and electrostatic interactions exist between the adsorbate and the adsorbent [44]. It refers to the phenomenon in which a component or components of a fluid accumulate at a solid surface when the fluid is in contact with the porous solid. Commonly used

adsorbents are activated carbon, silica gel, activated alumina, etc. It has been reported that adsorption technology using activated carbon as an adsorbent has become an effective method for removing micropollutants. Adams et al. [45] showed that the use of powdered activated carbon (PAC) could effectively remove drugs such as sulfamethazine, trimethoprim and dimethyl carbonate from water, and the removal rate ranged from 81% to 98%.

However, the adsorption process and adsorption effect of activated carbon are affected by many factors. They are not only related to the properties of activated carbon and EDCs but also related to the adsorption conditions, including pH, temperature, the dosage of adsorbent and interfering substances in water. Nam et al. [46] found that (1) temperature could affect the adsorption effect, and low temperatures reduced the adsorption of hydrophobic micropollutants; (2) dissolved organic matter (DOM) in surface water and micropollutants absorbed by activated carbon would exhibit competitive behavior; and (3) a high dose of adsorbent and long adsorption time could promote the adsorption effect, but at the same time, it could increase additional costs and energy demand. Therefore, in order to effectively remove EDCs in the environment, it is necessary to optimize the adsorption technology.

3.2. Chemical Advanced Oxidation

Chemical advanced oxidation (CAO) is a process in which strong oxidants are used to transform pollutants in wastewater into stable, low-toxic or nontoxic substances by a redox reaction. In general, the removal of EDCs by a CAO process involves ozonation, Cl_2 , ClO_2 , H_2O_2 , permanganate (MnO_4^-) and their combinations, such as UV/ O_3 , UV/ H_2O_2 , etc. [47–49]. Studies have shown that O_3 could remove a variety of EDCs [50,51]. For example, researchers have removed BPA and natural 17β -estradiol (E2) in an aqueous solution by ozonation (the concentration of O_3 was 0.1 mmol/L). However, the reaction between E2 and O_3 is higher than the reaction between BPA and O_3 . Additionally, the combination of UV radiation with O_3 seems to be more effective for EDC removal [52]. Ozone oxidation is also pH-dependent and is greatly affected by pH conditions. Some EDCs (TCS, E1, estriol) performed higher oxidation percentages at a pH of 6.6 than at 8.6 [47]. Another oxidant, chlorine, showed an incomplete chlorination reaction in the removal of EDCs. Researchers have used chlorine to remove BPA and E1 and found that the process produced many byproducts. Additionally, the estrogen activity of BPA in aqueous solutions did not decrease significantly after chlorination [53]. Therefore, removal of EDCs by a CAO process is not the most advisable option due to the above statement. It is obvious that chemical advanced oxidation requires strict technical conditions; water quality (e.g., pH) is a concern when operating. In addition, the high investment costs (e.g., generators of O_3 and Cl_2) have also become a limiting factor of chemical advanced oxidation technology.

To sum up, conventional water treatment technologies have certain limitations and disadvantages. Adsorption, as a physical treatment method, is not easy to adapt to the large-scale pollution treatment of natural water bodies. Chemical advanced oxidation techniques need to focus on the selection of highly effective oxidants and the optimization of operating conditions while ensuring that the generation of byproducts is reduced during the oxidation process.

Figure 1 shows several methods for degrading or removing EDCs from the environment, focusing on biodegradation and photocatalytic degradation in this review.

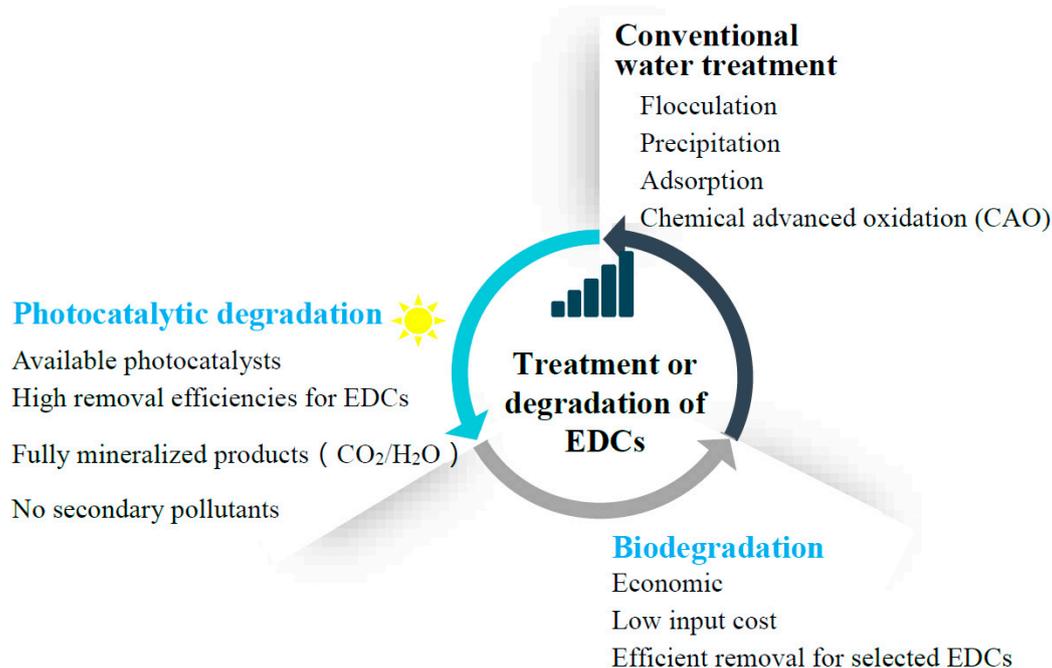


Figure 1. Treatment or degradation methods of endocrine-disrupting chemicals (EDCs).

4. Biodegradation of EDCs

Limited by conventional water treatment techniques, some experts have proposed biodegradation techniques for applying microorganisms or their enzymes in the treatment of soils or wastewater contaminated with EDCs. Biodegradation is considered one of the current treatment methods for EDCs. This method has many advantages for economic and environmental protection, such as low input costs, a wide scope of action, a long duration and simple requirements for equipment and space. A biodegradation method is more suitable for dealing with the pollution of natural water environments. Numerous studies have shown that some fungi and bacteria can effectively degrade EDCs. Acclimated activated sludge is widely used in sewage treatment and has a certain degradation effect on some EDCs. There are many reports on the biodegradation of BPA, which basically proves that BPA can be effectively degraded in both natural water and sewage.

When it comes to fungal strains, numerous studies on the fungal degradation of EDCs, such as branched-chain octylphenol (4-t-OP), mainly involve white-rot fungi (WRF), which can produce extracellular lignin-modifying enzymes for the biotransformation of aromatic compounds [54,55]. It was reported that WRF could remove various organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls, textile dyes, insecticides and EDCs [56,57]. For example, the white-rot fungus *Pleurotus ostreatus* HK35 [58], which is fairly easy to cultivate and to fructificate and has great potential for bioremediation, was tested in the degradation of seven typical representatives of EDCs (BPA, E1, 17 β -estradiol, estriol, 17 α -ethynylestradiol, TCS and 4-n-nonylphenol). Under model laboratory conditions, the degradation efficiency of *Pleurotus ostreatus* HK35 was greater than 90% in 12 days. *Trametes versicolor* is known as a multifunctional microorganism that could decompose various EDCs such as BPA and TCS [59,60]. It has also been observed that other microorganisms have the ability to metabolize EDCs in the environment. Some EDCs with endocrine activity, such as technical nonylphenol (tNP), 4-t-OP and 4-cumylphenol (4-CP), were degraded effectively by the nonligninolytic fungus *Umbelopsis isabellina* [61]. After 12 h of incubation, the removal rate of tNP, 4-t-OP and 4-CP (initial concentration: 25 mg/L) exceeded 90%.

Fusarium falciforme RRK20 [62], a filamentous fungal strain from wastewater samples in Taiwan, was applied in the degradation of 4-t-OP, which has higher estrogenic activity compared with other long-chain alkylphenols like NP. Then, the results showed that the degradation rate exceeded 70%.

Additionally, the strain RRK20 is capable of utilizing a variety of EDCs, including alkylphenol polyethoxylates, alkylphenols and natural and synthetic estrogens. The yeast *Candida rugopelliculosa* RRY5 [63] was proved to be able to utilize a variety of substances, such as 4-methylphenol, BPA and phenol, under aerobic conditions. Moreover, the degradation mechanisms of 4-t-OP by the strain RRY5 were by both the branched alkyl side chain and aromatic ring.

In addition to bacteria and fungi, the ability of algae to remove EDCs from water ecosystems has been demonstrated. Studies have found that *Chlorella fusca*, *Chlamydomonas*, *Chlorella vulgaris* and *Cyclotella caspia* could enrich and degrade EDCs. After EDCs were absorbed by algae, they could be degraded and transformed by glucosylation. Two microalgae, *Selenastrum capricornutum* and *Chlamydomonas reinhardtii* [64], were tested for possibly biodegrading the hormones β -estradiol (E2) and 17 α -ethynylestradiol (EE2). The complete removal of E2 and EE2 in the results indicated that microalgae were a low-cost photooxidation and/or biodegradation treatment system for pollutants. Freshwater microalgae, such as *Chlamydomonas mexicana* and *Chlorella vulgaris* [65], were able to biodegrade BPA.

As a basic biocatalyst, enzymes can participate in the regulation and metabolism of organisms. Biodegradable environmental EDCs by microorganisms or their enzymes have been applied. The ability of microorganisms to degrade EDCs comes from the enzymes that they secrete. Among these enzymes, the performance of manganese peroxidase (MnP) and laccase in the biodegradation of EDCs has been extensively studied. Hirano et al. [66] found that about 80% of BPA was removed in 12 days using *Pleurotus ostreatus*; the lignin-degrading enzyme MnP could effectively degrade BPA and convert it to phenol, diethylstilbestrol, 4-isopropylphenol and 4-isopropenylphenol. It was found that laccase extracted from *Coriolopsis polyzona* could simultaneously eliminate EDCs such as BPA, NP and TCS [67]. Two thermostable laccases [68] from *Pycnoporus sanguineus* after 8 h of treatment with 100 U/L at pH 5 were tested to degrade NP and TCS with more than 95% removal, as determined by means of high performance liquid chromatography (HPLC).

Nowadays, it is a fact that nanotechnology is rapidly evolving and has been widely used, such as nanoparticles and nanomaterials. At the same time, with the growing demand for nanomaterial design, environmental monitoring, biochemical engineering and biomedical applications, the opportunities for enzymes to link nanoparticles and nanomaterials are rapidly increasing [69]. Enzymes, nanoparticles and nanomaterials have become the research objects of many scholars; the interaction between them has gained great attention in the academic world [70,71]. According to reports, a major role or function of enzymes can be used to modify, decompose or manufacture nanoscale particles/nanomaterials since 2014. Due to the large use of nanomaterials, they enter the environment. It is reported that nanomaterials have certain environmental risks [72]. As a result, EDC-degrading microorganisms or enzymes may be exposed to these nanomaterials during the biodegradation of EDCs, and the biodegradation process may be disturbed. Chen et al. [73] have studied the incorporation of carbon nanotubes and/or graphene nanomaterials into the biodegradation process of EDCs and TCS mediated by manganese peroxidase (MnP) to analyze their interaction with MnP. The results clarified that the incorporation of nanomaterials changed the binding conformation of BPA, NP and TCS substrates to MnP, and the entire biodegradation process was also affected by this change.

Table 2 summarizes several microorganisms that can effectively degrade the main EDCs in the environment, including bacteria, fungi, algae and enzymes. It also briefly summarizes the optimal conditions for EDC degradation by various microorganisms and their removal efficiency.

Table 2. Biodegradation of EDCs.

Microorganism/Enzyme	Substrate	Removal Efficiency	Optimal Conditions	Reference
Rhizosphere bacteria TIK1 and IT4	Phenolic EDCs	Extensive	-	[74]
Purified LacI and LacII isoforms produced by <i>P. sanguineus</i> CS43	NP and TCS	95%	-	[68]
Nonligninolytic fungus <i>U. isabellina</i>	tNP, 4-t-OP, 4-CP	90%	90% of initially applied tNP, 4-t-OP and 4-CP (25 mg/L) were eliminated	[61]
<i>Fusarium falciforme</i> RRK20	4-t-OP	Most effective	-	[62]
Yeast <i>C. rugopelliculosa</i> strain RRY5	Alkylphenols	Effective	30 °C, pH 5.0, an initial 4-t-OP concentration of 30 mg/L	[63]
<i>S. yanoikuyae</i> SHJ	DEP	Effective	-	[75]
White-rot fungus <i>Pleurotus ostreatus</i> HK35	EDCs	>90%	-	[58]
Novel endophytic strain YJB3	DBP	82.50%	Under the optimal conditions	[76]
Freshwater microalgae, <i>Chlamydomonas mexicana</i> and <i>Chlorella vulgaris</i>	BPA	24%, 23%	-	[65]
Microalgae, <i>Selenastrum capricornutum</i> and <i>Chlamydomonas reinhardtii</i>	E2, EE2	88% to 100% of E2 was removed by <i>S. capricornutum</i> ; E2 and EE2 were completely removed by <i>C. reinhardtii</i>	-	[64]

5. Photocatalytic Degradation of EDCs

The advanced oxidation technology developed in recent decades has the ability to completely oxidize pollutants and does not produce harmful byproducts, so it has received great attention in water treatment. To the best of our knowledge, advanced oxidation technology is a method for effectively removing toxic pollutants from wastewater, which has a high removal efficiency, good photochemical stability, safety, nontoxicity and low costs [77,78].

There are many types of advanced oxidation technology. Among them, photocatalytic technology is considered the most promising water treatment method because of its high degradation rate and mineralization ability [79]. Photocatalytic technology is capable of decomposing and mineralizing recalcitrant pollutants (including organic matter, inorganic matter, etc.) into CO₂, H₂O and a small amount of simple inorganic compounds using sunlight as the excitation energy.

5.1. TiO₂ and ZnO Photocatalysts

At present, most of the photocatalysts studied are heterogeneous oxide semiconductor materials, of which pure and modified titanium dioxide (TiO₂) materials are the most widely used. TiO₂ is the most studied photocatalyst. For example, in addition to its unparalleled advantages, such as its nontoxicity, cheap price and affordability, suspended TiO₂ is also associated with the recovery of precious metals and photocatalysts [80]. Many studies have found that EDCs could be degraded effectively using TiO₂ as a photocatalyst. It was shown that nanofiber powder photocatalyst NnF Ceram TiO₂ [81], which is a powder photocatalyst based on TiO₂, decomposed progesterone and all types of estradiol without difficulty. Six pesticides, including malathion, quinalphos, fenitrothion, dimethoate, vinclozolin and fenarimol, were removed by two commercial TiO₂ nanopowders (Degussa P25 and Kronos vlp 7000 [82]) as photocatalysts. Benzophenone-3 (BP3) is one of the most commonly used UV filters and is widely used in sunscreen cosmetics, such as sunscreens and lotions. BP3 has a destructive effect on the endocrine system of different organisms. The photocatalytic degradation of BP3 by particles of TiO₂ [83] showed that after 300 min of treatment, about 67% of dissolved organic carbon was eliminated while reducing toxicity and increasing biodegradability, confirming that photocatalysis with TiO₂ is a potential method for removing BP3 from water.

Nano-TiO₂ has been considered an excellent photocatalytic material in the past decade, and scientists have conducted extensive research to evaluate the photocatalytic potential of other

metal oxides. Among the available semiconductor photocatalysts, zinc oxide (ZnO), as a promising photocatalyst, plays a key role in the degradation of organic pollutants in water environments, and it is a suitable substitute for TiO₂ due to its similar band gap energy and lower price [84]. Moreover, ZnO has high chemical stability and ultraviolet sensitivity, making photocatalysis a promising option for sustainable and environmentally friendly treatment [85].

5.2. ZnO Nanocomposites

Nevertheless, some factors affect the photocatalytic degradation process of EDCs. For ZnO, a major factor limiting the efficiency of ZnO photocatalytic processes is the quick electron–hole recombination. In the current research, experts have made considerable efforts to prevent the recombination of charge carriers in semiconductors and to increase the photocatalytic efficiency of ZnO catalysts, such as doping transition metal ions; depositing precious metals; and coupling with other semiconductors, like CeO₂–ZnO, ZnO–WO₃ and TiO₂–ZnO [86]. In this review, the progress of photocatalytic degradation of ZnO and TiO₂ nanocomposites was summarized.

Firstly, a nanorod ZnO/SiC nanocomposite [87] acted as an efficient catalyst for the degradation of diethyl phthalate (DEP). It was synthesized by a simple sol–gel method and exhibited enhanced UV and visible light photocatalytic efficiency. The prepared photocatalyst was nanoscale, with high crystallinity, a rough and porous surface and absorption in the UV and visible light regions, showing good reusability. Using a nanorod ZnO/SiC nanocomposite as a photocatalyst, the rate of DEP degradation was higher than 90% under UV and visible light irradiation. Secondly, perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA)–ZnO, the ZnO nanorods coupled with photosensitive molecules [88], could be applied in polluted surface water. The authors prepared the ZnO nanocomposite by incorporating four different photosensitive molecules, such as perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), heteropoly phosphotungstic acid (HPA), fluorescein and porphyrin, and showed that the PTCDA sensitized ZnO nanorods had the highest photocatalytic activity.

Secondly, Ce_xZn_{1-x}O nanocomposites were synthesized by the coprecipitation method. The prepared photocatalyst exhibited higher photocatalytic efficiency than pure ZnO during BPA degradation under sunlight irradiation and achieved almost complete BPA mineralization, indicating Ce_xZn_{1-x}O assisted photocatalytic degradation is an economical, environmentally friendly and effective approach for removing BPA in an aqueous system.

Thirdly, Bi₂O₃–ZnO nanorods [89] were a new photocatalyst. Nanoscale Bi₂O₃ particles were coated on ZnO nanorods (ZNRs) by combining hydrothermal technology with chemical precipitation. The results showed that the small Bi₂O₃ nanoparticles were evenly distributed on the surface of the ZNRs. Additionally, the Bi₂O₃–ZNR nanocomposites were characterized by high charge separation efficiency and •OH formation ability. More importantly, the Bi₂O₃–ZNR nanocomposites exhibited higher photocatalytic activity than a pure ZNR catalyst in the removal process of two EDCs, phenol and methylparaben. In addition, the Bi₂O₃–ZNR nanocomposites were easy to recycle and reuse due to their one-dimensional nanostructure properties.

5.3. TiO₂ Nanocomposites

Some experts have studied the combined use of TiO₂ composites with precious metals such as silver and gold. Among them, gold has become an attractive material because of its nontoxicity, stability and biocompatibility [90]. Gold nanoparticles can enhance photocatalytic activity by absorbing visible light. Research based on these predecessors, the gold-modified TiO₂ (Au–TiO₂) nanocomposites [91] synthesized with gold loadings of 0%–8% (wt %), were more efficient than P25 TiO₂ in the degradation of E1 under irradiation by UVA and visible LEDs, with a 4 wt % Au loading having the best photocatalytic activity.

A new photocatalyst called Ti-substituted hydroxyapatite (TiHAP) was developed in recent years. It was reported that TiHAP had high photocatalytic activity under ultraviolet light irradiation. Under the same conditions, the maximal adsorption amount of TiHAP for BPA was 19 times that of TiO₂ [92].

5.4. $Ag_3PO_4/LaCoO_3$ Composites

Silver orthophosphate (Ag_3PO_4) has attracted much attention due to its ability to absorb visible light and effectively degrade organic pollutants in the environment. It is a good photocatalyst. $LaCoO_3$ is a perovskite-type (ABO_3) transition metal oxide with magnetic properties, and it has attracted a lot of attention from many scholars because of its high catalytic activity, low costs and no environmental pollution.

For the photocatalytic performance and reactive species of $Ag_3PO_4/LaCoO_3$ composites, a study showed that a $Ag_3PO_4/LaCoO_3$ hybrid composite [79] has great potential environmental applications. Approximately 77.27% of the BPA was mineralized and degraded under 40 min of irradiation. Moreover, the prepared photocatalysts exhibit good performance and can be stably used and reused.

Table 3 describes the photocatalytic degradation of endocrine disruptors, summarizing several stable catalysts with high catalytic effects and preparation methods of photocatalysts.

Table 3. Photocatalytic degradation and nanomaterials.

Photocatalyst	Synthetic Method	Contaminant	Characterization	Reference
Anatase TiO_2	-	Diclofenac, chloramphenicol and estrone	Efficient	[93]
WO_3 -ZNR nanocomposites	Hydrothermal technique with a chemical solution	Phenol, BPA and methylparaben	Recyclable	[94]
ECT-1023t, N- TiO_2 and GO- TiO_2	-	BPA	ECT-1023t was the most efficient	[95]
Bi_2O_3 -ZnO nanorods	Hydrothermal technique and chemical precipitation	Phenol and methylparaben	Easily recovered and reused, high $\cdot OH$ generation ability	[89]
ZnO hierarchical micro-/nanospheres	A facile chemical solution route without any organic solvent or surfactant	-	Active species is $\cdot OH$	[96]
Ti-substituted hydroxyapatite	-	BPA	Large adsorption capacity for BPA	[92]
Nanopillars of TiO_2	Sol-gel template method	-	Efficient	[97]
MnO_2 nanoparticles	A food-grade carboxymethyl cellulose as a stabilizer	17β -estradiol	Promising for in situ oxidation of EDCs in groundwater	[98]
$Ag_3PO_4/LaCoO_3$ nanocomposites	Liquid deposition	-	Enhanced photocatalytic activity and stability	[79]
ZnO nanorods	A simple low-temperature hydrothermal	-	PTCDA sensitized ZnO nanorods showed highest photocatalytic activity	[88]
Nanorod ZnO/SiC nanocomposites	A simple sol-gel method	DEP	Crystalline, nanoscale, rough and porous on surface and possessed absorption	[87]

The biodegradation and photocatalytic degradation of environmental EDCs have obvious advantages, and they are hoped to make up for the weak removal effect of conventional sewage treatment technology on EDCs. Biodegradation is an environmentally friendly method that does not produce secondary pollution and often has no environmental risks. It can effectively reduce the estrogen activity of EDCs. Photocatalytic degradation is characterized by the reduction of persistent organic matter pollution, which means EDCs that are difficult to degrade in the environment can be removed by the catalytic action of photocatalysts. With the development of nanotechnology, it is naturally believed that more efficient and stable catalysts will be applied to the photocatalytic degradation of environmental EDCs in the future.

6. Conclusions

EDCs are now a global concern due to their widespread occurrence, persistence and bioaccumulation. It is a fact that the existing sewage treatment technology cannot effectively remove environmental EDCs. Compared with conventional wastewater treatment technologies, biodegradation and photocatalytic degradation have a promising future because the two approaches are more efficient and environmentally friendly. When it comes to photocatalytic degradation of EDCs, the selection of the

right photocatalyst is very important. The most commonly used photocatalysts at this stage are titanium dioxide and zinc oxide type semiconductor materials. On this basis, more and more nanoscale composite materials have been developed and experimentally proved that they all have excellent photocatalytic effects, such as nanorod ZnO/SiC nanocomposites, $Ce_xZn_{1-x}O$ nanocomposites, Bi_2O_3-ZnO nanorods, gold-modified TiO_2 (Au- TiO_2) nanocomposites, etc. Then, we need to understand the intermediates and degradation mechanisms produced by photocatalytic degradation, which is an urgent problem to be solved.

The biodegradation method has the advantages of economical environmental protection, low input costs, a long duration and simple requirements for equipment and space. It is more suitable for dealing with the pollution of the natural water environment. Studies have shown that some fungi and bacteria can effectively degrade EDCs. In addition to bacteria and fungi, the ability of algae to remove EDCs from water has also been demonstrated. The challenge, then, is to find a microbe or group of microbes that can degrade EDCs in a wide range of environments rather than just one type of endocrine disruptor.

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