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Robust strategies to eliminate endocrine disruptive estrogens in water resources

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Abstract

The widespread occurrence and ubiquitous distribution of estrogens, i.e., estrone (E1), estradiol (E2), and estriol (E3) in our water matrices, is an issue of global concern. Public and regulatory authorities are concerned and placing joint efforts to eliminate estrogens and related environmentally hazardous compounds, due to their toxic influences on the environmental matrices, ecology, and human health, even at low concentrations. However, most of the available literature is focused on the occurrence of estrogens in different water environments with limited treatment options. Thus, a detailed review to fully cover the several treatment processes is needed. This review comprehensively and comparatively discusses many physical, chemical, and biological-based treatments to eliminate natural estrogens, i.e., estrone (E1), estradiol (E2), and estriol (E3) and related synthetic estrogens, e.g., 17α-ethinylestradiol (EE2) and other related hazardous compounds. The covered techniques include adsorption, nanofiltration, ultrafiltration, ultrasonication, photocatalysis of estrogenic compounds, Fenton, Fenton-like and photo-Fenton degradation of estrogenic compounds, electro-Fenton degradation of estrogenic compounds, ozonation, and biological methods for the removal of estrogenic compounds are thoroughly discussed with suitable examples. The studies revealed that treatment plants based on chemical and biological approaches are cost-friendly for removing estrogenic pollutants. Further, there is a need to properly monitor and disposal of the usage of estrogenic drugs in humans and animals. Additional studies are required to explore a robust and more advanced oxidation treatment strategy that can contribute effectively to industrial-scale applications. This review may assist future investigations, monitoring, and removing estrogenic compounds from various environmental matrices. In concluding remarks, a way forward and future perspectives focusing on bridging knowledge gaps in estrogenic compounds removal are also proposed.

Keywords: Estrogens; Environmental impact; Occurrence; Toxicity; Elimination strategies

1. Introduction

Estrogens are a group of hormones available in either form, i.e., synthetically developed or natural. Among estrogens, i.e., estrone (E1), estradiol (E2), and estriol (E3) are three primary endogenous forms that have estrogenic hormonal activity and play a crucial health role. More specifically, these have been categorized as female sex hormones that are mainly responsible for the development and regulation of the reproductive system of females and the maintenance of secondary sexual characteristics. Besides natural estrogens, several synthetic forms have been developed via the chemical synthesis route. Synthetic estrogens are compounds that possess estrogenic activity, e.g., 17α-ethinylestradiol (EE2), estradiol valerate, estropipate, conjugate esterified estrogen, and quinestrol. Whereas diethylstilbestrol, hexestrol, dienestrol, methestrol, and benzestrol are some key examples of non-steroidal synthetic estrogens. Synthetic estrogens are being extensively consumed alone or in combination with progestins as an oral contraceptive pill, approved by the Food and Drug Administration (FDA) USA, treat menopause symptoms, osteoporosis prevention, hypoestrogenism, and metastatic breast and advance prostate prevention (Cobin and Goodman, 2017; Levin, 2018; Yang, He, et al., 2021).

Due to the control or uncontrolled consumption of estrogens, their ultimate excretion in urine and feces from humans and livestock in partially metabolized or relatively un-metabolized form finds its way to water matrices (Combalbert and Hernandez-Raquet, 2010; Yang, He et al., 2021). Estrogens are metabolized in the liver, and cytochrome 450 is mainly responsible for initiating estrogens' metabolism. This enzyme is abundantly expressed in the liver. Hydroxylation is the first step carried out by cytochrome 450 for the metabolism of estrogens. Metabolism alters the intensity of estrogens' action and also changes the profile of its effects on targeted organs (Tsuchiya, Nakajima, & Yokoi, 2005). Steroidal estrogens are increasingly being noticed in the water environment around the globe. Consequently, the hormonal compounds with estrogenic activities are unavoidably merged into the water matrices through ineffectively treated wastewater and runoff/disposal of animal wastes in freshwater or leakage into the groundwater bodies. Besides human and livestock waste, continuous discharge of estrogen-residual-containing industrial wastewater effluents adversely affects aquatic life. For instance, endocrine disruption is one of such adverse effects as these bioactive compounds disrupt the endocrine systems of aquatic organisms (Liang et al., 2020; Šauer et al., 2020), revealing evolving disorders in animals and humans. Estrogens stimulate developmental disorders in aquatic animals (Chiang et al., 2020; Wang et al., 2019). For instance, Šauer et al. (2021) reported the effects of synthetic estrogens, i.e., progestins gestodene and drospirenone, on the sex differentiation in common carp (*Cyprinus carpio*) from embryonic to juvenile stage. Drospirenone, gestodene, and their mixture have anti-gonadotropic activity in carp (*Cyprinus carpio*). Moreover, the exposure of test organisms to a binary mixture of drospirenone and gestodene triggered an enlarged frequency of intersex (32%) as compared to clean water and solvent control groups (both 3%). In an earlier study, Shi et al. (2020) reported the effects of synthetic progestin medroxyprogesterone acetate (MPA, 4.3 ng/L) or dydrogesterone (3.39 ng/L) on eye growth and the transcription of associated genes in zebrafish. The environmental protection agency (EPA) finalized the rule under the safe drinking water act necessitating water systems to monitor estrogen hormones as part of an unregulated contaminant monitoring program (Agency, 2011). The European Parliament has voted to add EE2 to the European Union watch list under the water framework directive, the EU's main water policy instrument for setting anti-pollution approaches (Chatain, 2013). Considering the above-mentioned scenarios, estrogens and related pharmaceutically active residues are increasingly being detected in our water bodies heavily consumed by humans, the livestock sector, and the biomedical sector. Advance wastewater treatment technologies are being globally focused on these days to reduce water pollution (Bilal, Rizwan, Adeel, & Iqbal, 2021; Gan et al., 2022, Rizwan et al., 2022, Rasheed et al., 2019). Water resources are reducing day by day, so challenges affiliated with the removal of estrogens have received great attention due to their harmful effects. Simply changing the operational mode of conventional wastewater treatment plants is not enough to mitigate estrogens. Advance treatments like nanofiltration (NF), membrane bioreactors (MBRs), reverse osmosis (RO) and ultrafiltration (UF), and advanced oxidation process (AOPs) are efficient to remove estrogens. However, these processes have the drawback of high cost (Shahid, Kashif, Fuwad, & Choi, 2021). Integrated treatment systems have been introduced recently to overcome the limitations of conventional and advanced processes. These integrated systems may combine physical, chemical, and biological treatments to obtain the significant removal of estrogens (Ensano, Borea, Naddeo, de Luna, & Belgiorno, 2019). Different biological treatments, including microbial strains and enzymes, have attained great attention as cost-friendly, sustainable and significant tools for the removal of estrogens (Bilal, Adeel, Rasheed, Zhao, & Iqbal, 2019; Ma, Shen, Tang, Li, & Dai, 2022; Singh, Bilal, Iqbal, & Raj, 2021). However, optimization and enzyme stability remained critical always in biological treatment systems. Several studies have reported the widespread distribution and existence of estrogens and related compounds of environmental concern (Combalbert and Hernandez-Raquet, 2010; Yang, He et al., 2021). Several treatment methods (physical, chemical and biological) have been proposed and deployed to tackle this issue of global concern. A detailed comparison was made by considering physical, chemical, and biological treatments (Table 1). However, no specific process exists to eliminate estrogens in wastewater treatment plants (Camacho-Munoz et al., 2012; Huang et al., 2019; Aguilar-Pérez et al., 2021). The current literature lacks a detailed overview of all possible methods in a single place. Thus, herein, an effort was made to spotlight the potential of all treatment processes. Among many reported methods, bio-based treatment systems that include the implementation of microbes as natural factories and their unique enzyme-based catalytic systems have governed a tremendous research consideration (Bilal et al., 2019; Singh et al., 2021a; 2021b; 2021c). So far, most of the available literature is focused on the occurrence of estrogens and related hazardous compounds with limited treatment options. A detailed review to fully cover the several treatment processes is needed. This paper comprehensively reviewed many physical, chemical, and biological treatments to eliminate estrogens and related environmentally hazardous compounds. The major objective of this review article includes a brief knowledge about estrogens, operational perspectives of various advanced physical, chemical, and biological processes to remove estrogens, knowledge about mechanisms involved in estrogen removal, and recognition of gaps for future developments.

2. Estrogens – Sources and environmental fate

Given a nonstop upsurge, discharge of estrogens and other pharmaceutically active compounds is likely to increase the bioaccumulation of estrogens into various receiving water systems (Jiang et al., 2013). Several steroidal estrogens, including E1, E2, E3, and EE2, have been extensively disseminated in different water matrices. For instance, liquid manure, feces, solid livestock waste, lagoon waste, and animal manure have been reported as the primary source of estrogens detection (Biswas et al., 2013). A plethora of literature is available that substantiates the occurrence of estrogens in groundwater, freshwater, and wastewater, though in different quantities from different sources. For example, Yang, He et al. (2021) reported the first large-scale assessment of 34 natural and synthetic sex hormones, including five other estrogens in soils. In addition, the occurrence and distribution of estrogenic substances in surface waters have been reported by Deich et al. (2021). According to the results obtained, natural estrogens, i.e., E1, E2, and synthetic EE2 were the most abundant, with maximum concentrations up to 1.1 ng L^{-1}, 0.7 ng L^{-1} and 0.6 ng L^{-1}, respectively. Regardless of the concentration and type, estrogens primarily enter the natural water matrices via sewage treatment plants and are consequently transported into the oceans (Xu et al., 2014; Deich et al., 2021). Routes of estrogens contamination to ground and surface water bodies are schematically shown in Figure 1.

3. Physical methods for removal of estrogenic compounds

Removing estrogens from water bodies was imperative due to their toxic nature and harmful effects. In this prospect, various physical, biological, and chemical methods have been used in accordance with requirements and efficiency toward removal. Such as, biological processes are beneficial for degrading many organic molecules but are limited to toxic inorganic materials (Gao et al., 2020). In addition, chemical methods such as the advanced oxidation process are useful for removing harmful estrogens with the formation of some byproducts and limiting their applications. These limitations allow biological and physiochemical characterization such as pH, the acid constant, the partition coefficient of water, polarity, hydrophilicity, and degradability measurement at first (Grelska et al., 2020; Simazaki et al., 2015). On the other hand, physical methods include adsorption, reverse osmosis, membrane filtration, nanofiltration, and ultrafiltration, which are very useful for removing inorganic molecules. However, membrane filtration shows limitations due to pore blockage, which causes fouling problems (Si et al., 2019; Katibi et al., 2021).

3.1. Adsorption of estrogenic compounds

The removal of estrogens compound by using solid-phase (adsorbent) in an aqueous phase is a useful technique due to its most efficient, effective and economic prospect. Efficiently, the ability of adsorbent and removal of the particular compound first monitored through specific sorption coefficient (ratio of adsorbed and dissolved targeted compound) and isotherms equations, respectively. Several adsorbents, including activated sludge, activated carbon (ACs), carbon nanotubes (CNTs), graphene oxide (GO), ion exchange resin, molecularly imprinted polymers, chitin, carbonaceous material from waste, and chitosan can be used for the removal of dissolved estrogens. Activated sludge removed estrogens through sorption and degradation after removing excess sludge and became a principal technique to purify sewage (Ren et al., 2007; Andersen et al., 2005; Johnson and Sumpter, 2001; Khanal et al., 2006). The involvement of two processes made this process unclear to understand which one is predominant in eliminating toxic estrogens (Ren et al., 2007). The solubility of natural estrogens in water is less than synthetic ones with a low Henry's law coefficient and less active toward biodegradability. This makes sense that their removal is mainly based on the adsorption process compared primarily to degradation, especially when the retention time with sludge is less (Ren et al., 2007). On the contrary, some researchers concluded that removing estrogen by adsorption process is less than 10 % (Andersen et al., 2003, 2005; Janex-Habibi et al., 2009; Joss et al., 2004; Muller et al., 2008; Ternes et al., 2004). This can be happened due to different experimental setups, as adsorption of estrogens mainly depends on particle size, temperature, total organic carbon, ions content, salinity, and pH. Activated carbon (ACs) is another efficient and effective adsorbent for removing many organic and inorganic estrogens from water bodies. It is widely used for adsorbents due to its efficiency and economical ease in availability (Babel and Kurniawan, 2003; Rivera-Utrilla et al., 2011). In this direction, activated carbon granulate shows high adsorption capacity, and the kinetically controlled process can be affected by environmental conditions (Zhang and Zhou, 2005). The pore size of activated carbon can also affect adsorption capacity, i.e., an increase in pore size reduces the adsorption of estrogens due to their high hydrophobic nature (Fukuhara et al. 2006). Another factor that controls the adsorption ability of ACs is the organic matter present in water bodies irrespective of estrogens due to their high speed of movement toward ACs as compared to estrogens and cover available sites for adsorption (Fukuhara et al., 2006; Kumar et al., 2009; Zhang and Zhou, 2005).

In addition, carbon nanotubes (CNTs) are very useful adsorbents for estrogens due to their excellent mechanical and electronic properties (Kurwadkar et al., 2019). A rolled graphene sheet is present at the surface of CNTs for single-walled CNTs, whereas multiple sheets of graphene are known as multiwalled CNTs (MWCNTs). Irrespective of

ACs, CNTs show considerably different properties as regardless of surface area and pore size, their adsorption ability mainly depends on purity, functionalities, and adsorption sites (Arora and Attri, 2020). The mechanism of estrogens removal is primarily based on pi-pi bond formation and van der Waals interactions among CNTs and estrogens and is responsible for adsorption performance (Kurwadkar et al., 2019). The adsorption ability of CNTs can be enhanced by increasing interstitial space and with the attachment of different functionalities according to the removal of specific estrogens. The application of CNTs on a larger scale is still in the process due to their more toxic effects than ACs (Das et al., 2018). Another family of adsorbent, molecularly imprinted polymers (MIPs) can be used for water treatment to remove toxic waste materials. Several MIPs have been synthesized for this purpose. MIPs adsorbent with an estradiol template is used to study water purification by adding some estrogens in deionized water. These MIPs can be reused after treatment with methanol/acetic acid followed by methanol (Meng et al., 2005). These MIPs can also functionalize with different materials to prepare an adsorbent with multiple adsorption sites. Gao and his coworkers functionalized MIPs with carbon nanotubes and removed estrogens with selectively fast kinetics and high capacity for the molecule’s uptake with an adsorption capacity of 113.5 mmol/g. These CNTs functionalized MIPs show efficiency of up to 95 to 98% and remain constant for different water bodies (Gao et al., 2011; Joseph et al. 2011). Graphene oxide sheets can also be used as an adsorbent for removing estrogens due to their excellent hydrophilicity, a more significant number of oxygens containing functional groups, and high surface area. The maximum adsorption capacity 149.4 mg/g of GO was reported by Jiang and coworkers (Gupta et al., 2017; Jiang et al., 2016). Cellulose is another promising material used for the adsorption of estrogen from water. Although cellulose shows less adsorption capacity towards estrogen in aqueous media with low reproducibility, several modified cellulose adsorbents have been used for water treatment applications (Adewuyi, 2020). Using cellulose for estrogen removal opens a path for using natural polymers having good sustainability and are highly effective at a low cost. These materials for water treatment are only limited to general water contaminants and are not widely applied to remove estrogens.

3.2. Nanofiltration of estrogenic compounds

Natural organic matter and micropollutants can be removed from wastewater and drinking water through the nanofiltration (NF) membrane technique. The separation of estrogen from water bodies through nanofiltration depends on steric hindrance and interaction of charged toxic pollutants with membranes (Berg et al., 1997). Many studies employed crossflow filtration and dead-end-cell filtration to remove estrogens by nanofiltrations. The estrogens removal ability of NF membranes ranges from 1 to 1000 ng/L depending on ionic strength, pH, charge, and contact angle of water with membranes materials (Nghiem et al., 2004; Schafer et al., 2003; Kimura et al., 2003). Different parameters affect various types of estrogens present in water bodies. Such as, the removal of hormones less depends on ionic strength whereas more depends on pH due to repulsive interaction between estrogens and membranes themselves. The mechanism of NF membranes technique is based on multiple processes, including adsorption, charge repulsion and size exclusion. These three mechanisms mainly decide estrogens' removal with different efficiency depending on the type of compound to be removed. The wastewater contains contaminants and estrogen forced toward the pores of the membrane (size 0.2 nm and

0.4 nm), and electrostatic charge and size help them attach to the membranes surface through adsorption (Kingsbury et al., 2013; Sun et al., 2017). The surface of NF membranes can be composed according to the required charge density in accordance with contaminants. During purification, divalent and multivalent ions stuck at the surface of the membrane and water with monovalent ions are allowed to pass (Dharupaneedi et al., 2019). In practical studies, NF method has been used to remove selective estrogens and achieve water with high quality and less organic matter. In this method, no chemical disinfectant is needed to remove microbes and viruses (Li et al., 2020; Datel and Hrabankova, 2020). The mechanism of selective removal of contaminants in NF membrane method is fundamental to understand. Semiao and coworkers found that the pore size plays a key role in the selective contaminant's reduction in NF membranes. Nevertheless, removing many pollutants with a single purification method is still difficult. Therefore, in many applications, the NF membranes method has been used in connection with other water treatments to purify water bodies in multiple steps efficiently.

3.3. Ultrafiltration of estrogenic compounds

Ultrafiltration (UF) is another membrane technology widely used to treat water bodies containing estrogens. Like nanofiltration, the contaminants are collected over a membrane through the filtration process. The filtration process can be changed by changing the pore size, surface charge density, and hydrophobic nature depending on which type of contaminant must be removed by membranes (Schäfer et al., 2011; Simmons et al., 2011). Similarly, hydrostatic pressure used to force water toward membranes also plays an essential role in controlling the particles at the surface of membranes. If the pore size of membranes is more significant, i.e., in micrometer, ultrafiltration becomes known as microfiltration and works on a standard atmospheric pressure (Zhou et al., 2010; Lu and Liu, 2010). On the other hand, membranes with pore size 0.001-0.1µm are used for filtration, known as ultrafiltration, and its efficiency depends on membranes type and the type of contaminants to be removed (Zhou et al., 2010; Lu and Liu, 2010; Acero et al., 2010; Cissé et al., 2011; Gao et al., 2011; Lidén and Persson, 2016). In the ultrafiltration method, membranes operate at low pressure with a crossflow separation. Due to the larger pore size of membranes, this method is mainly used to remove larger particles known as macromolecules. This is a secondary treatment method of considerable attention and extensive application with limited, targeted estrogens removal (Aziz and Ojuma et al., 2020). Patel et al. (2019) used ultrafiltration membranes to remove pharmaceuticals and found that only selected contaminants can be removed using this method. This happened due to the different working mechanisms of NF membranes and UF membranes. In NF membranes, the removal of contaminants is based on hydrophobic adsorption and size exclusion, whereas only hydrophobic adsorption occurs in UF membranes. Therefore, UF membranes are rare to use a single treatment purification of water bodies. Such as, it is very useful in combination with the reverse osmosis process as the contaminants allowed by UF membranes due to low molecular weight can be removed by reverse osmosis membranes. Sun and his teams concluded that particles of larger size could be rejected at the surface of membranes, whereas smaller particles remain concentrated with water bodies and pass-through reverse osmosis membranes with leachate effluents (Sun et al., 2015; Dharupaneedi et al., 2019).

3.4. Ultrasonication (US) of estrogenic compounds

The removal of estrogens using different techniques mainly depends on their physicochemical properties. Ultrasonication (US) method is now advantageous and is an advanced method for removing complex organic/inorganic contaminants from water bodies (Rao et al., 2016; Pokhalekar et al., 2016). This method is known as sonodegradation and produces H_2O_2, $OH^{\cdot}$, $OH_2^{\cdot}$, $OOH^{\cdot}$ Species by sonolysis of water at high temperature and pressure by nucleation collapse caused by ultrasound waves. These US waves cause chemical and thermal breakage of contaminants into gaseous and aqueous states (Naddeo et al., 2013). US treatment method is a clean, safe, and energy-saving method without producing secondary pollutants compared to other water treatment methods (Laxmi et al., 2010). During US treatment, the efficiency mainly depends on the size, acidity, shape, hydrophobicity, and functionality of estrogens and ultrasonication conditions. Another advantage of US treatment is the removal of contaminants in a small concentration compared to other water treatment processes. Im et al. (2014) performed the experiments to remove acetaminophen and naproxen by US treatment and found an excellent efficiency of about 99 % and 86.1 %, respectively. Further studies about the removal of estrogens revealed that efficiency mainly depends on the chemical structure of compounds. Such as a pharmaceutical contaminant, triclosan degraded 95 %, whereas iopromide and erythromycin removed about 50 %. Several factors can affect estrogens' removal by the US method, including promoters, catalysts background ions, water quality, pH, US frequency, temperature, reactor type, US power, and properties of estrogens (Chu et al., 2017). To get high performance by US treatment, all these factors need to be controlled. In this regard, low pH and high temperature and pressure push radical formations in US treatment and increase their efficiency. Similarly, many catalysts can also improve the cavitation bubbles for effective US treatment (Chu et al., 2017).

4. Chemical methods for removal of estrogenic compounds

Advanced oxidation processes are initiated through free radicals and various reactive oxidative species to degrade organic pollutants. Here we have discussed different Advance oxidation-based processes, including Fenton, Fenton like photo-Fenton, electro-Fenton, photocatalytic and various ozone-based processes for degradation of estrogens (E1, E2, E3, and EE2) (Figure 2).

4.1. Photocatalysis of estrogenic compounds

In photocatalytic treatment, the compound degradation is enhanced by activating a catalyst through light energy (Figure 3) (González-González et al., 2022a; González-González et al., 2022b). Catalyst plays a role in improving the reaction rate, and itself remains unaltered after reaction completion. Photocatalyst consists of semiconductor particles that contain a large surface area, valence band and conduction band. Between the valence and conduction bands, there is an energy difference called a bandgap. The photocatalytic reaction initiates when a photon of energy equal or greater to the band-gap is absorbed by the catalyst and promotes the electron transfer from the valence band to the conduction band, and this leads to the generation of a positive hole as well (Leyva, Moctezuma, Baines, Noriega, & Zarazua, 2018). After absorption of light by the photocatalyst, the valence band to conduction band electrons get to transfer, and holes (h^+) are produced in the valence band (Eq. 1). Then hydroxyl radicals are formed by the reaction of the positive hole with water molecules adsorbed on the catalyst's surface (Eq. 2). The target analyte that is adsorbed onto the catalyst's surface may react with the generated hole or electron (Eq. 3), and recombination of charged species is also possible. Superoxide radicals may also cause by the reaction of conduction band electrons with oxygen (Eq. 4). The most used photocatalysts involve ferric oxide (Fe_2O_3), tin oxide (SnO_2), zinc oxide (ZnO), zinc sulfide (ZnS), silicon, and titanium dioxide (TiO_2). Titanium dioxide is considered one of the best photocatalysts because it is photo-stable, commercially available, low toxic, and can degrade various molecules under ambient conditions. TiO_2 exists across multiple mineral forms like rutile, anatase, and brookite. Among them, anatase is considered the best choice as a photocatalyst because of the transport of excitons to the surface (Luttrell et al., 2014). P25, which consists of almost 85% anatase and 15% rutile, is the most widely employed TiO_2. Photocatalytic reactions involving TiO_2 have been described in Eq. 1-4, where h^+ represents hole forms through missing electrons and P_{ad} represents the adsorbed pollutant on the catalyst surface. Previously TiO_2 has been used widely to degrade estrogens by many scientists (Sornalingam, McDonagh, & Zhou, 2016).

$$TiO_2 + hv \longrightarrow TiO_2\,(e^- + h^+) \text{ ——— Eq .1}$$

$$TiO_2\,(h^+) + H_2O \longrightarrow TiO_2 + \dot{OH} + H^+ \text{ ——— Eq .2}$$

$$TiO_2\,(h^+) + P_{ad} \longrightarrow TiO_2 + P_{ad}^{+\bullet} + H^+ \text{ ——— Eq .3}$$

$$TiO_2\,(e^-) + O_2 \longrightarrow TiO_2 + O_2^{+\bullet} \text{ ——— Eq .4}$$

Menon reported photocatalytic degradation of E2 (17β-estradiol) and EE2 (17α-ethinylestradiol) by using TiO_2-ZnO nanocomposite under UV and visible irradiations. 100% degradation was obtained for both estrogenic compounds after 240 min@ $C_0 \leq$ 1 mg/L, while 25% degradation was obtained at $C_o \leq$ 10 mg/L under visible light. Fused rings of estrogens broke down into small molecules as byproducts which were mineralized through the removal of TOC. While under UV light, 30% and 20% mineralization was obtained for the E2 and EE2 respectively (@C_o 10 mg/L) while in visible light, 25%, 10% mineralization was obtained for E2 and EE2, respectively. The estrogen receptor-positive MCF-7 breast cancer cells were used to determine the estrogenicity through an E-screen assay. Analysis revealed that organic compounds obtained after degradation were sorbed on nanocomposite. Desorption was carried out following recalcintion (@ 600 °C) for 1 hour, leading to the regeneration of nanocomposite active sites. This enabled the reuse of nanocatalyst for 3 cycles under visible light without visible light activity loss (Menon, George, Tatiparti, & Mukherji, 2021). In the latest report, chemically activated g-C_3N_4 (graphitic carbon nitride) nanorods were utilized to degrade EE2 in visible light in water and real hospital wastewater. Pure and hydrothermally activated g-C_3N_4 photocatalysts were used, and activated g-C_3N_4 was found with an enhanced surface area due to intra-layer delamination and depolymerization. Activated g-C_3N_4 showed potential degradation of EE2 in water (96% @ 45 min) and hospital wastewater (HWW 99.09%, 30 min) in the presence of visible light. This research provides insight into the development of hetero-junction visible light photocatalyst. The estrogenicity of treated water samples was evaluated through the performance of the Yeast Estrogen Screen. Potential removal of estrogenic activity of EE2 was attained at almost 99% (<45 min, 3 mg/l) under visible light-activated g-C_3N_4. After 5 cycles, the loss of degradation potential (10%) was observed (Kumar, Avisar, Betzalel, & Mamane, 2020). Zinc oxide ZnO has also been used to degrade estrogens (Sornalingam et al., 2016). After titanium dioxide, the ZnO is the most common photocatalyst. The activity of ZnO decreases due to dissolution and pollutes the water by releasing free Zn ions. Bayode, Vieira, et al. (2021) reported the potential of p-n heterostructured ZnO/GO photocatalyst supported on clay to remove various steroids as E1, E2, E3, and EE2. The catalyst was fabricated through a microwave-assisted strategy. The existence of carbon interlayer (from *Carica papaya* seeds) and graphene oxide were important for the efficacy of photocatalyst. In a single solute system, the removal of estrogen was found >89 and as high as 98%, while in a mixed system, it was >91 and as high as 98 %. In real wastewater, the efficiency of photocatalyst ZnO/GO/C was found 65.9, 66.7, 62.6 and 77.7% for the removal of E1, E2, E3 and EE2, respectively. After 3 cycles of reuse, the efficacy of photocatalyst was >80%. The existence of humic acid reduced the removal potential upto >70% for tested estrogens, while the incorporation of 1 % hydrogen peroxide enhanced the estrogens' photo-degradation up to 100% within 10 minutes. COD test revealed the estrogen oxidation level after photo-degradation (51-77%). Photo-degradation was mainly through hydroxyl radicals ($OH_{\cdot}$) via superoxide radical ($\cdot O_2^{-}$) and hole (h^+) formation from the photocatalytic composite. In the ZnO and GO composite, the electron-hole pairs are formed under light. The holes and electrons migrate between ZnO and GO via a carbon interlayer (Figure 4). The carbon acts by hindering the quick recombination of electron-hole pairs through the transference of electrons between ZnO and carbon, which enhances the absorption of visible light and is responsible for increasing the photocatalytic potential of composite catalyst (Sun et al., 2016). A toxicity test was checked through *ceriodaphnia silvestrii* , and it was found that mild toxicity was found (LC_{50} = ca. 0.89 mg/L) (Bayode, Vieira, et al., 2021). Another efficient photocatalyst (Fe@PSK@GO) made from Kaolinite clay, Fe_2O_3, and graphene oxide was used to remove various estrogens (E1, E2, E3, EE2) under visible light. The synthesized catalyst oxidized the estrogens at >80% in water. Mineralization of estrogens was obtained in the range of 58-73%. The iron oxide presence in composite enhanced the photocatalytic potential, and further incorporation of graphene oxide increased the efficiency of photocatalyst. The incorporation of a carbon source doubled this potential. The holes and superoxide radicals were the main sources of photocatalytic efficiency of the nanocomposite. Toxicity assay showed that treated water proved safe for the use of human beings. The catalyst could be recycled three times without potential loss (Bayode, dos Santos, et al., 2021). CdS is a known photocatalyst that is responsive to light in a good way and has been widely used (Zhao et al., 2020). The novel CdS nanorod/TiO2 (B) nanobelt nanocomposite, through the hydrothermal process, was synthesized to remove EE2 in visible light. TiO_2-B type was crosslinked with the Cds nanorods to generate heterojunction with good removal (92%) than pure Cs nanorods within 120 minutes (Luo et al., 2019). Some commonly used photocatalysts for removing various estrogens have been presented in Table 2.

4.2. Fenton, Fenton like, and Photo Fenton degradation of estrogenic compounds

Fenton's approach is promising to degrade organic contaminants. Iron-based salts are utilized in this process to decompose hydrogen peroxide into hydroxyl radicals. Initially, the hydroxyl radicals and Fe^{+3} ions are generated through iron salts (Fe^{+2}) and hydrogen peroxide. In the next step, the Fe^{+3} reacts with other reaction intermediates and forms $Fe^{+2,}$ and this step is enhanced in the presence of light. This process has the advantage of the involvement of cost-friendly reagents (Eq. 5 & 6). The degradation potential of the Fenton process depends on the concentration of the catalyst, temperature, and pH of the reaction medium. In 2005, the first time degradation of estrogens was reported using UV-

Vis/Fe(III)/H_2O_2. Degradation efficiency was found dependent on the pH and concentration of Fe (III) and H_2O_2. E1 degradation was almost 98% after 160 min (Feng, Ding, Tu, Wu, & Deng, 2005). Iron (III) salts can replace iron (II) salts. This is known as the Fenton-like process, where Fe+3 and hydrogen peroxides are utilized. Hydroxyl radicals are produced due to the decomposition of H_2O_2, and Fe^{+3} is converted to Fe^{+2} (Eq. 7) Fenton-like process also generates peroxyl radicals (Eq 8, 9). The Fenton reaction performs efficiently at low pH values (2-5) to treat wastewater pollutants.

$$Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + OH^{-} + HO^{\bullet} \quad \text{———} \quad \text{Eq. 5}$$

$$Fe^{+3} + H_2O_2 \longrightarrow Fe^{+2} + H^{+} + HO_2^{\bullet} \quad \text{———} \quad \text{Eq. 6}$$

$$Fe^{+3} + H_2O_2 \longrightarrow Fe^{+2} + OH^{-} + HO^{\bullet} \quad \text{———} \quad \text{Eq. 7}$$

$$Fe^{+3} + H_2O_2 \longrightarrow FeOOH^{+2} + H^{+} \quad \text{———} \quad \text{Eq. 8}$$

$$FeOOH^{+2} \longrightarrow Fe^{+2} + HO_2^{\bullet} \quad \text{———} \quad \text{Eq. 9}$$

Conventional Fenton reaction has limitations like narrow pH range, catalyst recycling, etc. Yaping & Jiangyong (2008) synthesized a heterogenous Photo-Fenton catalyst, α-FeOOH coated resin. This catalyst degraded E2 efficiently in the presence of H_2O_2 under UV light over a wide range of pH (3-11) (Yaping & Jiangyong, 2008). Various iron-based heterogeneous Fenton catalysts, such as supported and unsupported iron catalysts of zero-valent iron, and multi-metallic systems iron oxides, proved efficient for the degradation of various organic contaminants. The Fenton process is enhanced by electricity, UV, Visible light, and complexing agents (Scaria, Gopinath, & Nidheesh, 2021). A heterogeneous catalyst nano-zero valent iron Fenton system loaded with citrate ligand (C-NZVI) was fabricated to degrade estrogens. Citrate contains the hydroxyl fragments and covers the surface. This can overcome the defects of nZVI and deal with acid corrosion, oxidation, and agglomeration. Hydroxyl and superoxides were formed and degraded the E2. Ligand performed as the ion transport channel and enhanced the excitation of formed radicals (hydroxyl and superoxide) and singlet oxygen (Figure 5) (Yang et al., 2021). Catalyst efficiently degraded the E2, with the degradation potential increasing by 4.59 folds (Yang et al., 2021). Mechanism of degradation of E2 exhibit that four rings may be destroyed alternatively starting from the benzene ring. Silva and coworkers carried out a study to degrade the various estrogens (E1, E2, E3, EE2) from real wastewater treatment plant (WWTP) effluents in the presence of white LED Photo-Fenton reaction. For the photo-Fenton response, the Fe^{+2} (Ferrous sulfate heptahydrate) and hydrogen peroxide were used at various concentrations, and white LED light ($\lambda = 455$ nm) was used for irradiation purposes. To quantify the estrogenic activity, the yeast estrogenic screen test was used. Under optimal conditions, the Photo-Fenton process resulted in 62% removal of estrogenic activity and 59% mineralization. Treated water samples were not found toxic to *Aliivibrio fischeri* , and almost 80% of estrogens were removed. Thus results of the study showed that LED irradiated photo Fenton reaction can be used to treat wastewater possessing estrogens (Silva et al., 2021). Some commonly used Fenton, Fenton like, and Photo Fenton processes for degradation of estrogenic compounds have presented in Table 3.

4.3. Electro-Fenton degradation of estrogenic compounds

The electro-Fenton process is based on the generation of H_2O_2 on the cathode, which produces hydroxyl radicals after dissociation in the Fe^{+2} catalyst via the Fenton reaction. This process occurs in acidic media due to the availability of more H+ ions to produce maximum hydrogen peroxide and avoid hydrogen peroxide decomposition into oxygen and water (Poza-Nogueiras, Rosales, Pazos, & Sanroman, 2018). The electro-Fenton process is a highly reported reaction for the degradation of various environmental pollutants from an aqueous solution, but its applications are not widely reported for estrogens degradation. In 2012, the Electro-Fenton process was reported to degrade estrogen hormones. EF was used to degrade E2 in an aqueous-acetonitrile mixture. Platinum anode and carbon felt cathode was used. The initial concentration effects of E2 were observed where 1, 5, and 10 mg/L of estrogen were completely degraded in 25, 30, and 40 min, respectively. The efficacy of the Electro-Fenton process was confirmed for high-rate degradation of E2 in an aqueous-acetonitrile mixture compared to the methanol (co-solvent). The 100% degradation of 5 mg/L of E2 was optimized (@ 0.2mM Fe^{+2} and 200 mA). In this study, the toxicity issue of obtained byproducts was not addressed (Naimi & Bellakhal, 2012).

4.4. Ozonation of estrogenic compounds

Ozone can react with organic pollutants due to its strong oxidation potential. This technique is highly employed for wastewater treatment. The ozonation process can be coupled with UV, H_2O_2 or photocatalysis to enhance the potential to degrade organic molecules. This may be attributed to an increase in the number of reactive radicals. Hydrogen peroxide can be cost-friendly and highly soluble in water (Vieira, de Farias, Spaolonzi, da Silva, & Vieira, 2021). Maniero et al. reported the degradation of 17β-estradiol and 17α-ethinylestradiol in the presence of ozonation and O_3/H_2O_2 processes under different pHs (3, 7 and 11). Through the YES assay, the estrogenic activity was evaluated. Ozonation and O_3/H_2O_2 were found effective in removing both estrogens in an aqueous medium. 17β-estradiol and 17α-ethinylestradiol were removed 100% and 99.5%

under pH 3, respectively. Estrogenic activity was removed completely in Ph for ozonation and O_3/H_2O_2 (Guedes Maniero, Maia Bila, & Dezotti, 2008). According to a report, various estrogens (E1, E2, E3 and EE2) were degraded in different oxidation processes as O_3, O_3/UV and $O_3/UV/H_2O_2$. Significant degradation was obtained in both O_3/UV and $O_3/UV/H_2O_2$, but it was comparatively low than O_3. And this may be attributed to presence of hydroxyl radical scavengers as carbonates and bicarbonate ions (Pešoutová, Stříteský, & Hlavínek, 2014). The clay was used as a catalyst in the ozonation process to degrade EE2 in an aqueous solution. Acid-activated bentonites and ion-exchanged montmorillonite (NaMt and Fe(II)Mt) exhibited catalytic potential during the ozonation of EE2. In the presence of Fe(II)Mt, the degradation of EE2 was obtained at almost 96% after one minute of ozonation. And after 15 minutes, under the same conditions, almost 99.9% degradation of EE2 was obtained. Acid-activated bentonites showed great potential for providing total mineralization within a short time of ozonation. The catalytic potential of clay correlates with its surface basic character and hydrophilicity. This study provides insights into soil behavior in the oxidative degradation of organic compounds (Boudissa et al., 2020). Perondi and his colleagues demonstrated the removal of E2 present in surface water under UVC (254 nm) light in the presence of various oxidants as O_3, H_2O_2 and TiO_2. Pseudo-first order kinetics were followed: $k_{UV/O3} > k_{UV/TiO2} > k_{UV/H2O2} > k_{UV}$. Efficient removal was obtained by photolysis (UV), photo-peroxidation (UV/H_2O_2), photocatalysis (UV/TiO_2), and photo-ozonation (UV/O_3). Eight transformation products were obtained. These may be obtained by ring-opening of E2 and hydroxyl radical (Perondi et al., 2020). Table 4 presents various ozone-based processes for the removal of estrogens.

5. Biological methods for removal of estrogenic compounds

5.1. Microbial degradation of estrogenic compounds

Biodegradation implicates the utilization of microbial strains like bacteria and fungi for the degradation and transformation of endocrine-disrupting chemicals and many other environmental contaminants. It has been considered a leading removal mechanism that affects the fate of endocrine-disrupting chemicals in the environmental matrices. Plenty of studies in the recent decade has investigated the biodegradation of various EDCs through diverse microorganisms (Husain and Qayyum, 2012; Zhang et al., 2016; Ahuactzin-Pérez et al., 2018). Lignin-degrading organisms, e.g., white-rot basidiomycetes, have gained attention as efficient candidates for degrading emergent micropollutants from the environment. Cabana and coworkers (2007) reported the WRF's capability for eliminating EDCs in different environmental compartments and recommended establishing reliable and robust biotechnological processes to treat EDC-loaded water and wastewater systems. In another study, Cajthaml (2015) substantiated the potentiality of ligninolytic fungi in degrading and transforming EDCs using a versatile lignin-modification enzymatic system and cytochrome P-450. Ligninolytic fungi-assisted EDCs degradation is likely via micropollutants polymerization or degradation by enzymes. It is worth noting that ligninolytic fungi are among the few microorganisms that efficiently degrade PCBs and EE2 (Cajthaml, 2015).

Ligninolytic bacteria are robust microbes for EDC degradation due to their ability to secrete lignin-degrading enzymes, including manganese peroxidase and laccase. Due to high tolerance in diversified environmental matrices and genomic maneuverability, bacteria possess a profound ability to catalyze EDCs biodegradation. In addition, integration of bacteria with physical approaches, i.e., adsorption, offers unique advantages with the excellent aptitude to eliminate EDCs in aqueous environments (Zhang et al., 2016). Nonetheless, the introduction of harmful microbes into the surroundings is the primary concern of adopting biodegradation approaches for removing EDCs, which may lead to antibiotics and multiple drug emergence issues. Thus, the enzymatic process involving extracellular ligninolytic enzymes is likely a more appropriate substitute.

5.2 Removal of estrogenic compounds by ligninolytic enzymes

The environmental risk of EDC exposure to humans and the inadequate efficiency of classical treatment strategies for complete EDC removal have rekindled the interest of researchers in exploring alternative options for EDC removal in wastewater. The exploitation of ligninolytic oxidative enzyme-based treatment processes has lately garnered much attention as a promising and eco-friendly alternative for eliminating EDCs. Ligninolytic enzymes, including manganese peroxidase (MnP), Lignin peroxidase (LiP) laccase, and versatile peroxidase (VP), have recently been used to degrade EDCs in water matrices efficiently. Becker et al. (2017) investigated the biocatalytic transformation of endocrine disrupters in real wastewater and artificial mixtures by laccases derived from *Myceliophthora thermophila* and *Trametes versicolor*. Results revealed the feasibility EDCs and hormones degradation even at a very low concentration of laccases. Adsorption onto support matrices was the effective elimination mechanism in the artificial mixtures. In binary solutions, immobilized biocatalyst presented high performance for EDCs removal in the initial 6 h (87% for *M. thermophila* and 83% for *T. versicolor*); however, adsorption superimposed this degradation during the experimental course (99%

after 24 h). A comparable removal pattern was detected in real wastewater but low adsorption efficiency and enzyme activity. The immobilized laccase-based biocatalytic system displayed the maximum removal efficiency of androgenic (99% removal after 6 h) and estrogenic (82% after 24 h) activity. Efficient degradation of EE2 by *Lentinula edodes* was attributed to the laccase since the induced production of laccase increased the degradation efficacy of tested pollutants from 50% to 80% (Eldridge et al., 2017).

A commercial laccase from *M. thermophila* was used to design an enzymatic membrane reactor to remove E1 and E2 continuously. The effects of hydraulic residence duration (1-4 h), oxygen frequency supply, and laccase activity (500-1,000 U/L) were also assessed. Interestingly, high degradation efficiencies between 64-100% were achieved with a corresponding degradation rate of 0.96-2.92 mg/(L·h). The estrogenic activity of effluent was diminished to over 95%, proving the practicality of laccase-assisted bioreactor for estrogenic compounds removal (Lloret et al., 2012). To improve the enzyme stability and degradation efficiency in a packed bed reactor, Eupergit supports immobilized laccase was operated in a fluidized bed reactor to remove estrogens. In addition to a significant improvement in biocatalyst stability (over 16 days), removal levels increased to 76 and 90%. The estrogenic activity of the effluent was also decreased up to 90%. In conclusion, immobilized laccase-based technology appears a promising tool for extending the exploitation of laccases in environmental bioremediation.

LiP is an emerging enzyme class produced by various fungal strains, i.e., *Phanerochaete chrysosporium*. These fungi also have veratryl alcohol (VA) as a secondary metabolite that regulates the functions of LiP. Mao et al. (2010) reported the effective removal and transformation of E2 via LiP-mediated catalytic reactions, which can be substantially boosted using VA. They evaluated enzyme reaction kinetics and LiP activity in the systems with or without VA. Experimental findings substantiated higher removal and transformation of E2 by VA through two effects, including mitigation of LiP inactivation and modification of enzymatic catalytic kinetics. MnP is another important lignin-modifying enzyme for the removal and degradation of EDCs. Tamagawa et al. (2006) treated steroidal estrone with *P. sordida* YK-624 in high-carbon and low-nitrogen culture medium ligninolytic conditions. After 5 days of treatment, E1 concentration was reduced by 98%. The disappearance of E1 was ascribed to the activities of ligninolytic enzymes MnP and laccase, which were detected during the treatment. HPLC analysis revealed the complete disappearance of E_1 in the reaction following 1 h exposure to either laccase or MnP. The yeast two-hybrid assay system evidenced that the estrogenic activity of E_1 was also completely eliminated by 2 h of enzymatic treatment.

VP has emerged as a promising biocatalyst to eliminate EDCs in the environment. VP integrates the substrate preference of LiP and MnP (Ruiz-Duenas et al., 2009). The catalytic cycle of VP relies on the concerted action of various compounds, like cofactors, substrates, and mediating agents that initiate and take part in the biocatalytic cycle. Taboada-Puig et al. (2011) formulated cross-linked enzyme aggregates (CLEAs) from glucose oxidase and VP to evaluate their potential to remove different EDCs, triclosan, NP, BPA, E2 and EE2. The as-synthesized CLEAs could remove all tested pollutants except for triclosan, and the elimination of estrogenicity was over 55% for all EDCs. Therefore, incorporating glucose oxidase with any other ligninolytic enzyme is suitable to remove EDCs. In another study, the same group used VP-induced Mn^{3+}-malonate oxidant for continuous elimination of triclosan, BPA, E1, E2, and EE2 from real and synthetic wastewaters in a two-stage (TS) system and observed a degradation efficiency in the range of 28 to 58 µg/L min, with negligible enzyme deactivation. Results revealed a 14-fold improvement in the VP-assisted removal efficiency of EDC in a TS system than enzymatic membrane reactor (EMR). Moreover, the functional challenges faced during EMR system were also circumvented. VP-coupled TS enzymatic system presented a 100% degradation rate for all studied EDCs, thus substantiating the feasibility of this system for efficiently eliminating EDC even at high concentrations (Taboada-Puig et al., 2015).

6. Transformation mechanisms and products

The disappearance of the parent molecule of estrogen is used to assess the removal. Estrogen-derived molecules have a significant impact on the environment. Therefore, it is important to understand the removal mechanism of estrogens and their formed by-products and intermediates. Determination of degradation routes identifies the hurdles of the process (Rathner, Petz, Tasnádi, Koller, & Ribitsch, 2017). Evaluation of final products may facilitate an increase in the purity of the final steam of products through an appropriate separation approach. Conclusively, the operational process and removal potential of estrogens may be enhanced. Different degradation methods provide various end products. Photocatalytic degradation of E2 and EE2 through TiO_2-ZnO nanocomposite under UV and visible irradiations was determined, and both estrogens were degraded. Fused estrogens rings were broken down into simple small compounds that were further mineralized by removing TOC (Total organic carbon) (Menon et al., 2021). Bisphenol A (BPA) was degraded using $S_2O_8^{2-}$/UV-C and H_2O_2/UV-C treatments. LC-MS/MS was used to evaluate the degradation products. A bioassay revealed that obtained by-products after degradation were more toxic and harmful than BPA at the initial point of H_2O_2/UV-C. After degradation, various ring-opening products like oxalic acid, succinic acid, fumaric acid, 3-methyl benzoic acid and 4-sulfobenzoic acid were obtained after degradation (Olmez-Hanci et al., 2015). Laccase and peroxidases oxidized the phenolic group and produced phenoxyl radicals (Beck et al., 2018). Sometimes, the phenoxy radicals combine to create a dimer of the initial molecule. In the next step, these formed dimers may get oxidized again through oxidoreductase enzymes and form trimmers up to oligomers (Xia et al., 2014). At the initial stage of the reaction, the production of phenoxyl radicals demonstrates the disappearance of the molecule monomer. The radical oxidation mechanism is involved in the enzymatic transformation of 17β-estradiol and this leads to the formation of dimers and trimmers. Xia and colleagues reported the removal of 17β-estradiol by using the laccase enzyme in the existence of organic matter. This happened because of electron resonation on phenoxide oxygen to benzene and the production of promising active sites on the estrogenic molecule (Xia et al., 2014). The mass spectrum showed the m/z peak at 271, showing the residue of starting of 17β-estradiol. The degradation pathway of 17a-ethinylestradiol showed the same mechanism as that of 17β-estradiol. Laccase was used to remove the 17a-ethinylestradiol and the main product of the reaction was found to dimer of 17a-ethinylestradiol with m/z peak at 591 after 60 minutes of reaction. However, at later stages of reaction the concentration of dimer decreased. This was because the dimer oxidation directally through laccase and indirect oxidation may occur with the help of monomer radicals. This may lead to 17a-ethinylestradiol oligomeric derivatives (Tanaka et al., 2009). Golveia et al. (2018) used laccase for the removal of 17a-ethinylestradiol.

Mass spectrum results combined with the electrospray ionization and detector (time of flight) exhibited a dimer as the main product of the transformation reaction. While mass spectrum obtained after 6 h has only one peak at m/z of 311, which shows the presence of a new degradation product. This new product was produced because of hydroxyl radical attack on 17a-ethinylestradiol, leading to dehydration and attack of hydroxyl radical, further providing 17a-ethinylestradiol semiquinone (Golveia et al., 2018). Trudeau et al. (2011) demonstrated the almost complete transformation of E1 into lumiestrone under illumination within 5 minutes. More radiation exposure leads to 100% E1 degradation (Trudeau et al., 2011). Mboula et al. (2015) carried out the photocatalytic degradation of E2 in solar light by employing various titanium dioxide catalysts. The obtained photo-products were examined. Intermediates possessed the phenolic moiety, which caused the estrogenic activity of the solution. Incorporation of hydroxyl moiety was suggested as a mass difference of 16 m/z was found of parent and intermediate ion. Intermediate having a mass of 288 g/mol was ascribed as 2-hydroxyestradiol or its resonating structure (10ε-17β-dihydroxy-1,4-estradien-3-one) (Mboula et al., 2015).

7. Toxicity and estrogenic activity assessment of transformed byproducts

AOPs are potential processes for removing a wide range of environmental pollutants from water bodies. But due to high operational costs and various studies, different byproducts are generated from parent compound degradation. The formed b-products are sometimes more toxic than parent molecules. Identifying and quantifying byproducts is still a challenge due to their low concentration and solution complexity (H.-C. Chen, Kuo, & Ding, 2009). Analysis of byproducts is necessary for the safety of living beings. Different analytical techniques and methods have been developed to identify photo-products qualitatively and quantitatively. Hyphenated techniques as GC/MS, LC/MS, LC/MS/MS, GC/MS/MS are employed to detect pollutants and their degradation byproducts. Several studies focused on photo-degradation of parent molecules, which is not enough to find the estrogenic effect of photo-products. Few intermediates show high estrogenicity compared to their parent molecules (Mboula et al., 2015), which forced them to evaluate their biological potential. It is also necessary to assess the estrogenicity of aquatic systems to check the synergistic effects caused by different photo-transformed byproducts (Yan & Song, 2014). Various methods are used to determine estrogenic activity and Yeast estrogen screen assay (Yes) is the most commonly used technique to measure the potency of estrogen hormones. Photocatalytic activity of TiO_2 removed the estrogenic potential of E1, E2 and E3 in 30 minutes, while only 37% removal was observed in the photolysis process. Removal of estrogenic activity followed the pseudo-first-order kinetics for photolysis and photocatalysis with the constant rate values of 0.0069/min and 0.0461/min, respectively (W. Zhang, Li, Wu, & Hu, 2012). Whidbey and his colleagues carried out the YES assay and photoproducts of E2 and EE2 showed no estrogenic activity under indirect photolysis. At the same time, E1 degradation formed the limestone, which showed moderate activity under direct photolysis. Degradation of the phenolic group of hormones is the cause of loss of activity (Whidbey et al., 2012).

Photoproducts of E2 showed no estrogenic activity in yeast estrogen-based assay (Ohko et al., 2002). Dimitroula et al. (2012) determined the removal of estrogenicity of a mixture of phenol, bisphenol-A and EE2 spiked in secondary treated STP effluent and observed loss inactivity (30%). Degradation of EE2 in wastewater exhibited 27% reduction in estrogenicity evaluated by YES assay. Degradation of E1, E2 and EE2 in wastewater provided 30% removal of estrogenicity even parent molecule has completely removed in 120 minutes, showing that few intermediates generated were also estrogenic (Frontistis et al., 2012). Estrogenicity of E2 photodegraded products was evaluated and it was found that estrogenic activity was not removed. Sample of reaction taken at 15 min exhibited high estrogenic effect in comparison of initial E2 solution. This may be due to the formation of byproducts that were highly estrogenic compared to E2 or this may also be due to the combined estrogenic potential of E2 and its photo-degraded products (Mboula et al., 2015).

8. Way forward and future perspective

The presence of pharmaceuticals in our water resources poses adverse effects on the environment. Treated wastewater is used for irrigation worldwide, but if it is not appropriately treated, the risk of estrogenic contamination increases. This study focuses on removing estrogens from water sources using various physical, chemical, and biological approaches. We have established multiple areas in which potential interventions may impact change. Firstly, there is a need to develop drugs based on green chemistry to be quickly metabolized by the body and undergo facile environmental biodegradation. Previously designed treatment plants had low capacities, so there is a need for their upgradation by integrating them with novel structures, disposal approaches, and monitoring systems, keeping in view the demands and focusing on the recovery of resources. The literature shows that treatment plants based on chemical (photocatalysis, Fenton, Fenton-like and Photo Fenton, electro-Fenton and ozonation-based degradation) and biological (microbial and enzymatic degradation) approaches can be potent cost-friendly for removal of estrogenic pollutants. Secondly, there is a need to properly monitor and dispose of the usage of estrogenic drugs in humans and animals, because sometimes drugs are disposed of intentionally in flushes and enter the sewer system. Industries involved in production and health care units that dispose of their wastes in the ecosystem are also significant sources of estrogenic waste.

The practices can be collecting expired and unused estrogenic products and regulating disposal norms. Previous developments regarding biosensors for estrogen detections have been reported. Electrochemical, cell-based, optical, and organism-based biosensors have been introduced for sensing estrogens in environmental matrices (Lu, Sun, & Sun, 2020). Dehalogenase enzymes have been an important tool for sensing halogenated molecules. Various biosensors based on dehalogenation enzymes have been reviewed in detail to sense halogenated molecules (Gul et al., 2021). Gul and colleagues also developed a 3-dimensionl platform integrated with smart phone ambient light sensor to detect halogen-based pollutants (Gul et al., 2021). Therefore, the attachment of different sensors with treatment plants can be helpful to find these compounds.

Thirdly, the provision of guidelines about the allowed limit of estrogens in wastewater treatment plant effluents may facilitate the researchers for practical applications of chemical and biological-based treatments and their potential to degrade these effluents in useful products. Finally, attention should be given to using microbes with hybrid treatment systems, keeping in more capacity of microbes to bear environmental stress. This review proposes that hybrid technologies can be a good choice for wastewater treatment for removing estrogens. These processes will help remove the drugs and protect the environment from damage efficiently.

9. Conclusions

Endocrine disruptive chemicals (EDCs) have been known to pose potential menaces to the environmental matrices and living entities. Considering the complexity and concentrations of estrogenic compounds, the development of appropriate treatment approaches is indispensable to ensure the effective elimination of disruptive endocrine estrogens in water resources. Various physical, biological, and chemical methods have been applied following the requirement and efficiency for removal. Physical processes, including adsorption, reverse osmosis, membrane filtration, nanofiltration, and ultrafiltration, have been widely adopted to remove EDCs. Applying adsorption-based treatments for eliminating EDCs are mounting using many adsorbents. Nevertheless, the assessment for continuous use at a large scale remains to be implemented. In addition, the membrane filtration showing good efficiency is restricted to only a few membranes. Additional studies are required to explore a robust and more advanced oxidation treatment strategy that can contribute effectively to industrial-scale applications. Exploiting ligninolytic oxidative enzyme-based treatment processes has recently gained prodigious attention as a promising and eco-friendly alternative for eliminating EDCs. Ligninolytic enzymes, including MnP, laccase, and VP, have efficiently degraded various EDCs in water matrices. However, a relentless improvement to overcome the limitations of all physicochemical techniques might outspread the EDCs removal performance, treatment, and applicability.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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List of Figures

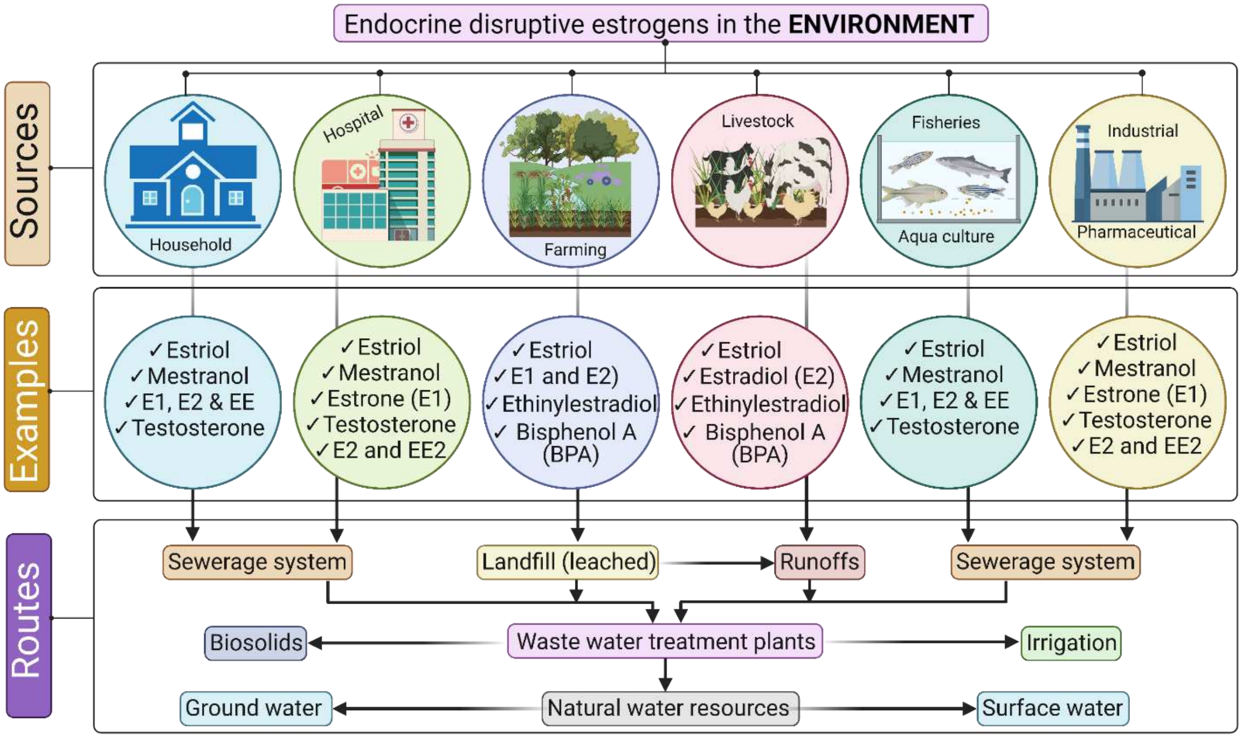


Figure 1 Routes of steroidal estrogens contamination to ground and surface water bodies. *Created with BioRender.com and extracted under premium membership.*

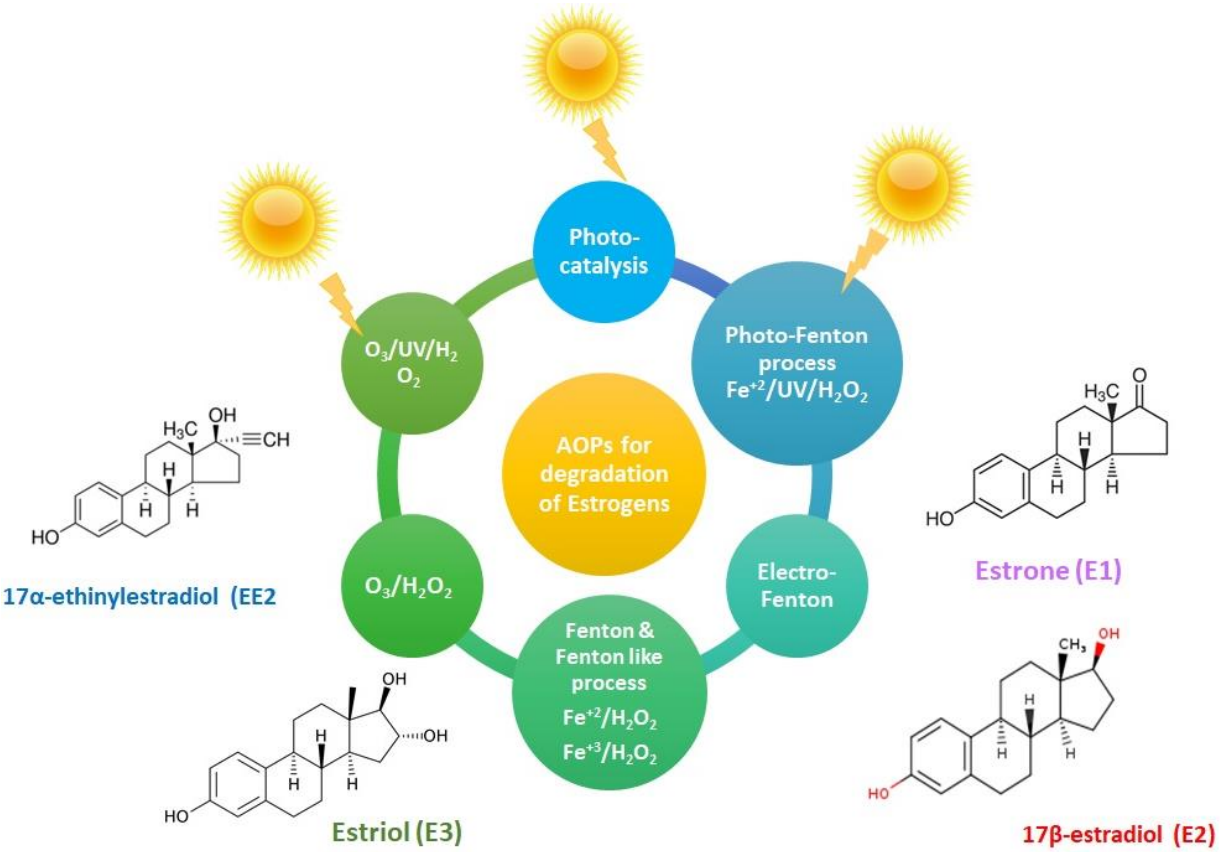
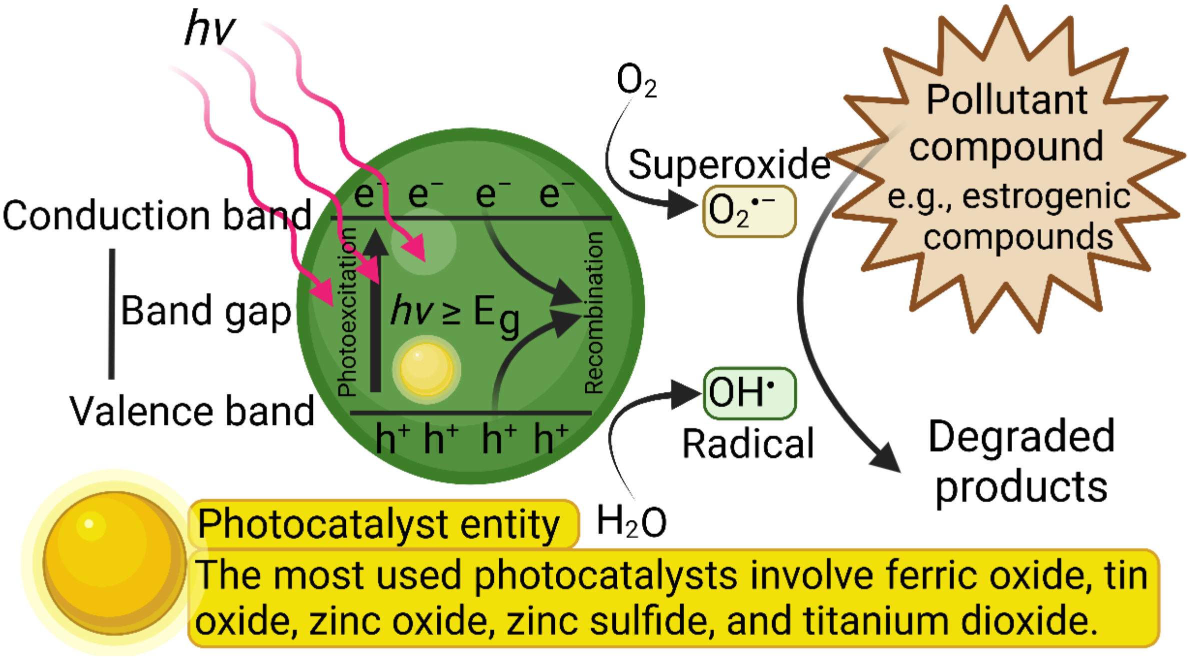


Figure 2 Advance oxidation processes for degradation of Estrogens.



The most used photocatalysts involve ferric oxide, tin oxide, zinc oxide, zinc sulfide, and titanium dioxide.

Figure 3 Schematic illustration of photocatalysis mechanism via the generation of free radicals and superoxide to catalytically degrade hazardous pollutants, e.g., estrogenic compounds. *Created with BioRender.com and extracted under premium membership.*

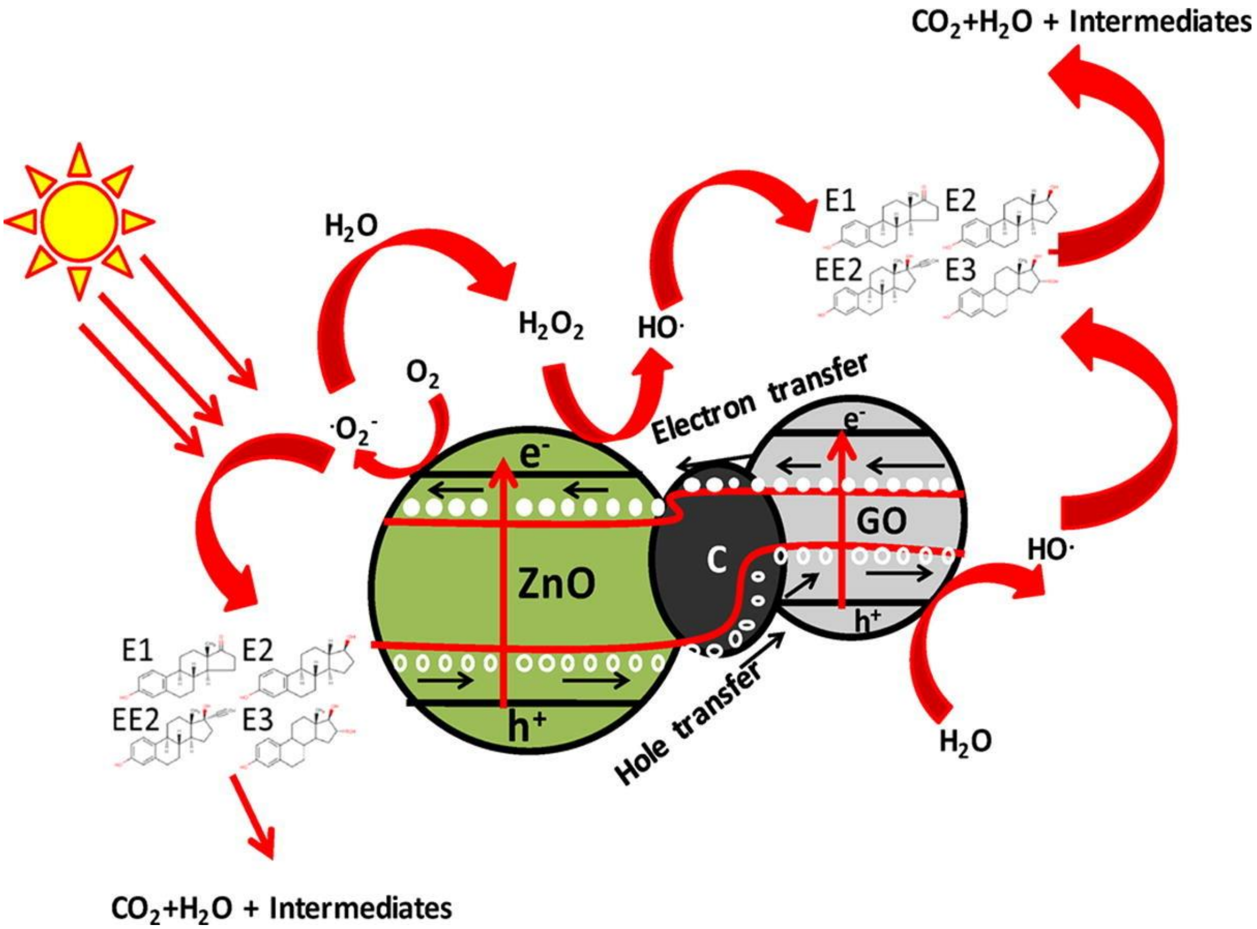


Figure 4 Proposed visible light photo-degradation mechanism of steroid estrogens over ZnO/C/GO composite. Reprinted from Ref. (Bayode, Vieira, et al., 2021) with permission from Elsevier. License Number: 5257771361802.

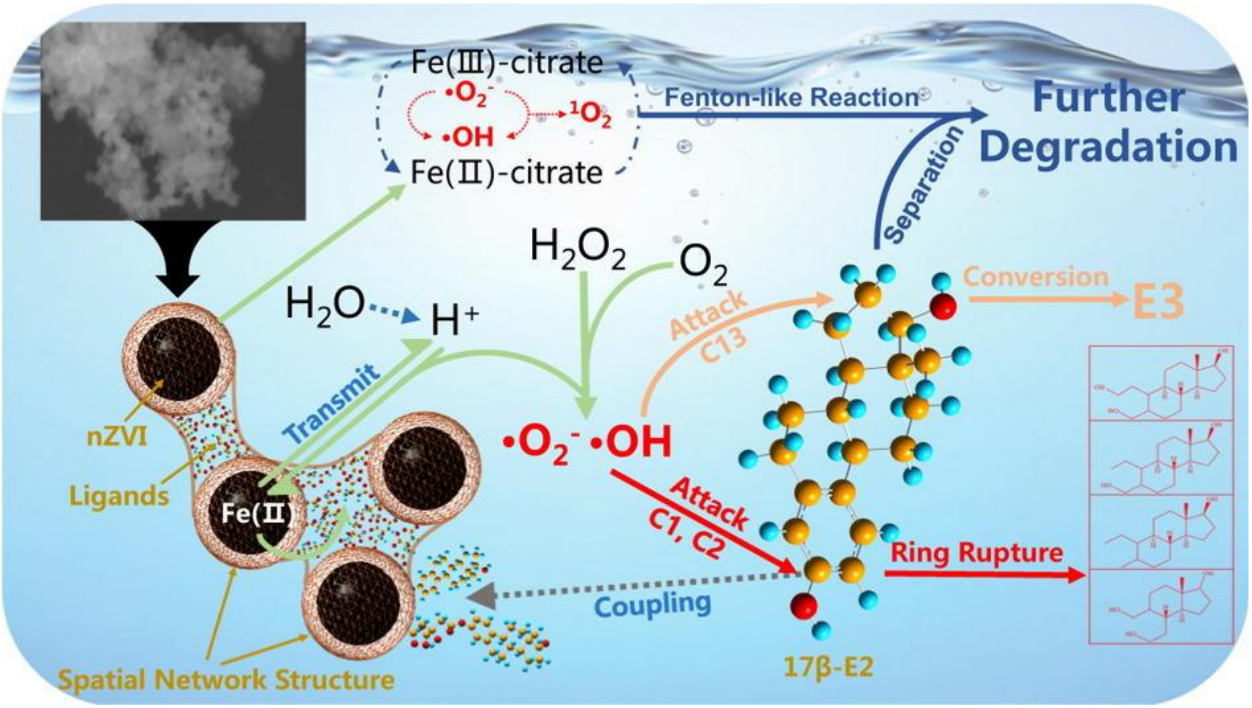


Figure 5 Proposed degradation mechanisms of C-nZVI to 7β-E2, Reprinted from Ref. (Yang et al., 2021) with permission from Elsevier. License Number: 5257780035840.

1362 **Table 1** Comparison of the physical, chemical, and biological based treatments.

Treatment methods	**Advantages**	**Disadvantages**	**References**
Physical methods			
Adsorption	Facile process, old technique, cost friendly, high surface area provision for removal	Poor selectivity, clogging issues, waste products formation, 50% removal of estrogens	(Brienza et al., 2014; Grover, Zhou, Frickers, & Readman, 2011)
Nanofiltration	Nanofiltration technique performs well in combination with other techniques, cost effective for small scale use, requires less room, facile, quick and highly effective even at high conc.	At inappropriate pressure the fouling of nanofilter membranes, maintenance cost high, removal of contaminants based on hydrophobic adsorption and size exclusion only	(Crini & Lichtfouse, 2019)
Ultrafiltration	secondary treatment method of considerable application with limited targeted estrogens removal leachate effluents, requires less space	only selected contaminants can be removed by using this method, removal based on hydrophobic adsorption only, useful in combination with other techniques like reverse osmosis	(Aziz and Ojuma et al., 2020, Patel et al., 2019, Sun et al., 2015)
Ultrasonication	Advance technique, Safe, energy saving, less formation of secondary contaminants in comparison of other tecgniques, removal of contaminants even at smaller concentration, estrogen removal	Efficiency depends on specific ultrasonication conditions, efficiency of method is dependent on various factors like temp, Ph , catalyst US power and characteristics of estrogens	Pokhalekar et al., 2016, Laxmi et al., 2010, Chu et al., 2017).
Chemical Methods			

Photocatalysis	Intermediates are not formed, efficiently removes all types of estrogenic compounds	Applications of this process is limited, duration of process is long, requires high energy	(Mayer et al., 2019; Ohko et al., 2002)
Fenton, Fenton like and Photo fenton degradation	Highly used for removal of estrogenic compounds, works under wide pH range (3-11), Efficient degradation of estrogens, almost 80% degradation of estrogens	Use of hydrogen peroxide and UV light	(Yaping & Jiangyong 2008, (Silva et al., 2021).
Electro-Fenton degradation	Electro-Fenton process was confirmed for high-rate degradation of E2 in an aqueous-acetonitrile mixture compared to the methanol (co-solvent)	Process occurs in acidic media, process is less reported for degradation of estrogens,	(Poza-Nogueiras et al., 2018). (Naimi & Bellakhal, 2012).
Ozonation	Less time consuming, removal rate is 90%	High treatment cost, by-products of process may be toxic	(Li, Zhang, Liang, & Yediler, 2013; Qi et al., 2020)
Biological methods			
Microbial degradation	Environmentally safe, less harmful chemicals are involved	Depends on different factors as specific microbes required, temp. and pH	(Brienza et al., 2014)
Enzymatic degradation	Efficient for removal of estrogens	Expensive process, stability of enzyme matters a lot, selective enzymes are required for every pollutant	(Becker et al., 2017; Logar, Brouwer, Maurer, & Ort, 2014)

Table 2 Photocatalytic degradation of estrogenic compounds.

Matrix	Compound	Catalyst	Light source	% Degradation	Reference
-	E2 EE2	TiO_2–ZnO nanocomposite	UV/Vis	At C_o <1 mg/L, 100%, at C_o ≤ 10 mg/L, ≥25%, under visible irradiation (240 min)	(Menon et al., 2021)
Water and Hospital wastewater (HWW)	EE2	activated g-C_3N_4	Solar light	Water = 96% (45 min) HWW = 99.09% (30 min)	(Kumar et al., 2020)
Real wastewater	E1, E2, E3, EE2	p-n ZnO/GO/C	Visible light	E1 = 65.98, E2 = 66.76, E3 = 62.66, EE2 = 77.72%	(Bayode, Vieira, et al., 2021)
Real wastewater, Tap water, Rainwater	E1, E2, E3, EE2	Fe@PSK@GO	Visible light	Real water; E1 = 66%, E2 = 67% E3 = 63% EE2 = 78% Tap water; E1= 75%, E2 = 79%, E3 = 79%, EE2 = 89% Rainwater; E1 = 77, E2 = 84, E3 = 77, EE2 = 91	(Bayode, dos Santos, et al., 2021)
Aqueous system	17α-methyltestosterone	doped TiO_2 with Sm^{3+} or Gd^{3+} @0.3 and 0.5 %wt	Solar light	-	(Arévalo-Pérez et al., 2020)
-	EE2	CdS nano-rod/TiO_2 (B) nano-belt composite	Visible light	92% (120 min)	(Luo et al., 2019)
Synthetic water	E2, EE2	TiO_2-P25/H_2O_2	UVC	E2 = 51/32% EE2 = 48/30%	(Castellanos, Paulo Bassin, Dezotti, Boaventura, & Vilar, 2020)
Aqueous system	E2	Pd(II)-porphyrin-coated membranes	Visible light	98%	(Lyubimenko, Gutierrez Cardenas, Turshatov, Richards, & Schäfer, 2021)
Aqueous system	E2	TiO_2	UV	85% (60 min)	(Orozco-Hernández et al., 2019)

Synthetic solution	E3, EE2	Au-TiO_2	11 W UVA (λ = 365 nm) or Cool White (λ > 410 nm) LEDs	Potential results	(Sornalingam et al., 2020)
-	E2	Carbon fibers/TiO_2/MIL-101(Fe)	Visible light	87.4% (60 min)	(Y. Zhang et al., 2021)
Blended system	E2	E2-TiO_2-NR photoanode	300 W-lamp equipped with UV reflector in photoelectrochemical quartz reactor	64%	(Cai et al., 2021)
-	EE2	Zn-doped titanium oxides	UVA-LED, λ = 365 nm,	-	(Engelhardt, Schmitz-Stöwe, Schwarz, & Stöwe, 2020)
Real discharged water	EE2	Persulpahte	UV/heat	Significant degradation obtained	(Chainarong, Chanat, Tunlawit, Tharisara, & Athaphon, 2020)
-	E1, EE2	Ti-0.5wt%W alloy (NT/Ti-0.5W)	UV/Vis	UV light; E1 = 54, EE2 = 66% (2 min) Visible light; E1 = 50% (1.8 min), EE2 = 50% (4.6 h)	(Escudeiro de Oliveira, Barroso, de Almeida, Moraes, & de Arruda Rodrigues, 2020)

Abbreviations: estrone = E1; 17β-estradiol = E2; estriol = E3; 17α-ethinylestradiol = EE2; PSK = Crushed *carica papaya* seeds, kaolinite, $ZnCl_2.6H_2O$, 20 mL 0.1 M NaOH

Table 3 Various advanced oxidation processes (AOPs) for removal of different estrogens.

Matrix	**Compound**	**AOPs**	**Catalyst**	**Light source**	**% Degradation**	**Reference**
WWTPE	E1, E2, E3, EE2	Photo-Fenton	Fe^{+2}/ H_2O_2	White LED (λ = 455 nm)	Significant degradation obtained	(Silva et al., 2021)
Wastewater	E2	Fenton	*cis*-$[Fe(cbc)Cl_2]^+$ (Fe(L 1)/ H_2O_2	-	Approx. 90%	(M. Chen et al., 2019)
-	E2	Fenton	Fe/HC- H_2O_2	-	Significant degradation obtained	(Yu et al., 2019)
Aqueous system	E2	-	nZVI/PGBC/PS	-	100% (45 min) by activating sodium persulfate (PS)	(Ding et al., 2021)
Wastewater	E2	-	Fe/GBC/PS	-	100% (90 min)	(P. Zhang et al., 2019)
Wastewater	EE2	Coupled Fenton process	up-flow anaerobic sludge blanket reactors (UASB) coupled with Fe^{+2}/ H_2O_2	-	Significant degradation obtained	(López-Velázquez, Villanueva-Rodríguez, Mejía-González, & Herrera-López, 2020)

Abbreviations: estrone = E1; 17β-estradiol = E2; estriol = E3; 17α-ethinylestradiol = EE2; kaolinite, $ZnCl_2.6H_2O$, 20 mL 0.1 M NaOH; HC = hydrochar; PGBC = porous graphitized biochar

Table 4 Various ozone-based processes for degradation of estrogens.

Matrix	**Compound**	**Catalyst**	**Light source**	**% Degradation**	**Reference**
Aqueous medium	E2, EE2	O_3/H_2O_2		100%, 99.5 (pH 3)	(Guedes Maniero et al., 2008)
Municipal watewater	E1, E2, E3, EE2	O_3/H_2O_2/UV	(λ = 455 nm)	99.4% E1, 98.2% E2, 98.7% E3, 99.6% EE2	(Pešoutová et al., 2014)
Solvent free process	EE2	O_3/benonite (Fe(II)Mt,	-	96% (1 minute)	(Boudissa et al., 2020)
Surface water	E2	UVC/O_3	UVC (λ = 254 nm)	Significant degradation obtained	(Perondi et al., 2020)

Abbreviations: estrone = E1; 17β-estradiol = E2; estriol = E3; 17α-ethinylestradiol = EE2; kaolinite, $ZnCl_2.6H_2O$, 20 mL 0.1 M NaOH