Electrochemical Technologies for the Abatement of Endocrine Disrupting Compounds

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Research Article

Abstract

Endocrine disrupting compounds (EDCs) are a class of emerging contaminants capable of interfering with the normal hormonal functioning of humans and other organisms. Even minute concentrations of EDCs in natural receiving water bodies can be minacious and are raising concern globally due to their connection with rising cases in reproductive, immune system, and developmental-related health disorders. These EDCs are released from anthropogenic sources and are routinely detected in the natural environment especially in wastewater. Incapacitated by poor infrastructure and design, conventional wastewater treatment facilities fail to satisfactorily remove the recalcitrant organic pollutants like, parabens, phenols, pesticides, etc., making them one of the biggest sources of EDCs discharged into the environment. Neoteric techniques such as, electrochemical oxidation, electro-Fenton process, electrocoagulation, and other electrochemical technologies (ETs) have emerged as a robust technology for eliminating biorefractory contaminants from different effluents. The setups used in ETs are easy to fabricate, require low chemical additions, produce minimal sludge, and their faster/efficient degradation of recalcitrant compounds give them an edge over their conventional counterparts. However, expensive electrodes and substantial power consumption limit the scale-up application of ETs. Thus, this review attempts to present a holistic view of the applicability and feasibility of ETs with respect to EDCs attenuation from contaminated water and their advancement as a mainstream wastewater management technology.

1. Introduction

The advent of any novel material and technology is inherently followed by the formation of new types of waste products and contaminants. As these contaminants are newly identified, as these are from a new origin, and currently not or partially regulated by concerned regulatory bodies, hence these are often termed as 'emerging contaminants'(EmCs). The prevalence of EmCs in the aquatic environment is rampant and is well documented by many researchers (Ashton et al., 2004;Behera et al., 2011;Gros et al., 2012;Hughes et al., 2013) owing to the advancement in analytical technologies (Richardson, 2009). Arrays of anthropogenic activities, such as industrial operations, wastewater discharge, etc., are the major sources of release of these pollutants into the environment, though they can be of natural origin as well (Cabeza et al., 2012;Rout et al., 2021). There are innumerable EmCs present in the environment and can be broadly classified into three categories based on their origin, namely (a) personal care products, (b) pharmaceuticals, and (c) endocrine disrupting compounds (EDCs) (Gogoi et al., 2018).

Among these three types of EmCs, EDCs are considered the most potent ones due to their inherent ability to impede hormonal homeostasis, which subsequently develops into serious health related disorders. Any natural or synthetic chemical compound that is cable of interfering with the normal working of the endocrine system or hormonal functions of the body, such as the release of reproductive hormones, different metabolic activities, sustaining homeostasis, etc., is termed as EDC (Kabir et al., 2015;Kavlock et al., 1996). Many products and commodities of daily use, such as plastics products, food packaging, construction materials, personal care, and hygiene products, medications, pesticides, insecticides, and so on possesses some kind of EDCs in the form of paraben preservatives, bisphenol A (BPA), triclosan (TCS), phthalates, estrone (E1), estradiol, estriol (E3), etc., in their ingredients (Dodge et al., 2015; Kabir et al., 2015; Monneret, 2017).

Such widespread use of materials containing EDCs has led to their deposition and accumulation in the environment, especially in natural water bodies. The existence of EDCs is ubiquitous in the aquatic environment as evidenced by different investigations ascertaining their presence in surface water, groundwater, and wastewater, which is mainly due to industrial discharges and inadequate wastewater treatment systems (Vymazal et al., 2015;Zhang et al., 2015). Prolong residence of EDCs in the environment poses an imminent threat to both humans and natural biota due to their ecotoxicological effects. The EDCs have been known to cause serious health concerns in human beings including

hormonal imbalance, hindering neurological functions, birth defects, and other developmental impairments in children (Monneret, 2017). Besides, exposure to EDCs can also lead to diseases like breast cancer in females, obesity, diabetes as well as reproductive ailments (Jambor et al., 2017; Legler et al., 2015; Nohynek et al., 2013). A similar adverse effect of EDCs has been observed in animals and aquatic biota like, interfering with the immune system, malfunctioning of hormone-secreting and reproductive organs, and formation of malignant tumours (Casanova-Nakayama et al., 2011; Fowler et al., 2012; Xie et al., 2018). Hence, the removal of EDCs from sewage and industrial effluents is imperative for safeguarding humans and natural ecosystems from any such deleterious effects.

Conventional wastewater treatment plants (WWTPs) are not designed to handle and remove EDCs from wastewater and consequently, they exhibit limited removal of EDCs from wastewater. Moreover, the recalcitrant and biorefractory nature of EDCs makes them resistant to degradation in biological treatment processes, such as activated sludge process, tricking filter, etc. Non-conventional and advanced treatment technologies like adsorption, membrane filtration, advanced oxidation processes (AOPs), etc., have been employed for the treatment of EDCs (Sun et al., 2017; Vieira et al., 2020); however, all of these methods have some inherent drawbacks associated with their operation. In adsorption, the contaminant is not degraded rather only phase transformation occurs demanding separate attenuation for the safe disposal of the rejects. Moreover, regeneration of the adsorbent, once it has been spent during the adsorption, is a costly affair. On the other hand, membrane filters suffer from frequent fouling due to pore blockage and thus require regular replacement of filters, which becomes problematic while handling a large volume of wastewater. The AOPs are effective methods for eliminating ECs; nonetheless, expensive chemicals are required during their application for wastewater treatment that incurs a high cost for operation and maintenance of the these AOP-based treatment units (Priyadarshini et al., 2021).

The electrochemical technologies (ETs), such as electrochemical oxidation (EO), electro-Fenton process (EF), electrocoagulation (EC), electroflotation process, etc., have emerged as cost-effective and eco-friendly technique for the efficacious abatement of EmCs from wastewater due to minimal chemical requirements, reduced sludge production, non-selective degradation of a vast variety of pollutants, lesser footprint and requirement of lesser detention time. The ETs are capable of effectively eliminating the target compounds by completely mineralizing them into carbon dioxide, water, and simple inorganic compounds via direct anodic oxidation (AO) and hydroxyl radical ($\bullet$OH) mediated indirect oxidation (in case of EO and EF) or by separating out the contaminants from bulk solution either by skimming them from the surface (during EF) or by coagulation of contaminants followed by settling as in EC.

Many investigations have demonstrated the competency of EO, EF, and EC for the elimination of EmCs from the wastewater, such as caffeine, dyes, antibiotics, beta-blockers, parabens, phenolic compounds, and many more (Oturan, 2014; Raj et al., 2021; Seibert et al., 2020). Such promising result shown by ETs in the degradation of ECs exemplifies their robustness in handling pollutants not amenable to biodegradation, rendering them as a potential solution for the treatment of wastewater containing EDCs and other persistent complex organic contaminants.

This review attempts to highlight the most recent developments made in the application of different ETs for the mitigation of EDCs and focuses on their removal efficiency, performance governing parameters, and salient features of each technology along with some key challenges in the upscaling of ETs for broader and field-scale implementation. Additionally, the benefits and shortcomings of ETs have been critically reviewed, incorporating comparative economic analysis of ETs with conventional treatment methods and other advanced chemical treatments techniques. The attenuation capacity of ET-based hybrid systems and other advanced treatment techniques has also been briefly introduced to elucidate the integration abilities of ETs. To the best of our knowledge, no such review is available in the literature, which comprehensively presents the performance of ETs for EDCs abatement from wastewater. Besides, the review will also serve as a comprehensive guidebook for budding researchers interested in exploring ETs for the

attenuation of EmCs from the aquatic environment, while the experts, presently working in the associated field, will be benefited from the updated literature, and would be enlightened with the recent insightful information pertaining to ETs that could assist their ongoing research. Moreover, the article also puts forward the research gap in the field of ETs, which could be exploited by the researchers working in this domain for addressing the critical drawbacks for abetting ETs to realise their full potential.

2. Endocrine Disrupting Compounds: Classification, Ecotoxicity, And Occurrence

2.1 Classification

The EDCs are a highly heterogeneous group of compounds, which have the potential to disrupt the endocrine (hormonal) system of the human body or any other organism. According to the definition given by the United States Environmental Protection Agency, EDCs are "an agent that interferes with the synthesis, secretion, transport, binding, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development and/or behaviour" (Crisp et al., 1998). In other words, any compound capable of triggering abnormal hormonal responses causing adverse health effects and hindering the natural growth and development of the body is categorized as an EDC. Classification of EDCs is a cumbersome task as there are innumerable substances that can affect the endocrine system of an organism directly or indirectly, and it requires a series of tests, and experiments for ascertaining the endocrine disrupting potential of a chemical compound and its metabolite. Moreover, most of these contaminants overlap with other subcategories of EmCs, making the categorisation of EDCs even more perplexing and complicated.

Diamanti-Kandarakis et al. (2009) and Pojana et al. (2007) bifurcated EDCs into two categories, namely, synthetic chemicals, such as industrial solvents and their by-products, plasticizers, pesticides, etc., and natural chemicals like phytoestrogens. On the other hand, researchers proposed a product-based classification of EDCs, dividing them into three categories depending upon the commodities or material in which they are used or found, namely, pesticides, chemicals in products, and food contact materials (Forio and Goethals, 2020; Peña-Guzmán et al., 2019). Nonetheless, considering the heterogeneous nature of these chemicals and for the sake of simplicity in understanding, EDCs are broadly classified into six major groups in this article as (i) pesticides, (ii) phenolic compounds, (iii) phthalates, (iv) paraben compounds, (v) steroid estrogens, and (vi) estrogenic heavy metals, which are elaborated in the following section. Application and associated health hazards of the different classes of EDCs have been depicted in Table 1.

Table 1
Occurrence of EDCs in different types of aquatic environments.

Water body/type	Location	EDCs detected	Concentration (µg/L)	Reference
Lagos lagoon	Nigeria	MP	0.453	Folarin et al. (2019)
Pearl river estuary	China	BPA, BPS, BPF, MP, EP, PP,	0.0308, 0.0123, 0.0467, 0.0076, 0.000276, 0.00168	Zhao et al. (2019)
WWTP sludge	USA	MP, EP, PP, BP	204*, 2.6*, 7.7*, 4.3*	Chen et al. (2017)
Nzoia basin river	Kenya	EP, MP, DEET, metolachlor, atrazine, diuron	0.5, 1.16, 0.08, 0.25, 0.07, 0.041	K'oreje et al. (2018)
Arkavathi river, its tributaries and lakes	India	TCS, BPA	1.716, 0.088	Gopal et al. (2021)
Somme river	France	DMP, DEP, DBP, DEHP, lindane, chloroneb	0.25, 6.98, 3.86, 20.76, 0.355, 0.633	Net et al. (2014)
WWTP effluent	Italy	BPA, 4-NP, NP1EO, NP2EO	0.207, 0.0054, 0.0196, 0.121	Spataro et al. (2019)
Household grey water	India	DEHP, DEP, DBP, DOP, TCS, BPA, 4-OP, 4-NP	0.38, 1.57, 4.77, 0.712, 5.82, 11.08, 2.21, 5.96	Delhiraja and Philip (2020)
Drinking water	Serbia	BPA, OP, NP	0.0356, 0.0037, 0.0079	Čelić et al. (2020)
Wastewater	South Africa	4-NP, 4-t-OP, BPA, DCP, TCS	6.72, 1.68, 1.684, 2.20, 2.85	Farounbi and Ngqwala (2020)
Mangrove water	Singapore	Atrazine, BPA,	0.366, 1.918	Bayen et al. (2016)

*Data unit is in ng/g of dry sludge; BP = Butyl paraben; BPA = bisphenol A; BPF = Bisphenol F; BPS = Bisphenol S; ; DMP = Dimethyl phthalate; DEP = Diethyl phthalate; DBP = Dibutyl phthalate; DEHP = Di(2-ethylhexyl) phthalate; DEET = N,N-diethyl-meta-toluamide; DOP = Dioctyl phthalate; EP = Ethyl paraben; MP = Methyl paraben; NP = Nonylphenol; 4-NP =4 Nonylphenol; 4-n-NP = 4-n-nonylphenol; NP1EO = Nonylphenol mono ethoxylate; NP2EO = Nonylphenol di ethoxylate; OP = Octylphenol; 4-t-OP = 4-t- Octylphenol; PP = Propyl paraben

2.2.1 Pesticides

Pesticides are a group of chemical compounds frequently used for safeguarding plants and crops from pest infestation, weeds, and different microbial infections, in turn, enhancing agricultural yield. With an annual global consumption of four million tons, the application of pesticides is considered as one of the largest xenobiotic releasing anthropogenic activity (Maggi et al., 2019). Dichloro-diphenyl-trichloroethane (DDT), kepone, and organo-phosphorus pesticides are among the most widely applied pesticides, which are known to cause estrogenic imbalances in rats (Gellert, 1978). Adverse estrogenic activities of pesticides have been widely reported and DDT was among the first few compounds identified as EDCs (Fisher et al., 1952).

Despite worldwide agreement on curbing down the use of pesticides due to their devastating hormone-related disorders on wildlife and human health, the use of pesticides such as DDT is rampant, especially in developing countries like India, Ethiopia, Namibia, South Africa, etc., and it is responsible for causing acute toxicity and another health-related hazard in addition to endocrine disruption (Abhilash and Singh, 2009). The presence of pesticides and their metabolites is ubiquitous in the environment owing to the continuous application notably in the agriculture sector and

poses an imminent threat. Thus, advanced treatment techniques, like EO and EF, are required to eliminate the spread of pesticides in the natural water bodies.

2.1.2 Phenolic compounds

Phenolic compounds are chemicals carrying an aromatic ring with one or more hydroxy substituents. Petrochemical, pharmaceuticals, oil refineries, paper and pulp, paint, textiles, and other industrial effluents are the prime source for the discharge of phenolic compounds in the environment. Among others, TCS, BPA, 4-nonylphenol (4-NP), 2,4-dichlrophenol, and 4-tert-octyphenol (4-t-OP) are the most frequently detected phenolic compounds in the aqueous environment (Li et al., 2012). These phenolic compounds are often designated as priority pollutants by the United States Environmental Protection Agency due to their ubiquity and hazardous nature. Chronic symptoms of phenol exposure include diarrhoea, vertigo, abnormal urination, etc., whereas prolonged exposure can severely affect the central nervous system and even cause fatality in some cases (Villegas et al., 2016). Moreover, phenols toxication has been known to cause developmental and birth defects in infants. The presence of phenolic compounds in different hydric sources is an alarming situation and requires immediate attention to curtail its perilous effects on the environment.

2.1.3 Phthalates compounds

Phthalates or phthalates esters are chemical substances widely used as plasticizers in the production of PVC, lubricants in manufacturing different industrial goods, and as a solvent in the preparation of household commodities. Di(2-ethylhexyl) phthalate (DEHP), diisononyl phthalate, di-2-propyl heptyl phthalate, etc., are some of the examples of commonly used phthalates in industries. In fact, the large-scale application of phthalates has caused pervasive human exposure and associated health hazards. Phthalates are non-steroidal EDCs and their exposure can result in reproductive ailments in humans, low birth weight, and asthma (Yang et al., 2020a). Moreover, phthalates are perennially discharged in to the receiving water bodies with the wastewater treatment plant effluent, which has resulted in innumerable malfunctioning and ill effects on the exposed flora and fauna. Hence, it is imperative to contain phthalate contamination of the natural water bodies for safeguarding human health as well as the aquatic ecosystem.

2.1.4 Parabens

Paraben compounds are defined as alkyl esters derived from p-hydroxybenzoic acid, such as methylparaben (MP), ethylparaben (EP), butylparaben (BP), etc. They are extensively used as preservatives, chiefly in cosmetics, personal care products, and pharmaceuticals, which have made their presence ubiquitous in the environment. The extend of human exposure to parabens can be exemplified by the fact that 95% of urine samples collected worldwide were found to contain MP and propylparaben (PB) (Quirós-Alcalá et al., 2018). Investigations have demonstrated conclusive shreds of evidence linking paraben exposure to breast cancer and metabolic alterations (Zhao et al., 2020). Moreover, maternal paraben exposure during pregnancy can be perilous for the health of the mother as well as for the offspring. Despite efforts in discouraging the use of paraben compounds in daily use products, these preservatives are regularly discovered in natural receiving water bodies, thereby exposing the aquatic biota to adverse ecotoxicological effects.

2.1.5 Estrogenic heavy metals

Heavy metals are inorganic non-biodegradable contaminants that are released into the environment primarily from industrial activities, such as tanning industry, plating-electroplating industry, metal mining and smelting, battery manufacturing, fertilizers and pesticides, petrochemical sectors, textile plants, and so on (Qasem et al., 2021). Lead, cadmium, arsenic, mercury, and other heavy metals are capable of impeding the normal metabolism of steroid hormones either by binding to hormone receptors or through biological mimicry. Some metals like Cd, which can mimic

estrogen are often classified as metalloestrogen and have been linked to obesity, diabetes, and other metabolic disorders (Safe, 2003).

2.1.6 Steroid hormones

Different kinds of hormones also act as an EDC and can have adverse effects on the human body and aquatic organisms. Researchers have reported that different natural and synthetic estrogen, and other micro-pollutants that mimic estrogenic activity persist in soil sediments, surface water, and sub-surface aquifers, which can impede the hormonal system of living beings. Different hormones such as progestin and natural estrogens like E_1, 17β-estradiol (E_2), and estriol E_3, and synthetic estrogen-like 17α-ethinylestradiol (EE_2) are well known for their high estrogenic activity (Cook et al., 2016;Torres et al., 2021).

Generally, these micro-pollutants are released in natural water bodies due to their incomplete removal through conventional wastewater treatment plants, effluents leached from various pharmaceutical industries, and other anthropogenic activities (Forio and Goethals, 2020; Peña-Guzmán et al., 2019). Therefore, the presence of these types of EDCs in varied hydric sources is a serious threat to the environment as well as for the human health. Moreover, natural and synthetic estrogen have the proficiency to cause various common illnesses, such as nausea, breast tenderness, vomiting, headaches, stomach cramps, weight gain, and hyper-pigmentation, loss of hair, vaginal itching, abnormal uterine bleeding and anaphylaxis, etc. (Forio and Goethals, 2020; Peña-Guzmán et al., 2019; Torres et al., 2021).

2.2 Presence of endocrine disrupting compounds in the aquatic environment

The presence of EDCs in the natural water bodies can have dire health consequences on the aquatic ecosystem and human health. Human contact with EDCs is almost inevitable as they are found in a plethora of everyday products like, cosmetics, food packaging, plastic containers, medication, and so on. Unfortunately, most of these estrogenic compounds ultimately end up in the environment via different pathways (Fig. 1) and pose serious maladies to the exposed organisms. The presence of these EDCs in different water bodies is frequently reported in the literature and it has been summarized in Table 1.

Treated effluent discharged from wastewater treatment plants is considered as the prime source of EDC contamination in the aquatic environment as the majority of EDCs are biorefractory in nature and are not subdued during conventional biological treatment processes. For instance, Pothitou and Voutsa (2008) discovered the presence of 1.574 µg/L of 4-NP and 0.445 µg/L TCS in the influent of a sewage treatment plant (STP) in Greece. The concentration of 4-NP and TCS in the effluent of the STP was found to be 0.786 µg/L and 0.076 µg/L, respectively; whereas, 1.089 µg/g of 4-NP and 0.461 µg/g of TCS was also quantified in the sludge of the STP indicating a reduction in effluent concentration was majorly due to phase change of contaminants rather than actual degradation (Pothitou and Voutsa, 2008). Similarly, 31 different EDCs including, parabens, alkylphenol compounds, organophosphorus flame retardants, TCS, BPA, etc. were identified in rivers of the Iberian peninsula in concentrations ranging from ng/L to µg/L (Gorga et al., 2015). Moreover, 4-NP, E1, BPA, 4-t-OP, and other EDCs are also routinely detected in wastewater irrigated soils, receiving waters, and groundwaters (Chen et al., 2011;Li et al., 2015).

More recently, phthalate esters, like diethyl phthalate and dibutyl phthalate with an average concentration of 1.57 µg/L and 4.77 µg/L, respectively, were detected in household greywater collected from Chennai, India (Delhiraja and Philip, 2020). In addition, the same greywater sample also contained 5.82 µg/L TCS, 11.08 µg/L of BPA, and 5.96 µg/L of nonylphenol (NP) (Delhiraja and Philip, 2020). Discharge of inadequately treated/untreated wastewater causes contamination of rivers and other natural water bodies, as it was evident during the investigation carried out by

Renganathan et al. (2021). In this investigation, they identified the presence of different pharmaceutically active compounds including 10.39 ng/L of TCS, 205.62 ng/L carbamazepine, and 28.51 ng/L diclofenac in the river Cauvery and its tributaries, which serves as the prime source of the freshwater supply for many states in southern India.

Though EDCs compounds may undergo degradation by means of sorption, biotransformation process, etc., under natural aerobic conditions, a substantial fraction of these xenobiotic compounds tend to settle at the bottom of the river bed, where they don't degrade further due to the absence of oxygen and thus accumulate in the sediments over a period of time (Koumaki et al., 2018). This may further aggravate the risk of toxic chronic exposure and bioaccumulation of EDCs in the flora and fauna inhabiting the contaminated water body. In the liver tissue of fishes of the Pearl River system in south China, a maximum concentration of 40.920 μg/g of BPA and 5.978 μg/g of NP was discovered, which was suggestive of the bioaccumulation potential of these EDCs (Lv et al., 2019). Furthermore, fish samples from the Magdalena River in Colombia were detected with 32 μg/kg of MP and 90.80 μg/kg of carbamazepine, wherein the water sample taken from the same river had 8.03 μg/L of carbamazepine, while MP was not detected (Zhao et al., 2019). Thus, it is evident that biomagnification tends to accumulate the concentration of EDCs and other xenobiotic compounds in aquatic organisms, which is many folds higher than the surrounding environmental concentration, thus intensifying the exposure risk to humans.

Oceans are the sink for natural drainage systems and are bound to get contaminated if the incoming water is polluted. Many toxic chemicals of anthropogenic origin are frequently traced across different oceanic ecosystems and are known to cause detrimental environmental impacts on marine life. Estuaries and seawater of the coastal Iberian region were found to have NP in a concentration ranging from 0.031 μg/L to 0.056 μg/L, while BPA was measured in a concentration level of 0.020 μg/L to 0.054 μg/L (Salgueiro-González et al., 2019). In the coastal country of Kuwait, high levels of diethyl phthalate (DEP), di-2-ethylhexyl phthalate (DEHP), and dibutyl phthalate (DBP) were detected in seawater with a maximum concentration of 0.52 μg/L, 2.91 μg/L, and 1.22 μg/L, respectively (Salgueiro-González et al., 2019). Moreover, 2176.6 μg/kg of DEP, 11236.4 μg/kg of DEHP, and 1316.5 μg/kg of DBP was also measured in the sediment samples collected from the sea bed (Salgueiro-González et al., 2019). Clearly, the presence of EDCs is ubiquitous in the aquatic environment owing to the mishandling and mindless dumping of contaminated effluents into the natural drains. Thus, imminent measures are required to bring down the level of EDCs in the receiving waters and to check further recontamination of the same.

2.3 Ecotoxicity and adverse health impacts of endocrine disrupting compounds

Hormones maintain the internal homeostasis of an organism using different chemical and biological stimuli. The EDCs can produce inadvertent exogenous chemical signals in an organism's body, causing interference with the normal functioning of the endocrine system. Endocrine disruption can have several adverse health impacts and fatalities (Table 2), therefore the presence of EDCs in the aquatic environment is considered as one of the most critical toxicological hazards (Casanova-Nakayama et al., 2011). Many investigations have already presented clinical evidence on the ill effects of EDCs on human health and toxicity towards others (Hamid et al., 2021).

Fishes ingesting EDC contaminated food sources suffer from an imbalance in sex-steroid activity and immune homeostasis, which makes them more susceptible to pathogenic infestations (Milla et al., 2011). Similar perturbations were observed in the immunological responses of intertidal mud crab exposed to 1 μg/L to 30 μg/L of BPA and DEHP, while a 100 μg/L of BPA and DEHP exposure caused abnormal cellular development in chironomid larvae (Park et al., 2019;Park and Kwak, 2010). Another investigation revealed that non-ionic surfactant nonylphenol ethoxylate (NPEO) and its degradation product NP produced oxidative and cellular stress on *Caenorhabditis elegans* (De la Parra-Guerra and Olivero-Verbel, 2020).

Moreover, NP was found to be more toxic than NP-9 with 24 h 50% lethal concertation (LC_{50}) for *C. elegans* being 26.88 mg/L and 1916.14 mg/L, respectively, for both compounds (De la Parra-Guerra and Olivero-Verbel, 2020). In a separate investigation, Sun and Liu (2017) observed embryotic malformations in zebrafish, when exposed to 0.6 mg/L of butyl benzyl phthalate. Furthermore, the presence of additional contaminants, such as microplastic can elevate the toxicity of NP. For example, the growth inhibition ratio (expressed as (increased density of control - increased density at different concentrations)/ increased density of control) of *Chlorella pyrenoids* was 69.2% for only NP, while it was 15.1% for NP combined with polyamide 1000 (Yang et al., 2020b). Whereas, DBP in presence of polyethylene fragments inhibited the growth and aggravated the cell wall disruption in roots of *Lactuca sativa L.* (Gao et al., 2021).

The EDCs compounds have also been associated with the rising rate of health issues in humans like, developmental abnormalities, reproductive disorders, birth defects, etc. Parabens and phenols are known to alter the level of reproductive and thyroid hormones in pregnant women. Further, MP and BP increased the level of sex hormone-binding globulin (7.70%) and free thyroxine (5.64%), respectively; whereas, BPA, 2,4-dichlorophenol, and 2,5-dichlorophenol were found to diminish the amount of progesterone released (Aker et al., 2016). Similarly, urine samples of 105 men were found to have an average BPA concentration of 0.10 μg/g of creatinine, 10.69 μg/g of creatinine DEHP, and 19.3 μg/g of creatinine mono n-butyl phthalate, also some among 105 subjects displayed anomalies in the semen quality (Caporossi et al., 2020).

Dichloro-diphenyl-dichloro-ethylene is the most environmentally prevalent metabolite of DDT that can cause an imbalance in androgens activity by binding with the hormone and has been moderately associated with the development of diabetes (Lind and Lind, 2018). Investigations on exposure of EDCs during pregnancy also suggest that these compounds can pass through the placenta and cause developmental and cognitive impairments of the foetus (Yang et al., 2019). More interestingly, Zhang et al. (2021) concluded that even preconception exposure of parents to phenols and phthalates augment the risk of preterm birth, indicating chronic sex hormone irregularities induced by EDCs.

Paraben compounds are widely used in cosmetics as preservatives and are believed to have carcinogenic properties. This tenet is cemented by the investigation of Amin et al. (2019), who traced the presence of paraben compounds in malignant breast tissues of exposed women. Additionally, maternal exposure to paraben has also been associated with childhood obesity among children of age up to 8 years (Leppert et al., 2020). There is no gainsaying the fact that endocrine disruption caused by EDCs is one of the most critical health hazards for both humans and other species. Different investigations have already correlated EDCs exposure to escalating health disorders and if remained unchecked in the environment, these xenobiotics compounds can potentially have a long-lasting detrimental effect on the environment.

Table 2
Different class of EDCs with their applications and associated health hazards.

EDC class	Common compounds	Applications	Health hazard on exposure	Reference
Pesticides	DDT, pyriproxyfen, malathion, fenoxaprop-ethyl, acaricide, thiram	Insect, pest, rodents and related diseases control in crops and trees	Carcinogenic, reproductive disorder, damage to CNS and thyroid, failure of vital organs	Rani et al. (2021); Mima et al. (2018)
Phenols	BPA, BPS, NP, TCS	Production of polycarbonate plastics, epoxy resins, flame retardant, surfactants, antimicrobial agent in personal care products	Osteoporosis, obesity, lower sperm count, infertility, low birth weight, increased susceptibility to autism, diabetes	Vitku et al. (2018); Ma et al. (2019); Rathnayake et al. (2016)
Phthalates	MEP, DEHP, DEP, DBP	Used as plasticizers in manufacturing of PVC, building materials, cosmetics, toys, food packaging, automobiles, lubricants, solvents, insecticides	Obesity, antiandrogenic effects in the prostate, hepatotoxicity, dermal toxicity, diminished sperm count and quality	Costa et al. (2017); Vitku et al. (2018); Schettler (2006);
Parabens	Methyl paraben, ethyl paraben, propyl paraben, butyl paraben	Preservative for cosmetics, food products, pharmaceuticals, toiletries	Osteoporosis, obesity, breast cancer, childhood overweight, allergy development, thyroid dysfunction, preterm birth, ADHD in children	Vitku et al. (2018); Kizhedath et al. (2019); Leppert et al. (2020); Yim et al. (2014); Baker et al. (2020); Amin et al. (2019)
Heavy metals	Pb, As, Cd, Hg, Cu, Ni	Used in electronic devices, mobile phones, solar panels, pharmaceuticals, electrical appliances, industrial applications	DNA damage, reproductive toxicity, diabetes, obesity, damage to nervous system, anaemia, cardiovascular diseases	Mima et al. (2018); Gupta et al. (2020); Mitra et al. (2017); Jiang et al. (2020);

EDC = Endocrine disrupting compound; DDT = Dichlorodiphenyltrichloroethane; BPA = Bisphenol A; BPS = Bisphenol S; NP = Nonylphenol; TCS = Triclosan; MEP = Monoethyl phthalate; DEHP = Di(2-ethylhexyl) phthalate; DEP = Diethyl phthalate; DBP = Dibutyl phthalate; Pb = lead; As = Arsenic; Cd = Cadmium; Hg; Mercury; Cu = Copper; Ni = Nickel; CNS = Central nervous system; DNA = Deoxyribonucleic acid; ADHD = Attention-deficit hyperactivity disorder

3. Removal Of Endocrine Disrupting Compounds Through Conventional Wastewater Treatment Plants

The presence of EDCs in treated effluent and receiving water in itself is evidence for the inefficacy of conventional methods adopted in traditional wastewater treatment plants. Compounds like BPA, TCS, 4-NP, 4-t-OP, etc. have been frequently discovered in the WWTP effluent and sludge across the globe (Table 3). In the effluent of wastewater treatment plant located in Greece, an average of 0.352 µg/L, 0.029 µg/L, and 0.042 µg/L of NP, TCS, and BPA was detected, while parabens, like MP, EP, PP, etc., have been traced in the treated effluent of different WWTPs across India in varying concertation of 0.0039 µg/L to 0.041 µg/L (Karthikraj et al., 2017; Pothitou and Voutsa, 2008). Benotti et al. (2009) reported the presence of 0.001 µg/L of TCS, 0.025 µg/L of BPA, and 0.1 µg/L of NP in the treated water of drinking water treatment plants in the United States of America, indicating recalcitrant nature of these EDCs capable of

escaping relatively rigorous treatment provided for drinking water. A mass balance analysis of EDCs entering and leaving a WWTP in Xiamen, China estimated that a total of 42.2 g of EDCs entered WWTP every day out of which 6.15 g was discharged with the effluent and 7.60 g escaped with the sludge, thus exposing the inadequacy of these conventional wastewater treatment facilities in remediating complex organic contaminants (Ashfaq et al., 2018).

Aerobic treatment is generally preferred over anaerobic methods for the elimination of xenobiotic contaminants, chiefly due to the robustness of aerobic microorganisms in handling complex substrates and the slower degradation rate of anaerobic systems. For instance, more than 98% of MP and PP having an initial concentration of 10 mg/L were readily removed through activated sludge process after 90 min; whereas, during anaerobic treatment, 70.1% of MP and 97.8% of PP was eliminated with an incubation time of 72 h and 48 h, respectively (Wu et al., 2017). Some EDCs like phenolic compounds are less amenable to biological degradation depending on the complexity of their structure. During a sequencing batch reactor treatment of 15 µg/L of BPA, the maximum removal efficiency of only 39% was attained revealing the recalcitrant nature of BPA (Kassotaki et al., 2019). Sometimes metabolites of readily degradable EDCs may be more recalcitrant than the parent compounds. In this regard, Karthikraj and co-researchers investigated five WWTP of India and found out that overall mean removal efficiency for different paraben compounds across all WWTPs ranged from 82–100%; however, only 28%-76% of paraben metabolites like, 3,4-dihydroxy benzoic acid, benzoic acid, ethyl protocatechuate, etc. were eliminated from the wastewater (Karthikraj et al., 2017). Hence, analysis of intermediate formation during the treatment process is imperative to ascertain the authentic removal of the target pollutants and their metabolites.

Additionally, a significant quantity of EDCs has been detected in sludge coming out of aerobic treatment implying that bulk removal mechanism in such system is by phase change of contaminants via adsorption on the sludge surface rather than actual degradation. For example, during a comprehensive analysis of wastewater sludge from 40 WWTPs in Korea, an average of 71 µg/g of DEHP, 22 µg/g of diisononyl phthalate, and 4.3 µg/g of di-n-butyl phthalate was quantified (Lee et al., 2019). Similarly, during the investigation of seven treatment plants in Taiwan all employing activated sludge process as secondary treatment, the cumulative concentration of phthalates in sludge was detected in the range of 7.4 µg/g to 138.6 µg/g (Dong et al., 2020). Anaerobic digestion is the most commonly adopted method for sludge management, which is rather ineffective in the elimination of xenobiotic compounds, and treated sludge could further serve as a source of EDCs contamination after disposal. These shortfalls of conventional treatment processes necessitate the requirement of advanced treatment of wastewater to subdue persistent pollutants.

Neoteric technologies like AOPs, electrochemical advanced oxidation, bio-electro-Fenton process (BEF), etc. have manifested potential in containing EmCs including EDCs, Nevertheless, EO and EF are preferred because of reduced sludge production, minimal chemical requirements, and most notably, the ability to completely mineralize biorefractory contaminants into simpler inorganic constituents, carbon dioxide and water. Also, EC is being increasingly adopted for facilitating a higher degree of contaminant removal via coagulation in a much shorter duration. Overall, ETs present a plausible solution for tackling the proliferation of EDCs and other similar xenobiotic compounds in the aquatic environment.

Table 3
Removal of EDCs in conventional wastewater treatment plants

EDC	WWTP location	Treatment scheme	Influent concentration (ng/L)	Effluent concentration (ng/L)	Sludge concentration (ng/g)	Reference
Methyl paraben	China	Primary + ASP + UV disinfection	721	28.7	94.2	Ma et al. (2018)
DEHP	India	Primary + ASP + oxidation pond	115000	95000	NR	Shivaraju et al. (2021)
Bisphenol A	China	Membrane bioreactor	271.8	233.4	183.6	Qian et al. (2021)
Triclosan	India	Primary + ASP+ chlorination	1703	650	NR	Mohan and Balakrishnan (2019)
Nonylphenol	Vietnam	Primary + ASP + disinfection	487	109	NR	Ho and Watanabe (2017)
Triclosan	China	Sample from 46 treatment plants	NR	NR	3890	Zhu et al. (2019)
Bisphenol A			NR	NR	1210	
Propyl paraben			NR	NR	57.1	
ASP = Activated sludge process; DEHP = Di(2-ethylhexyl) phthalate; EDC = Endocrine disrupting compounds; WWTP = Wastewater treatment plant; UV = Ultraviolet; NR = Not reported						

4. Electrochemical Technologies For The Abatement Of Endocrine Disrupting Compounds
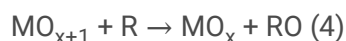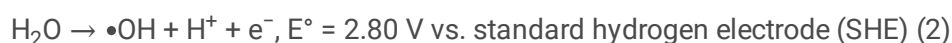
Over the last few decades, the release of EDCs into natural water sources has become a global concern due to their substantial noxious effects on humans and wildlife. Different kinds of emerging pollutants especially, EDCs like polychlorinated biphenyls, dixons, and polybrominated biphenyls, BPA have been perceived in aquatic environments as a result of different anthropogenic activities. Therefore, the removal of these emerging pollutants from surface and groundwater remains a priority in research as it is of utmost necessity to alleviate the associated health risk to humans and other wildlife. Although, different removal technologies consisting of physical, chemical, and biological processes have already been developed; however, researchers have shown keen interest to employ electrochemical-based advanced technologies for the removal of EDCs from wastewater prior to its discharge (Ahmad et al., 2021).

Moreover, electrochemical treatment processes possess the proficiency to eliminate a wide range of EDCs effectively from aquatic environments (Table 4) (Azizi et al., 2021;De Luna and Bensalah, 2021). Additionally, electrochemical treatments are quite easy to operate with the requirement of minimal chemicals and don't generate too much sludge, which makes this process a sustainable and effective panorama for wastewater remediation (Ifelebuegu and Ezenwa, 2011). Consequently, the requirement of applied potential and utilization of expensive catalysts and electrodes can render these treatment technologies uneconomical for large-scale applications. Therefore, further research is required to develop low-cost electrodes along with the reduction in the overall energy consumption of the system, which will take these technologies towards commercialisation.

A typical lab-scale electrochemical system comprises of a reactor fitted with electrodes along with arrangement for power supply and mixing/recirculation of the wastewater. Sometimes to reduce electricity consumption, supplementary power source like solar power can also be used (Fig. 2).

4.1 Electrochemical oxidation

Wastewater treatment through EO can be accomplished through different techniques, such as direct EO and indirect EO (Fig. 3). Generally, the direct EO process is also sometimes referred to as AO because transportation of electrons occurs between the anode and organic contaminant via the surface of anode (Eq. 1) without the involvement of any other intermediate oxidising species, such as hypochlorous acid (HClO), sulphate ions ($SO4^{2-}$), which may be formed due to the presence of different inorganic salts in the solution (Ambauen et al., 2020).

$R \rightarrow ze^- +$ oxidized product (1)

$H_2O \rightarrow \bullet OH + H^+ + e^-$, $E° = 2.80$ V vs. standard hydrogen electrode (SHE) (2)

$MO_x(\bullet OH) \rightarrow MO_{x+1} + H^+ + e^-$ (3)

$MO_{x+1} + R \rightarrow MO_x + RO$ (4)

$MO_x(\bullet OH) + R \rightarrow CO_2 + H_2O + H^+ + e^-$ (5)

Where, R represents the contaminant, z is the number of electrons, $MO_x(\bullet OH)$ is anodic-bonded $\bullet OH$, and MO_{x+1} denotes higher metal oxide.

On the other hand, in the indirect EO process, in addition to anodic degradation, pollutants are also subjected to oxidation by *in situ* electrochemically generated $\bullet OH$ in the bulk solution. Highly reactive $\bullet OH$ are generated at the surface of the anode through the splitting of H_2O by applied potential (Eq. 2), which can facilitate the oxidation of contaminants (Fig. 3). The $\bullet OH$ thus formed gets adhered to the surface of the anode either via physisorption or chemisorption, depending upon the nature of the anode material employed during the electrochemical process (Ganiyu et al., 2021). Electrodes having low oxygen overpotential, like Pt, graphite, ruthenium dioxide, etc., tend to develop a stronger surface bond with $\bullet OH$ that leads to the formation of higher metal oxides at the anode surface, which further reacts with the contaminants present in the wastewater (Eq. 3 and Eq. 4). On the other hand, non-active electrodes such as boron-doped diamond (BDD) and PbO_2 grow a much weaker bond with $\bullet OH$, promoting direct oxidation of pollutants via $\bullet OH$ (Eq. 5). Various other redox reagents, such as Cl^- and HClO, also generate electrons by either anodic or cathodic EO process and also act as intermediators to shuttle the electrons towards the electrode (Ahmad et al., 2021;Martínez-Huitle and Panizza, 2018). The EO process is the most significant technology employed in wastewater treatment among the different electrochemical treatment technologies employed for the removal of recalcitrant and complex micro-pollutants due to its efficient pollutant degrading capacity (Raj et al., 2021).

The degradation of EDCs has been widely investigated through the EO process owing to their efficacy in subduing recalcitrant contaminates. To date, EO has been successfully applied for the removal of different organic and inorganic components, like benzoic acid, carboxylic acids, phenol, and phenolic compounds, aromatic compounds, chlorophenols, and chloromethylphenoxy herbicides; however, to the best of our knowledge, only a few researchers have reported the degradation of tenacious EDCs and other emerging micro-pollutants via the process of EO (De Luna and Bensalah, 2021). In this regard, Frontistis et al. (2011) removed different estrogen hormones, like E_2 and EE_2, from effluent of municipal wastewater treatment plant through the EO process utilizing BDD as the anode and zirconium as

the cathode. Within 7 min, complete mineralization of 100 µg/L of E_2 and EE_2 was successfully attained by applying a current density of 2.1 mA/cm^2.

Similarly, 250 to 500 µg/L of E_2 was successfully mineralized in 30 to 40 min through BDD thin film electrode reactor at an applied current density of 25 mA/cm^2 (Murugananthan et al., 2007). Furthermore, Feng and his research group developed Ti-based SnO_2 anode for the degradation of EE_2 in presence of 28.4 mg/L of Na_2SO_4 as the electrolyte in aquatic solution through electro catalytic oxidation (Feng et al., 2010). The maximum 96.5% of EE_2 was degraded in 15 min with the removal of 78.5% of total organic carbon (TOC) in 8 h at the current density of 10 mA/cm^2 (Feng et al., 2010). However, high power consumption during the EO process is one of the major bottlenecks to scale-up this process for field-scale applications. To overcome this lacuna, Sakakibara et al. (2010) demonstrated that complete degradation of different kinds of EDCs like BPA, NP, 4-t-OP, and E_1 (ranging between 0.01 to 150 µg/L) is be possible by applying extremely low energy input of 1 to 10 Wh/m^3 through granular bed electrochemical reactor. Therefore, an electrode having a high specific surface area possesses the proficiency for the high rate treatment of E_1, E_2, and EE_2 and other endocrine disrupting compounds through the electrolytic reactor (Reis and Sakakibara, 2012).

4.2 Electrocoagulation

The EC process is an advanced electrochemical technique employed for the removal of a broad spectrum of pollutants and emergent contaminants from wastewater as it is a combination of the functions of three processes, namely coagulation, floatation, and electrochemistry (Fig. 4). In the first phase of this electrochemical technique, coagulant formation occurs via the suspension of metal ions released from an anode electrode, and thereafter pollutants and other suspended particles are destabilized via neutralization of their repulsive forces that keep them in suspension in water. After the neutralization of repulsive forces, the suspended particles agglomerate to form flocs and are easily separated from water through the process of sedimentation (Meunier et al., 2006).

The EC process has extensive advantages over other conventional chemical coagulation or flocculation process. For example, external chemical coagulants like metal salts, polyelectrolytes, etc., are not required as the coagulants are generated *in situ* through electrolytic oxidation of suitable anode material, resulting in lower sludge formation as compared to chemical precipitation (Brillas and Martínez-Huitle, 2015). Among different metal compounds, mostly aluminium and iron are extensively utilized as the metallic anode material in the process of EC due to its high dissolution rate, favouring the production of hydroxides, polymeric hydroxides, and oxyhydroxides. As an example, Cook et al. (2016) developed a bench-top EC unit fabricated with aluminium blades as anode for the degradation of different estrogenic EDCs, such as E_1, E_2, E_3, EE_2, BPA, and NP. The maximum 61%, 63%, 56%, 64%, 66%, and 81% of E_1, E_2, E_3, EE_2, BPA, and NP, respectively, were removed from municipal wastewater spiked with these six types of EDCs via EC. Likewise, Symonds et al. (2015) also removed up to 78% of personal care products from domestic wastewater utilizing a benchtop EC unit. Furthermore, complete removal of phosphate and 89.7% of nitrate removal was achieved through this EC treatment along with a maximum 7 log scale reduction of pathogens (Symonds et al., 2015). Therefore, these investigations exemplify that a wide range of EDCs and other micro pollutants can be successfully eliminated through the process of EC.

4.3 Electro-Fenton treatment for the disruption of EDCs

In the cathode-based electrochemical advanced oxidation systems, the most well-known technique is the EF process, wherein H_2O_2 is externally added or produced *in situ* at the cathode in the presence of O_2 (Eq. 6), and the Fe(II) catalyst is also regenerated on the surface of the cathode (Martínez-Huitle and Panizza, 2018) following Eq. 8. *In situ* production of H_2O_2 can be facilitated via two-electron reduction of oxygen at the cathode surface (Ganiyu et al., 2018).

Generally, during the EF reaction, oxidation of organic contaminants is mediated by electrochemically generated homogeneous •OH, which is swiftly produced in the bulk solution through the decomposition of H_2O_2 in the presence of catalytic reaction of ferrous ions (Eq. 7) in addition to the •OH generated in the vicinity of anode surface (Fig. 5) (Trapido et al., 2009).

Table 4
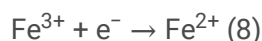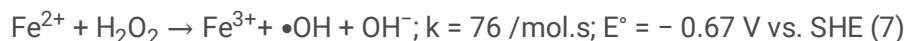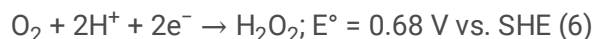Removal of broad-spectrum EDCs through different electrochemical processes

Electrochemical process	Operating condition	Removed EDCs	Removal efficiency	Reference
EO	Electrodes: carbon fiber; Applied cell potential: 0.7-1.0 V	BPA, BPS, Diphenoli acid (1 mM of EDCs in 14.2 g/L Na_2SO_4 solution)	100% of removal efficiency after 10 min of treatment	Kuramitz et al. (2004)
EO	Electrodes: Ti/BDD, $Ti/Sb-SnO_2$; j:10-50 mA/cm^2	Bisphenol A (100 mg/L)	100% mineralization of BPA at 10 mA/cm^2 with $Ti/Sb-SnO_2$ and Ti/BDD anodes	Cui et al. (2009)
EO	Electrodes: BDD; 8.7 g /L of K_2SO_4 solution j: 1.35 to 21.6 mA/cm^2	Methyl paraben (MP)	Complete mineralization of 100 mg/L of MP in 300 min	(Steter et al., 2014)
EO	Anode: BDD, Steel, Pt; j: 50 mA/cm^2; Electrolytes: 14.2 g/L Na_2SO_4	Butyl paraben (BP)	Total mineralization of 100 mg/L of BP in 15 min with BDD anode; 40% and 18% removal of BP with steel and Pt anode, respectively	(Pueyo et al., 2020)
EC	Electrodes: carbon felt; j: 16.6, 33.3 and 66.6 mA/cm^2	Micro-plastics and fabrics from real effluent of washing machine	93.4% of total micro-plastics and fabrics mineralization after 360 min; 90% and 85% removal of TOC and COD, respectively	Duran et al. (2018)
	Electrodes: carbon steel; pH: 5.95; Energy consumption (< 0.742 kWh/m^3)	Algestone acetophenide and estradiol enanthate	Removed 88.9% and 91.8% of algestone acetophenide and estradiol enanthate, respectively after 60 min	Morais et al. (2019)
EC-EO	EC: Iron electrodes; j: 8.88 mA/cm^2; EO: Anode-BDD; Cathode-Ti; j: 22.2 mA/cm^2	Mixture of steroid estrogens E_1, E_2, E_3, and EE_2 (200 µg /L)	90% removal of DOC after 30 min through EC; 80% removal of steroid estrogens after 8 min through EO	Maher et al. (2020)
EF	Molar ratio of Fe^{2+}/H_2O_2: 0.012 to 0.100; pH: 3	BPA (13 to 300 mg/L)	Complete BPA degradation and significant DOC and TOC conversion	Escalona et al. (2014)
EO	Anode: BDD; Cathode: Pt; Electrolyte: $NaNO_2$; pH:4; j:9.04 mA /cm^2	BPA (50 mg/L)	63.7% removal of TOC after 60 min	Dong et al. (2019)
EO	Anode: BDD; Cathode: SS; j: 40 mA /cm^2	NP7EO (500 mg/L)	90% removal of TOC after 8h	Armijos-Alcocer et al. (2017)

Note: *Value calculated directly from the data reported in the article; BDD = Boron-doped diamond; EC = Electrocoagulation; EO = electrochemical oxidation; AO = Anodic oxidation; EC-EO = Electrocoagulation-electrochemical oxidation; j = Applied current density; DOC = Dissolved organic carbon; E_1 = Estrone; E_2 = 17β-estradiol; E_3 = Estriol; and EE_2 =17α-ethynylestradiol; NP7EO = Nonylphenol ethoxylate-7; DiBP = di-isobutyl phthalate

| Electrochemical process	Operating condition	Removed EDCs	Removal efficiency	Reference
EF	Anode: BDD; Cathode: Graphite felt; pH: 3; j: 6.25 mA /cm^2*	MP (100 mg/L)	98.68% removal of TOC after 120 min	Rosales et al. (2018)
EF	Electrodes: Iron; pH: 5; j: 6.95 mA /cm^2; Na$_2$SO$_4$: 2 g /L; H$_2$O$_2$: 40 μL	DiBP (10 mg/L)	93.7% removal of DiBP after 25 min	Yang et al. (2020c)
EC	Anode: mild steel; cathode: iron mesh; j: 3.8 mA /cm^2; pH: 3	Cr(VI) (26 mg/L)	Complete removal of Cr(VI) in 21.47 min	Khan et al. (2019)
EC	Electrodes: Aluminum; j: 6 mA /cm^2	Phenol (120 mg/L)	57% removal of phenol in 120 min	Zambrano and Min (2019)
Note: *Value calculated directly from the data reported in the article; BDD = Boron-doped diamond; EC = Electrocoagulation; EO = electrochemical oxidation; AO = Anodic oxidation; EC-EO = Electrocoagulation-electrochemical oxidation; j = Applied current density; DOC = Dissolved organic carbon; E$_1$ = Estrone; E$_2$ = 17β-estradiol; E$_3$ = Estriol; and EE$_2$ =17α-ethynylestradiol; NP7EO = Nonylphenol ethoxylate-7; DiBP = di-isobutyl phthalate				

Oxidation of target pollutants and simultaneous electrochemical regeneration of Fe(II) at the cathode is proceeded by the reaction given in Eq. 8 and Eq. 9, respectively.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2; E° = 0.68 \text{ V vs. SHE (6)}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + •OH + OH^-; k = 76 \text{ /mol.s}; E° = -0.67 \text{ V vs. SHE (7)}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \text{ (8)}$$

$$•OH + EDCs \rightarrow \text{By-products} + H_2O \text{ (9)}$$

Moreover, •OH generated by H$_2$O$_2$ and ferrous salts during Fenton's oxidation process, has a high oxidation potential to mineralize the toxic EDCs effectively. Therefore, the production rate of H$_2$O$_2$, the concentration of Fe(II), properties of contaminants, and solution pH have a significant effect on the efficacy of the EF process. Surplus production of •OH in the EF system has made it possible to treat concentrated wastewater laden with recalcitrant pollutants with appreciable efficiency. For instance, 99.1% removal of 4 mg/L dimethyl phthalate was accomplished via EF degradation using iron electrodes (Dolatabadi et al., 2021). However, the sluggish production rate of H$_2$O$_2$ and strict pH requirement of 3.0 are among the major roadblocks of the EF process. The application of heterogeneous Fenton's catalysts such as, pyrite, chalcopyrite, etc. has made it possible to operate the EF process in neutral and circumneutral solution pH (Ganiyu et al., 2018).

For the further enhancement of the treatment efficiency, researchers have applied ultraviolet-visible (UV-Vis) light or solar irradiation in the EF process, which is formally recognized as photo-electro-Fenton oxidation (PEF) (Ganiyu et al., 2018). The PEF system works on the principle of EF treatment along with irradiating UV light, wherein emerging micro pollutants are degraded via the formation of •OH at the surface of the anode as well as the photolytic reaction due to

the UV radiation (Eq. 10). Also, in the PEF process, photodecomposition of intermediate compounds such as Fe(III)-carboxylate complexes occurs through Eq. 11.

$$Fe\,(OH)^{2+} + h\nu \rightarrow Fe^{2+} + \bullet OH \quad (10)$$

$$Fe\,(OOCR)^{2+} + h\nu \rightarrow Fe^{2+} + CO_2(g) + R\bullet \quad (11)$$
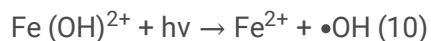
Furthermore, researchers also developed a novel PEF, formally known as solar-assisted PEF for the improvement of the degradation rate of EDCs and other emerging pollutants by applying sunlight as the UV source. In this veneration, Ganiyu et al. (2018) and Steter et al. (2018) removed parabens, one of the major endocrine disruptors, through SPEF using BDD and RuO_2-based anode from urban wastewater. The complete removal of organic parabens like MP, EP, and PP was achieved through BDD assisted SPEF after 180 min; whereas, relatively lower removal efficiency (95%) was noticed after 240 min of reaction time via RuO_2-based SPEF with the dosage of 11.2 mg/L Fe(II) at pH 3.0 with 10 mA/cm^2 of current density (Steter et al., 2018).

In another investigation, a maximum of 69% mineralization of the antibiotic erythromycin along with the 78% removal of TOC was attained from erythromycin solution through a solar plant-based filter-press flow reactor equipped with Ti/Pt and graphite-felt as an anode and cathode, respectively, by applying an external cathodic potential of −0.35 V vs. SHE in 300 min (Pérez et al., 2017). Likewise, Fonseca et al. (2011) applied direct solar radiation for the degradation of E_1, E_2, E_3, and EE_2. After 126 days of continuous operation, the degradation rate of all these EDCs varied between 75% and 100% with an average light irradiance of 5.2 kWh/m^2. Therefore, different types of EF treatment can successfully mineralise diverse groups of EDCs and other noxious pollutants effectively, which can assist to prevent endocrine disruption hazards in both humans and natural biota.

4.4 Factors affecting the performance of electrochemical systems

There are various factors that can affect the efficiency of ETs employed for the treatment of wastewater. Nonetheless, electrode material, applied current density, supporting electrolyte, electrolyte pH and initial organic load/contaminant concentration are the most critical parameters influencing the performance of electrochemical systems. Over the past decades, AO has been considered as the most effective process for the abatement of persistent contaminants and other micro-pollutants from wastewater. The selection of anode material is one of the most significant parameters that affect the performance of AO for carrying out the electrochemical reaction. In this veneration, different conventional metal and metal composites like Pt, RuO_2, SnO_2, PbO_2, and IrO_2 based anodes have been extensively applied for the production of $\bullet OH$ (Zhuo et al., 2017). During the EO treatment of 0.5 mg/L of BP at an applied current density of 50 mA/cm^2, complete elimination of BP was secured in just 15 min of electrolysis time using BDD anode, while removal efficiency of only 40% and 18% was achieved by employing stainless steel and Pt as an anode, respectively, for the same electrolysis period (Pueyo et al., 2020).

The superior performance of BDD anode can be attributed to the fact that it is a non-active anode and therefore generates physisorbed $\bullet OH$ in greater quantity than active Pt and stainless-steel anode, where chemisorbed $\bullet OH$ is formed, which further reacts with anode to produce higher metal oxides that are relatively less potent than $\bullet OH$ in oxidising the organics. Similarly, complete degradation of 100 mg/L solution of MP through EO using the dimensionally stable anode of Ti/Ru and Ti cathode was obtained in 40 min; however, the TOC removal efficiency peaked at 36% implying partial degradation of MP (Dionisio et al., 2020). This could be because of the lower availability of $\bullet OH$ that remained confined in the vicinity of the anode and hence, only partial mineralization of MP was possible.

Despite the condescending electrocatalytic potential of BDD anodes, their large-scale application is ceased by exorbitant material cost. Inactive anodes made up of PbO_2 have shown promise as an economical alternative to BDD for degrading xenobiotics compounds like BPA and DBP (Chen et al., 2021;Samarghandi et al., 2021). Comparable performance was observed during EO of 100 mg/L norfloxacin, which resulted in 70% and 90% of TOC removal, when PbO_2 and BDD were employed as anode, respectively (Sánchez-Montes et al., 2018). However, anodes with high oxidation potential, such as PbO_2, are less stable and are less durable rendering them unfeasible for long-term operation (De Luna and Bensalah, 2021).

In addition to anode material, cathode also plays a vital role in determining the ultimate removal efficiency of contaminants in the EF process. Cathode material capable of facilitating a two-electron oxygen reduction reaction can electrochemically generate *in situ* H_2O_2, which can dramatically increase the concentration of •OH in the wastewater, thereby boosting the degradation efficiency of the system. In this context, Sopaj et al. (2020) evaluated different materials for H_2O_2 generation and advocated the use of carbon sponge and carbon felt as a cathode in the EF process as they produced 102 mg/L and 40.8 mg/L of H_2O_2 at an applied current of 50 mA with pH of 3. These porous carbon electrodes possess macrostructure that is capable of bonding with oxygen in •OOH, which abets H_2O_2 generation on the cathode surface and exemplifying higher pollutant removal efficiency.

Supporting electrolytes are also instrumental in the performance of ETs, as they not only improve the conductivity of the electrolyte medium rather also give rise to supplementary reactive species in the bulk solution that can aid pollutant abatement. Fajardo et al. (2017) demonstrated complete removal of total phenolic content during EO of six phenols namely, 3,4,5-trimethoxybenzoic acids, 4-hydroxybenzoic acids, gallic acids, protocatechuic acids, and veratric acids, each with an initial concentration of 100 mg/L using Ti/RuO_2 anode at an optimized concentration of 10 g/L of NaCl as supporting electrolyte. While only a 30% reduction in total phenolic content was achieved, when Na_2SO_4 was used as a supporting electrolyte in the same quantity (Fajardo et al., 2017).

The oxidation of NaCl generates active chlorine species, such as Cl_2, HClO, and OCl^-, which is much more reactive than the $S_2O_8^{2-}$ that are formed during the oxidation of Na_2SO_4 and therefore ameliorated the removal efficiency of phenol. Concurring results were obtained during electrochemical degradation of phenol with an initial concentration of 100 mg/L using Ti mesh electrodes, wherein the addition of 10 mg/L of NaCl attained 98.21% removal efficiency for phenol, which was 9.5 times higher compared to the removal efficiency achieved using 10 g/L of Na_2SO_4 as supporting electrolyte (Zambrano and Min, 2019).

Current density is another vital parameter, which has a direct influence on the kinetics of electrochemical reactions occurring during the operation of ETs. Usually, increasing the current or current density results in faster degradation of contaminants due to augmented formation of •OH and other oxidising agents in the electrolyte. Accordingly, during the EF treatment of 19.24 mg/L fungicide thiram using Pt and BDD anodes, electrolysis time for complete degradation was reduced from 10 mins to 5 min, when the applied current was elevated from 50 mA to 300 mA (Mbaye et al., 2022). The higher degradation rates can be explained by the escalated generation of •OH at anode and H_2O_2 at the cathode by applying higher potential. Notably, an increase in the current further from 300 mA didn't augment the degradation rate of contaminants as at higher applied current, parasitic reactions, such as cathodic evolution of hydrogen, and reduction of H_2O_2 to H_2O may occur that can reduce the overall efficiency of the electrochemical system (Mbaye et al., 2022). Moreover, the higher current density may also form a stable oxide layer on the anode surface causing the isolation of the anode surface, making electrodes susceptible to corrosion or passivation, especially in the sacrificial anodes used in EC (Garcia-Segura et al., 2017).

Electrolyte pH significantly affects the efficiency of ETs, notably during EC and EF treatment. A homogeneous EF system requires maintaining the pH of the electrolyte around 3.0 to optimise Fenton's reaction for the generation of •OH. Moreover, a slight change in pH can cause the dissolution of Fe(II) ions, which may hamper system efficiency and result in excessive sludge formation. The advent of heterogeneous EF systems has made it possible to carry the degradation of contaminants at neutral and circumneutral pH ranges, thus evading the requirement of regulating the electrolyte pH (Wang et al., 2021). Similarly in EC, the pH of the solution determines the solubility and type of coagulating species formed (Garcia-Segura et al., 2017). Slightly acidic electrolyte results in greater removal efficiency during EC, when compared to alkaline environment. For example, attenuation of *Escherichia coli* in EC employing $FeSO_4$ significantly improved from 2 to 4.3 log removal, when pH was altered from 7.5 to 6.6 (Delaire et al., 2015). The amplified attenuation capacity of *E. coli* in the EC process could be attributed to the transient presence of Fe(II) in the electrolyte at lower pH, which contributes to higher Fe(III) precipitate formation as well as triggers the generation of strong oxidants via Fenton type reaction that are effective in reducing the bacterial load of the wastewater (Delaire et al., 2015).

Furthermore, the initial concentration of target pollutants determines the electrolysis time required for their mineralisation, which in turn affects the operational cost of ETs. Higher initial concentration requires larger electrolysis time to attain the required level of mineralisation. On the contrary, the rate of degradation of pollutants is proportional to its initial concentration, as at higher concentration greater number of contaminant molecules are available that can be targeted by •OH, thus avoiding parasitic side reactions of •OH. A similar trend was witnessed by Zhang et al. (2020a) during the degradation of p-aminophenol in a varying concentration range of 50 mg/L to 200 mg/L. Nevertheless, increasing initial concentration beyond 200 mg/L didn't have any significant improvement on the degradation rate of p-aminophenol as at a given applied current density, the amount of •OH generated in the system remains constant (Zhang et al., 2020a). Hence, optimizing cell parameters and other operational factors of ETs is instrumental in producing appreciable abatement of targeted EDCs and similar xenobiotic pollutants.

5. Other Emerging Technologies For The Removal Of Edcs From Aqueous Environments

Over the past few decades, different electrochemical processes have gained a lot of interest in the field of wastewater treatment as different recalcitrant organic, inorganic, and synthetic pollutants are mineralized efficiently through this process. Moreover, the utilisation of hybrid technology, i.e., coupling of electrochemical techniques with other biological or chemical treatments has great potential to eliminate the majority of the contaminants from the aqueous medium. In this veneration, de Vidales et al. (2014) developed a hybrid electrochemical unit fabricated with UV-light and ultrasound irradiation by applying conductive BDD as anode and SS as cathode for the degradation of progesterone hormone. After 40 min of treatment, total mineralization of progesterone (initial concentration of 100 mg/L) was achieved at an applied current density of 30 mA/cm^2 along with ultrasound irradiation at 24 kHz wave with 200 W of ultrasonic power and UV treatment at 254 nm wavelength with 4 W of power (de Vidales et al., 2014).

However, the utilization of costly anode for EO can hinder the large-scale application of this technology (Das et al., 2021a;Das et al., 2019a). Therefore, cost-effective and sustainable biological treatment techniques should be implemented to mitigate these roadblocks (Das et al., 2021b;Das et al., 2021c). For instance, floating and submerged aquatic plants also possess the potential to degrade the trace phenolic EDCs utilizing peroxidases enzymes (Reis and Sakakibara, 2012). The complete destruction of BPA, 4-t-OP, 2,4-dichlorophenol, and NP occurred with 100 µg/L of an initial concentration of each EDCs through the bio-Fenton process in the presence of H_2O_2 at pH ranging between 3.0 and 9.0 (Reis and Sakakibara, 2012). More recently, facile modifications of conventional microbial fuel cells have made it possible to implement cathodic Fenton's oxidation of biologically recalcitrant contaminants without the need for external power supply, thereby significantly curbing the operating cost of the so-called BEF system (Sathe et al., 2022).

The efficacy of such a BEF system was illustrated during the investigation by Sathe et al. (2021) in which 87.4% sodium dodecyl sulphate surfactant with initial concentration of 10 mg/L was mitigated via BEF treatment in a contact period of 4 h and produced a maximum power density of 105.67 mW/m^2, concomitantly, thus illustrating BEF as a green wastewater remediation technology.

Moreover, researchers have also demonstrated that microalgae are capable of confiscating EDCs and other emerging pollutants from aqueous medium (Das et al., 2019b; Silva et al., 2019). In this regard, Bai and Acharya (2019) removed most common EDCs, such as BPA, by cultivating green algae *Nannochloris* sp. in both BPA mixed ultra-filtered and ozonized wastewater. After 7 days of cultivation, a maximum of 46% of BPA was removed from ultra-filtered water; whereas, BPA still remained after treatment through microalgae (Bai and Acharya, 2019). Additionally, two robust microalgal species *Picocystis* sp. and *Grasiella* sp. destructed 72% and 53% of BPA, respectively, from aqueous media; whereas, green cyanobacteria *Clamydomonas reinhardtii* accumulated 0.16 pg BPA/cell after 96 h of treatment with the exposure to 30 mg/L of BPA (Esperanza et al., 2020;Ouada et al., 2018).

Therefore, biological treatment coupled with ETs represents a significant hybrid method for the removal of EDCs and other micropollutants from wastewater. However, further investigation is required to improve the holistic understanding of the biodegradation pathway of microbiota as well as the essential parameters that enhance the degradation efficiency of EDCs. Also, by-products and secondary metabolites, which are released during the biodegradation process need to be characterized and quantified because occasionally by-products can be more intoxicating and persistent compared to the parent compounds.

6. Benefits And Drawbacks Of Electrochemical Technologies With Economical Perspective

The ETs have many advantages over other existing and advanced wastewater treatment systems (Fig. 6), though the most salient feature of ETs is the ability to mineralize a wide array of recalcitrant xenobiotic compounds at a relatively higher rate. Rosales et al. (2018) reported complete mineralization of 100 mg/L of MP in 120 min through EO process using BDD anode and carbon felt; whereas, complete abatement of MP was accomplished during the same investigation in only 60 min via EF treatment. The ameliorated degradation rate in the EF process is attributed to the surplus formation of •OH via the catalysis of *in situ* cathode-generated H_2O_2 in addition to the •OH produced at the anode surface. Moreover, elevated •OH level in EF process also abets higher mineralization of target pollutant as observed during the degradation of 20 mg/L of 2,4-dichlorophenoxyacetic acid using BDD electrodes, during which TOC elimination efficiency of EF was 20% higher than that achieved during EO (49%) under identical experimental conditions (Cai et al., 2020).

Similarly, while treating wastewater with 50 mg/L of NP, mere 30% of degradation was achieved through 60 min of ozonation; whereas, 70% removal efficiency was attained via EF treatment for the same experimental period, thus ascertaining the faster degradation kinetics achieved in the EO of pollutants (Barrera-Díaz et al., 2018). Besides the removal of recalcitrant persistent contaminants, EO and EF have also shown efficacy in subduing antibiotic-resistant bacteria and antibiotic-resistant genes that are not readily removed by other disinfection treatments like, chlorination, UV irradiation, and ozonation. However, EF treatment is considered superior to EO as antibiotic-resistant genes are not efficiently destroyed during EO. In this regard, EF inactivation of antibiotic-resistant genes yielded 3.8, 4.1, 5.2, and 4.8 log removal for intracellular *tetA*, intracellular *ampC*, extracellular *tetA*, and extracellular *ampC*, respectively in 120 mins at an applied current density of 21.42 mA/cm^2 and Fe(II) concentration of 56 mg/L (Chen et al., 2020). Clearly, ETs not only attenuate xenobiotics contaminants rather they are also capable of simultaneously disinfecting the wastewater by

destroying the microorganisms infesting the wastewater, which can considerably reduce the cost required for disinfection.

Chemical-based treatment methods like, UV/H_2O_2, ozonation, and other AOPs also degrade recalcitrant compounds relatively swiftly. Nevertheless, the amount of chemicals consumed during the degradation process is much higher in comparison to ETs. Moreover, the chemicals used in the ETs, especially in EO and EF processes are relatively inexpensive and readily available, when compared to other advanced chemical treatments. For instance, 30 mg/L of ozone and 6.5 mg/L of chlorine dosage were employed for the degradation of 4 mg/L of TCS through ozonation and chlorination degradation, respectively; while, 21 mg/L of Na_2SO_4 was utilized during EO treatment and 11 mg/L of Fe(III) ion was employed as a catalyst along with 7 mg/L of Na_2SO_4 in EF process from the removal of 10 mg/L and 50 mg/L of TCS, respectively (Mei et al., 2021; Sires et al., 2007). The reduced chemical consumption of the ETs is owed to the *in situ* electrochemical production of the H_2O_2 and regeneration of Fe(II).

Furthermore, *in situ* production and electrochemical regeneration of chemicals in ETs circumnavigates the need for transporting and storing these chemicals, which minimises the operational cost of the treatment. Many investigations have illustrated the lower treatment cost of ETs, when compared to other AOPs, such as photocatalysis, UV-O_3 treatment, Fenton process, etc. M. Rodríguez-Peña et al. (2019) estimated the treatment cost per kWh/L for 4-NP contaminated wastewater to be $0.2493 for EO, while abatement of 4-NP with AO and UV-O_3 amounted $0.4556 and $0.2707, respectively (Barrera-Díaz et al., 2018; Felis and Miksch, 2015; Rodríguez-Peña et al., 2019).

Mousset et al. (2021) devised novel criteria for juxtaposing diverse AOP for wastewater treatment using accumulated oxygen-equivalent chemical-oxidation dose. Accordingly, the overall treatment cost for 99% removal of 137.5 mg/L (TOC of 100 mg/L) of phenol per gram of TOC removed considering power consumption, chemical utilization, and sludge management was evaluated as $141.5 for EF, $601 for PEF, $697 for Fenton process, and $ 3625 for ozonation (Mousset et al., 2021), thereby advocating EF as the most cost-effective treatment option among different AOPs. Likewise, per kg phosphorous recovery from the supernatant of anaerobic sludge incurred approximately $1.92 via EC employing iron electrodes, while it was estimated to be $3.13 for precipitation using Fe(III) salt, thus demonstrating the substantial savings that can be obtained by replacing conventional coagulation process with EC (Huang et al., 2017).

Another major advantage of ETs is reduced sludge production, notably during EO and EF treatment, as both the process rely on mineralization of the target compound rather than phase change. Though, during the homogeneous EF process surfeit addition of Fe(II) ions may lead to the formation of Fe(OH)$_3$ flocs leading to the formation of a thick scum layer (Badellino et al., 2007). On the contrary, the electrochemical formation of Fe(OH)$_3$ is promoted in EC to coagulate impurities present in the wastewater. However, the amount of chemical input required and sludge produced during EC is significantly lower than that required during the conventional coagulation process as highly pure coagulants are generated *in situ* electrochemically, thus demonstrating higher removal efficiency (Garcia-Segura et al., 2017). Facile construction and operation, neutral and circumneutral pH of operation and broader application are a few other beneficial attributes of ETs that make them a propitious technology for abatement of EmCs from the wastewater.

Despite being propitious for the efficient removal of recalcitrant xenobiotic compounds, wide-scale application of ETs is still restricted to lab-scale investigations, chiefly due to exorbitant operating costs involved in the treatment process. A cost comparison analysis of different ETs, hybrid systems, and other existing technologies has been highlighted in Table 5. The major share of initial start-up cost is contributed by the cathode catalysts and expensive electrodes such as, BDD, dimensionally stable electrodes, different noble metal electrodes, etc.; whereas, a significant amount of power is also consumed during the operation incurring substantial operating charges. In this regard, Kaur et al. (2019) estimated the treatment cost of real textile wastewater by EF method as $3.13 per m^3 of wastewater and $5.76/kg of

chemical oxygen demand removed, which was much higher than the average operating cost of $0.28/m^3 for conventional treatment plant including nutrient removal (Molinos-Senante et al., 2010).

Table 5
Comparison of the treatment cost for different electrochemical technologies, hybrid systems, and other advanced treatments

Wastewater/ contaminant	Cost of treatment ($)					Remarks	Reference
	EF	EO	EC	ET-hybrid	Other treatment		
Synthetic textile wastewater	1.442/kg COD.m^3	NR	4.274/kg COD.m^3	NR	NR	Remazol black B mineralization was 80% by EF and 19.8% by EC	Suhan et al. (2020)
Waste activated sludge	2.37/ton VSS	NR	NR	NR	1.46/ton VSS (ozonation)	Dry sludge production was reduced by 94.5% and 10% after EF and ozonation, respectively	Olvera-Vargas et al. (2019)
Nonylphenol	NR	0.136/L	NR	0.124/L (O$_3$-EO)	3.656/L (UV+O$_3$)	70% and 30% COD removal by EO and O$_3$, respectively	Barrera-Díaz et al. (2018)
Pharmaceutical wastewater	2.54/m^3	52.28/m^3	0.6/m^3	NR	27.56/m3 (coagulation + photocatalysis)	COD removal was 100% for EF, 71% for EO and 54.7% for EC	Olvera-Vargas et al. (2021)
Coal plant tailings	NR	NR	5.15/ton of solid sludge	NR	23.86/ton solid sludge (chemical coagulation)	Al electrode was used for EC and AlSO$_4$ salt was used for chemical coagulation	Eskibalci and Ozkan (2018)
Phenol	141.5/g TOC	NR	NR	NR	36245/g TOC (ozonation)	Cost reported for 99% mineralization of phenol	Mousset et al. (2021)

COD = Chemical oxygen demand; EF = Electro-Fenton process; EO = Electrochemical oxidation; EC = Electrocoagulation; ET = Electrochemical technology; TOC = Total organic carbon; UV = Ultraviolet irradiation; VSS = Volatile suspended solids; NR = Not reported.

A more suitable economical representation for the treatment cost of ETs would be as the amount of energy consumed per unit of contaminant or kg of organics removed as electricity tariffs and operating cost may vary from place to place. In this regard, Monteil et al. (2019) approximated the energy requirement for xenobiotics containing wastewater to be at least 0.39 Wh/g of TOC removed that again is unsustainable while dealing with a larger volume of wastewater. In EO and EF process, the high current density is imposed on the electrodes to facilitate contaminant degradation that

causes electrodes corrosion, while in EC sacrificial iron anodes are used for the formation of iron flocs in the solution, thus frequent replacement of electrodes is required in ETs for the consistent reactor performance.

Furthermore, a major concern during electrochemical degradation of biorefractory contaminants is the formation of toxic intermediates and metabolites due to partial mineralization. Degradation by-products like, 4-isopropyl phenol, phenol, divinyloxyethane, acetylacetone, and isobutyric acid were detected, when 20 mg/L of BPA was subjected to heterogeneous EF treatment (Zhang et al., 2020b). Likewise, the degradation of surfactant NPEO forms metabolites, such as 4-NP, ethylene glycol, etc., which has higher estrogenicity than NPEO (da Silva et al., 2015;He et al., 2020). Usually, mineralization efficiency reduces with time due to limiting substrate concentration and scavenging of oxidising species. Therefore, a much longer retention period is required to degrade resistant intermediates for attaining a higher degree of mineralization, which makes the treatment uneconomical. Concurring results were reported during the abatement of furosemide and ranitidine, where an increase in electrolysis time from one hour to eight hours caused a drastic surge in treatment cost from $10.10 to $56.82 for furosemide and $12.30 to $61.72 for ranitidine for each gram of TOC subdued (Olvera-Vargas et al., 2016). Hence, making ETs economically viable remains the prime challenge in scaling-up these innovative treatment techniques for broader applications.

7. Future Scope

The non-selective destruction of contaminants by *in situ* electrochemically generated •OH radical in AO and EF makes them a very effective technology for managing xenobiotic pollution of hydric sources, while EC has displayed superior contaminant removal efficiency in comparison to the conventional coagulation process. Nonetheless, the application of ETs is still confined to lab-scale investigations owing to their prohibitive operating cost and power demand. Comprehensive research pertaining to the development of inexpensive durable electrodes and low-cost catalysts is required to reduce the initial investment and maintenance cost of ETs. Further investigations on holistic designing of continuous flow and energy-efficient reactors to suit more pragmatic applications will abet in the commercialisation of these neoteric technologies. More experiments on pilot-scale prototypes of ETs should be carried out to assess the behaviour of different cell parameters and associated operational difficulties in the up-scaled reactors. Moreover, analysis of pilot-scale reactors will also aid in a better understanding of the hydrodynamic and electrochemical behaviour of the degradation process, which can be used for optimising the design of electrochemical reactors.

More recently, researchers are coupling ETs with different AOPs to boost the destruction of persistent contaminants such as, photo-EO process, photo-EF process, EF-peroxi coagulation, etc. (Li et al., 2017;Li et al., 2021;Thor et al., 2020). Such systems have demonstrated ameliorated performance though at the cost of higher energy consumption and/or additional chemical inputs. Integrating biological systems with ETs may prove to be a better hybridisation scheme as it may reduce the overall power consumption as well as the time of electrolysis. In this regard, BEF systems, in which Fenton's oxidation of pollutants is carried without imposing an external power supply, has emerged as a plausible solution for circumnavigating the drawbacks of the EF process. Besides, ETs enhance the biodegradability of wastewater by disintegrating complex organic compounds to simpler metabolites, thus making them an ideal pre-treatment process prior to subjecting the wastewater to biological units. Different combinations such as, up-flow anaerobic sludge bed-EO, sequencing batch reactor-EO, EC-membrane filtration, sequencing batch reactor-EF have been employed to good effect for the abatement of recalcitrant pollutants (Ganzenko et al., 2020;Liu et al., 2017;Vinduja and Balasubramanian, 2013). However, there is a dearth of wholesome understanding of bio-ET integrated processes. Additional research to explore the broad facets of hybrid systems can be instrumental in dodging the bottlenecks of ETs and can catapult their advancement as a mainstream wastewater remediation technology.

8. Conclusion

The presence of EDCs in different hydric sources is an imminent threat to the wellbeing of the aquatic ecosystem and human health. Exposure to EDCs can have dire health consequences, such as hormonal imbalance, impairment of the reproductive system, cancer, obesity, developmental disorder in children, and so on. Conventional wastewater treatment plants are not designed to remove EDCs from wastewater and thus are the main culprit for EDCs discharge into natural receiving water bodies. The ETs have emerged as an effective process for the elimination of EDCs from contaminated water owing to their non-selective degradation of organic contaminants using highly potent •OH and other reactive species. Nevertheless, the broader application of ETs is flawed by unreasonable operating costs and the high energy demand of these systems. Researchers have coupled ET with other AOPs and biological systems in order to overcome the roadblocks encountered during the operation and upscaling of ETs. Hybrid systems like, BEF, EF/EO-MBR, EC-EF, etc. have shown promise in abatement of EmCs, though these are still in the embryonic phase and require more exploration. Further comprehensive pilot-scale investigations must be executed so that the ETs can be streamlined as an integral part of the wastewater treatment facility.

Declarations

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Data availability statement

Some or all data, models, or codes that support the findings of this study are available from the corresponding author upon reasonable request.

Authors' contributions

Rishabh Raj: Conceptualization, Formal analysis, Investigation, Methodology, Roles/Writing - original draft, Writing - review & editing

Swati Das: Validation, Visualization, Roles/Writing - original draft, Data curation, Writing - review & editing, Investigation

Sovik Das: Software, Visualization, Roles/Writing - original draft, Writing - review & editing

Makarand Madhao Ghangrekar: Funding acquisition, Project administration, Resources, Supervision, Validation, Writing - review & editing

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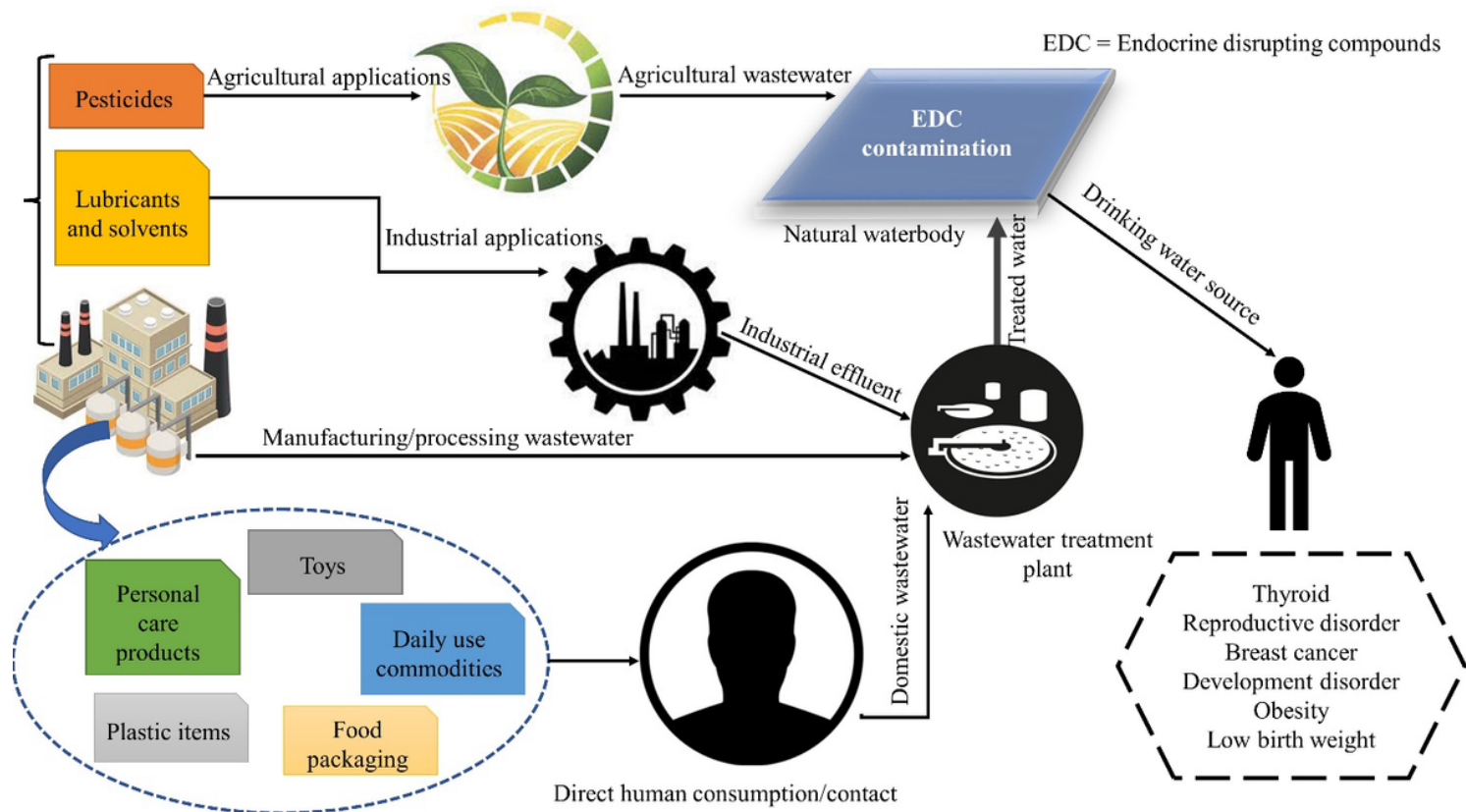
Figures

Figure 1

Probable pathway of EDCs into the aquatic environment

Figure 2

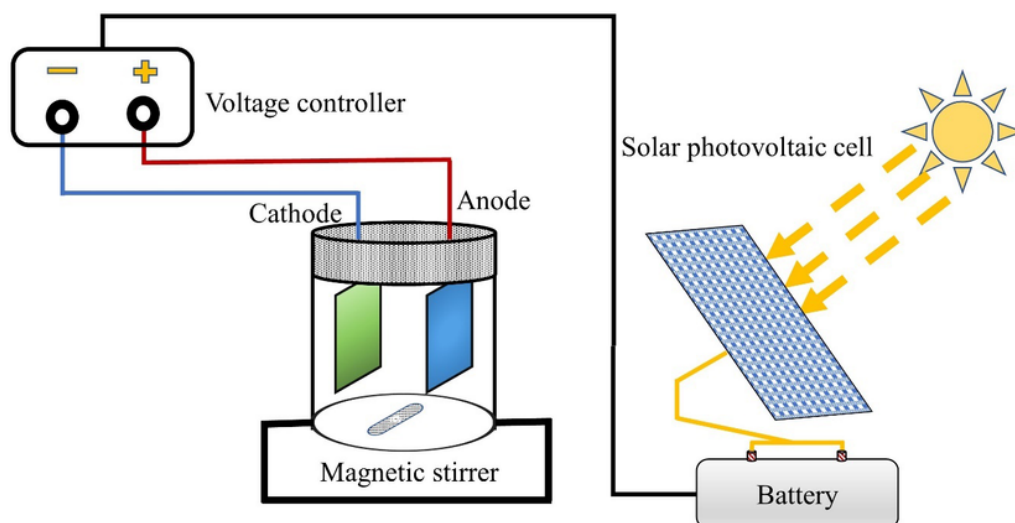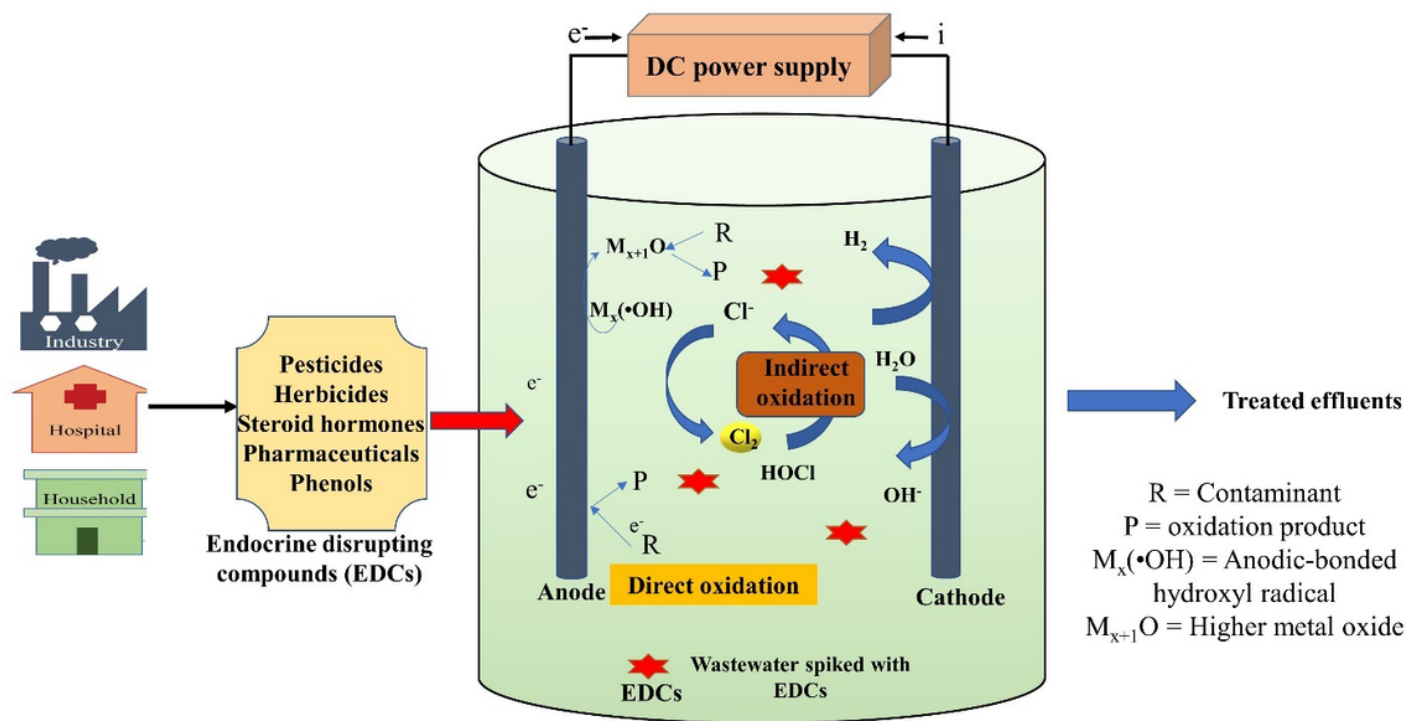Lab-scale electrochemical reactor setup operating with solar-generated electricity

Figure 3

Treatment of endocrine disrupting compounds via electrochemical oxidation
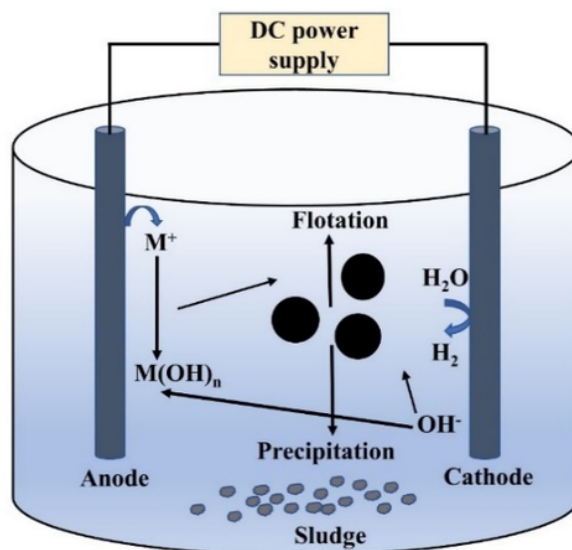
Figure 4

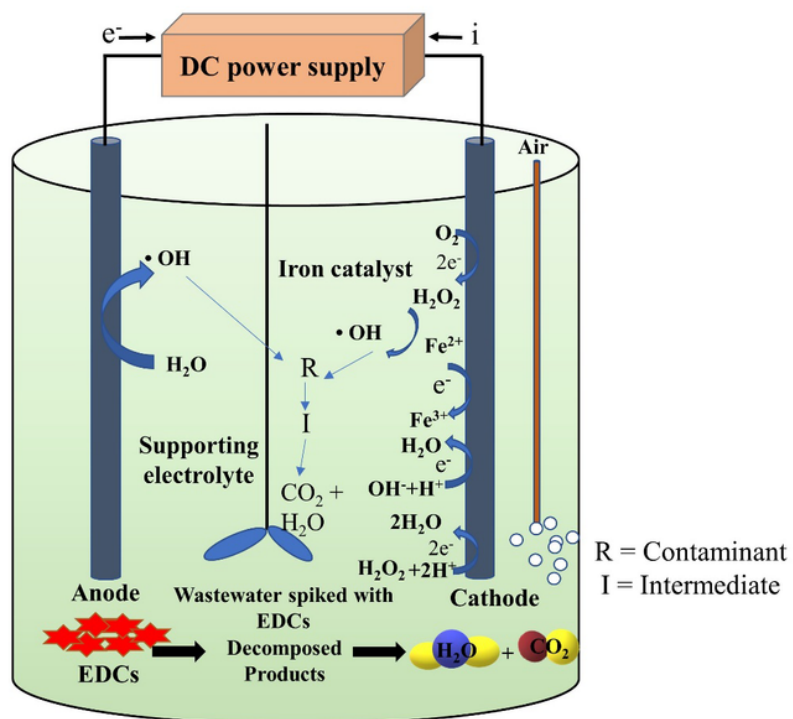Schematic representation of electrocoagulation process

Figure 5

Schematic representation of different electrochemical reactions occurring during electro-Fenton treatment
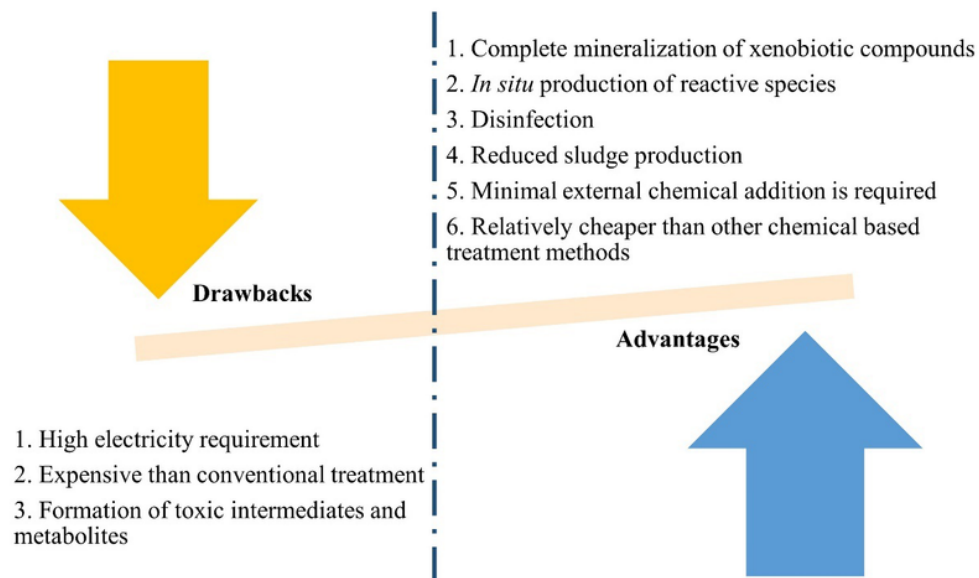

Drawbacks

1. High electricity requirement
2. Expensive than conventional treatment
3. Formation of toxic intermediates and metabolites

Advantages

1. Complete mineralization of xenobiotic compounds
2. *In situ* production of reactive species
3. Disinfection
4. Reduced sludge production
5. Minimal external chemical addition is required
6. Relatively cheaper than other chemical based treatment methods

Figure 6

Advantages and limitations of electrochemical technologies