



# Water Reuse: Emerging Contaminants Elimination—Progress and Trends

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**How to cite this paper:** Ghernaout, D. and Elboughdiri, N. (2019) Water Reuse: Emerging Contaminants Elimination—Progress and Trends. *Open Access Library Journal*, 6: e5981.

<https://doi.org/10.4236/oalib.1105981>

**Received:** December 9, 2019

**Accepted:** December 24, 2019

**Published:** December 27, 2019

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## Abstract

This work concentrates on the review paper published by Ahmed *et al.* [1] which is dedicated to the elimination of emerging contaminants (ECs) using biological, chemical and hybrid techniques in effluents from wastewater treatment plants (WWTPs). Endocrine disruption chemicals (EDCs) are better reduced by a membrane bioreactor (MBR), activated sludge, and aeration processes between various biological processes. Surfactants, EDCs and personal care products (PCPs) may be well reduced using activated sludge processes. Pesticides and pharmaceuticals manifested convenient reduction performances by biological activated carbon. Microalgae treatment techniques may diminish nearly all sorts of ECs to a certain degree. Additional biological methods were observed less efficient in dealing with ECs. Chemical oxidation techniques (like ozonation/H<sub>2</sub>O<sub>2</sub>, UV photolysis/H<sub>2</sub>O<sub>2</sub>, and photo-Fenton) may greatly eliminate up to 100% of pesticides, beta-blockers, and pharmaceuticals; at the same time, EDCs may be better reduced via ozonation and UV photocatalysis. Fenton method was observed less efficient in treating any sorts of ECs. A merged setup founded on ozonation pursued by biological activated carbon was manifested hugely efficacious in eliminating pesticides, beta-blockers, and pharmaceuticals. An integrated ozonation-ultrasound device may eliminate until 100% of numerous pharmaceuticals. Next research orientations to boost the elimination of ECs have been suggested.

## Subject Areas

Environmental Sciences

## Keywords

Water Reuse, Emerging Contaminants (ECs), Endocrine Disruption Chemicals

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(EDCs), Membrane Processes, Wastewater Treatment, Advanced Oxidation Processes (AOPs)

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## 1. Introduction

Emerging contaminants (ECs) are mainly synthetic organic chemicals that have been lately found in natural mediums [1] [2] [3] [4] [5]. ECs are a huge and comparatively novel group of unregulated complexes [6] and may easily induce harmful influences in aquatic and human life at naturally pertinent levels, which are beginning an increasing worry [2] [7] [8]. They are the components predominantly found in urban sewage, daily household products, pharmaceutical production facilities, wastewater, hospitals, landfills, and natural aquatic mediums [9] [10] [11]. ECs levels may extend from a few ng/L to a few hundred µg/L [10] [12]. Such levels in the aquatic medium may produce ecological hazards like interference with the endocrine system of high organisms, microbiological resistance, and accumulation in soil, plants, and animals [13], because such ECs are not totally eliminated throughout traditional wastewater treatment techniques [8] [14] [15]. ECs comprise mainly pharmaceutical organic pollutants, personal care products (PCPs), endocrine disrupting compounds (EDCs), surfactants, pesticides, flame-retardants, and industrial additives among others [1].

Pharmaceutical organic contaminants and PCPs contain analgesics, lipid regulators, antibiotics, diuretics, non-steroid anti-inflammatory drugs, stimulant drugs, antiseptics, analgesics, beta-blockers, antimicrobials, cosmetics, sunscreen agents, food supplements, fragrances, and their metabolites and transformation products [1]. They may touch water quality and greatly influence potable water supplies, ecosystem and human health [15] [16] [17]. Their environmental bioaccumulation worsens the abnormal hormonal control inducing reproductive impairments, diminished fecundity, augmented incidence of breast and testosterone cancers, and persistent antibiotic resistance [18]. More important, antibiotic residues may cause the development of antibiotic-resistant genes hugely favoring superbugs [8].

EDCs are exogenous substances or mixtures that modify the roles of the endocrine systems and then induce negative health influences in an intact organism, or its progeny or populations [19]. The impacts linked to EDCs are breakage of eggs of birds, fishes, and turtles, problems in reproductive systems, alteration in the immunologic system of marine mammals, a decrease of sperm of human organ, elevation in the incidence of breast, testicle and prostate cancers, and endometriosis [16]. Pesticides have immune-depressive impacts in fishes, mammals and may alter hemopoietic tissue of anterior kidney [20]. Surfactants can touch the physical stability of human growth hormone formulations and are responsible for the endocrine activity [1] [21].

A set of diverse physical, chemical, and biological techniques have previously been utilized to eliminate or decompose the remains of ECs during the past years [22] [23]. Biological treatment techniques remain the most largely employed for eliminating ECs, comprising activated sludge, constructed wetland, membrane bioreactor (MBR), aerobic bioreactor, anaerobic bioreactor, microalgae bioreactor [24] [25], fungal bioreactor, trickling filter, rotating biological reactor, nitrification, enzyme treatment, and biosorption. Several non-biodegradable organic micropollutants cannot be enough reduced employing biological treatment techniques [5] [26] [27]. Chemical treatment processes are also largely employed for decomposing such micropollutants [26] [27], involving traditional oxidation techniques like Fenton, ozonation, photolysis, and advanced oxidation processes (AOPs) [28] [29] like ferrate [30] [31] [32], photo-Fenton, photocatalysis, solar-driven processes, ultrasound process, and electro-Fenton method. Furthermore, numerous hybrid systems have newly been implemented to improve the elimination of a large span of ECS. **Table 1** lists the benefits and dares of diverse methods for eliminating ECs [1].

The plurality of polar and semi-polar pesticides and pharmaceuticals will stay partitioned in the aqueous phase because of their comparatively elevated water solubility; for this reason, their reduction via physical processes like sedimentation and flocculation is not efficient [67] as it has been mentioned to be less than 10% [68] [69]. As a result, additional debates of those methods are not revised here. The debate of extra physical treatment techniques like membrane [70], reverse osmosis (RO), ultrafiltration (UF), microfiltration (MF), NF, and adsorption methods is also kept out from this work, even if such physical approaches can be a piece of hybrid or integrated treatment techniques for eliminating ECs [1] [71].

Therefore, this work aims to deeply assess the viability of biological, chemical, and hybrid treatment processes as a tool to eliminate ECs from wastewater. Particularly, the paper presents an outline of the efficacy of diverse wastewater treatment techniques for eliminating ECs. It also estimates traditional wastewater treatment methods along with amelioration and hybrid treatment techniques for reducing ECs. It also assesses the dares and the actual comprehension inabilities restricting the performance of biological and chemical treatment technologies. Several of the future research trends are as well proposed.

## 2. Biological Treatment Techniques

Biological treatment techniques have been largely used for eliminating ECs mostly via the pathway of biodegradation. Biodegradation is the method during which large molecular weight ECs are decomposed by microorganisms like bacteria [72] [73] [74] [75], algae [76] [77], and fungi into small molecules [6], and even biomineralized to simple inorganic molecules like water and carbon dioxide. During the traditional biodegradation method, microorganisms employ organic complexes as first substrates for their cell development and induce

**Table 1.** Benefits and dares of diverse techniques in eliminating ECs [1].

Treatment method	Benefits	Dares
<i>Traditional</i> Biological activated carbon	A large variety of ECs reduction from wastewater. Reduction of remaining disinfection/oxidation products [33] [34] [35] [36]. Not producing hazardous active products.	Comparatively elevated cost in running and maintenance. Regeneration and disposal hurdles of high sludge. Processing of sludge may elevate global cost by 50% - 60%.
Microalgae reactor	Resource recovery of algal biomass, employed as fertilizer [37] [38] [39]. Elevated quality effluent & no acute toxicity danger linked with ECs.	Reduction efficiencies touched by cold season. EDCs cannot be decomposed conveniently.
Activated sludge	Lower capital and operational costs than AOPs. More environmental friendly than chlorination [40] [41] [42].	Low efficiencies for pharmaceuticals and beta-blockers. Large amount of sludge containing ECs. Unsuitable where chemical oxygen demand levels are greater than 4000 mg/L.
<i>Non-traditional</i> Constructed wetland	Low energy consumption and low operational & maintenance costs. High performance on removal of estrogens, PCPs, pesticides and pathogens.	Clogging, solids entrapment and sediments formation. Biofilm growth, chemical precipitation and seasonal dependent. Needs large area of lands and long retention time.
MBR	Effective for the removal of bio-recalcitrant and ECs. Small footprint.	High-energy consumption, fouling, and control of heat and mass transfer. High aeration [43] cost and roughness of membrane [44] [45]. Pharmaceutical pollutants have low efficiencies.
<i>Chemical process</i> Coagulation	Reduced turbidity arising from suspended inorganic and organic particles [46] [47] [48]. Increased sedimentation rate through suspended solid particles formation [49] [50] [51].	Ineffective micropollutants removal [52] [53] [54]. Large amount of sludge [55] [56] [57]. Introduction of coagulant slats in the aqueous phase [58] [59] [60] [61].
Ozonation	Strong affinity to ECs in the presence of H <sub>2</sub> O <sub>2</sub> . Selective oxidant favoring disinfection and sterilization properties [62].	Interference of radical scavengers.
AOPs	Major ancillary effects on removal of ECs such as EDCs, pharmaceuticals, PCPs and pesticides. Short degradation rate.	Energy consumption issues, operational & maintenance cost. Formation of toxic disinfection by-products [63] [64]. Interference of radical scavengers.
Fenton and photo-Fenton	Degradation and mineralization of ECs. Sunlight can be used by avoiding UV light.	Decrease of •OH forming chloro and sulfato-Fe(III) complexes or due to scavenge of •OH forming Cl <sub>2</sub> • and SO <sub>4</sub> • <sup>-</sup> in the presence of chloride and sulfate ions.
Photocatalysis (TiO <sub>2</sub> )	Degrading persistent organic compounds. High reaction rates upon using catalyst. Low price and chemical stability of TiO <sub>2</sub> catalyst and easier recovery.	Difficult to treat large volume of wastewater. Cost associated with artificial UV lamps and electricity. Separation and reuse of photocatalytic particles from slurry suspension.
<i>Physical process</i> Micro-orultra-filtration	Can remove pathogens. Applicable for heavy metal removal.	Not fully effective in removing some ECs as pore sizes vary from 100 to 1000 times larger than the micropollutants. High cost of operation.
Nanofiltration (NF)	Useful for treating saline water and wastewater treatment plants (WWTPs) influents. Can remove dyestuff and pesticides.	High-energy demand, membrane fouling and disposal issue [65]. Limited application in pharmaceutical removal.
Reverse osmosis	Useful for treating saline water and WWTP influents. Can remove PCPs, EDCs and pharmaceuticals.	High-energy demand, membrane fouling and disposal issue [66]. Corrosive nature of finished water & lower pharmaceutical removal.

enzymes for their ingestion [12] [78] [79] [80]. Several ECs are poisonous and resistant to microbial development thus blocking biodegradation, in which situation a growth substrate is required to keep microbial development for biodegradation, a phenomenon recognized as cometabolism [12]. Biodegradation techniques have conventionally been utilized in wastewater treatment devices for eliminating ECs [81] [82]. They may be classified into aerobic and anaerobic techniques. Aerobic implementations involve activated sludge, MBR, and sequence batch reactor. Anaerobic techniques implicate anaerobic sludge reactors and anaerobic film reactors. The wastewater features have a fundamental contribution in choosing biological techniques [9] [83]. The wastewater treatment methods may be largely categorized as traditional processes and non-traditional processes, which are depicted in next sections [1] [66] [84].

The decomposition potential of ECs is a function of the chemical and biological persistence of ECs, their physicochemical characteristics, the technique applied and running parameters. For the highly polar substances (such as most pharmaceuticals and their corresponding metabolites), the most substantial removal mode is via the biological conversion or mineralization by microbes. The elimination yields greatly depend upon the treatment method, the working factors, and pointed pollutants [85]. Distinguishing decomposition products in environmental samples is hard work since not only are they found at so small concentrations but also they are existing in complex matrices that may interfere with detection [85] [86].

More details about progress and challenges in traditional treatment methods may be found in [1].

### 3. Chemical Treatment Techniques

Biological wastewater treatment techniques may be efficacious in eliminating several categories of ECs following the target chemicals, nature of wastewater, and running parameters [1] [87]. For instance, polar pharmaceuticals and beta-blockers depicted changing reduction performances in diverse biological techniques. Thus, chemical treatment processes have to be examined as replacements with the objective of discovering appropriate finishing technologies to more eliminate ECs [88] [89]. Such techniques are largely described as aqueous phase oxidation processes founded on the intermediary of highly reactive chemical species [90]. Oxidation reactions have mainly been employed to complete rather than substitute classical setups and to ameliorate removing ECs [91]. Chemicals like chlorine, hydrogen peroxide, ozone as well as the integration of these oxidants involving transition metals and metal oxides based catalysts in the so-called AOPs are needed for eliminating ECs from wastewater [92] [93]. Moreover, an energy source like UV-vis radiation, electric current, solar [94], gamma-radiation, and ultrasound are also utilized [95] [96]. In AOPs, oxidizing ECs is founded on generating free radicals, especially, hydroxyl radicals that ease the transformation of contaminants to less poisonous and more de-

composable compounds [95] [97]. The final goal of chemical oxidation is the mineralization of contaminants, with their transformation to carbon dioxide, water, nitrogen, and other minerals. The rate constants for most reactions involving hydroxyl radicals in water are frequently in the order of  $10^6 - 10^9 \text{ M}^{-1}\cdot\text{s}^{-1}$  [1]. Chemical oxidation techniques may modify pharmaceuticals' polarity and the number of functional groups, which in turn influence their functionality in the organisms.

Progress and dares in classical oxidation methods are well explained by Ahmed *et al.* [1].

#### 4. Progress and Challenges in Hybrid Systems

The classical wastewater treatment methods are not appropriate for eliminating efficiently several ECs [98]. A collection of hybrid treatment techniques is mentioned in the literature. Throughout the past decade, huge ameliorations have been reached in their usage in wastewater treatment, to avoid the liberation of ECs into the aquatic environment by effluent discharge [99]. Most of the hybrid systems are composed of biological-based treatment setup pursued by some physical or chemical treatment devices. Chemical oxidation founded treatment, as ozonation is the most largely employed method to merge with the biological processes. Several illustrations of these integrations comprise ozonation assisted by biological activated carbon, MBR-RO/UF/MF/ozonation, filtration and activated sludge pursued by UF [1]. MF and UF are ever more being viewed as replacements to granular media filtration [100].

#### 5. Future Tendencies

Diverse biological and chemical-founded processes may efficiently eliminate distinct ECs; however, there are up to this time insufficiencies in the total elimination of ECs. Several additional research domains are proposed in **Table 2** [1].

#### 6. Conclusions

The main points drawn from this work may be given as:

- 1) Various biological techniques were observed to boost the reduction performance of diverse categories of ECs. As an illustration, the traditional activated sludge method has manifested better reduction performances for surfactants, EDCs, and PCPs than trickling filter and biofilm reactors, nitrification and denitrification techniques. Biological activated carbon method has been mentioned with ameliorated performances in the reduction of pesticides, analgesics, and antibiotics. MBR process has been detected to be hugely efficient in eliminating EDCs, PCPs, and beta-blockers than constructed wetlands. The new microalgae founded technique has the most elevated performance in eliminating diverse classes of ECs particularly pharmaceuticals and PCPs, even if no information was published on their elimination of beta-blockers, antibiotics, and surfactants [1] [110].

**Table 2.** Ten investigation areas suggested for the future [1].

Research field	Description
Research field #1	There is a shortage of elaborated knowledge about the decomposition pathways implicated, the effect of running factors on ECs elimination, reaction kinetics and reactor conception for excellent efficiency.
Research field #2	Amalgamation of present treatment setups with nanoscale science and technology.
Research field #3	Dares related to wastewater sample preparations, analytical methods and validation protocols for the reliable analysis of ECs in complicated environmental samples [101] [102].
Research field #4	Reduction efficiency of various WWTP techniques at changing working situations has to be re-estimated employing appropriate sampling procedures.
Research field #5	Employing solar irradiation has to be examined as a substitutional AOP technique for diminishing the prices of huge-scale commercial implementations.
Research field #6	Composite techniques founded on merged chemical and biological treatment methods (like UV photolysis in the existence of H <sub>2</sub> O <sub>2</sub> pursued by MBR or biological activated carbon, ozonation in the existence of H <sub>2</sub> O <sub>2</sub> pursued by MBR or biological activated carbon, photo-Fenton pursued by MBR or biological activated carbon) have to be more tried.
Research field #7	Integrating physical methods (like gamma radiation and ultrasound with adsorption on activated carbon) may as well be performed inside the actual wastewater treatment setups [103] [104].
Research field #8	Ferrate method is a comparatively green technology and has to be more widely investigated for industrial-scale utilizations [105] [106] [107] [108].
Research field #9	Fresh comprehension in genetic engineering has to be inserted to choose and develop the most efficient microbes for decomposing ECs, which will decrease hydraulic contact period and economize capital cost in reactor conception.
Research field #10	The hardness and feasibility of full-scale chemical oxidation techniques require to be widely studied to guarantee ECs elimination performances and reduce poisonous by-products [109].

2) Chemical oxidation processes (like ozonation/H<sub>2</sub>O<sub>2</sub>, UV photolysis/H<sub>2</sub>O<sub>2</sub>, and photo-Fenton) have been observed to be the best techniques for reducing pesticides, beta-blockers, and pharmaceuticals. Ozonation and UV photocatalysis techniques are greatly efficacious in eliminating EDCs. The Fenton process has been illustrated to be the minimum efficient between all sorts of classical and AOPs treatment techniques. Reducing surfactants and PCPs via chemical techniques has not so far been well-tried [1].

3) Merged setups (like MBR pursued by RO, NF or UF) are better for eliminating EDCs and pharmaceuticals; however, they are less performant in reducing pesticides. Ozonation pursued by a biological activated carbon hybrid system has been found to be efficient in decreasing pesticides, beta-blockers, and pharmaceuticals. Ozonation pursued by ultrasound hybrid system may eliminate to 100% of some pharmaceuticals like salicylic acid, ibuprofen, naproxen, acetaminophen, cocaethylene, benzoylecgonine, enalapril, nor-benzoylecgonine, ketoprofen, atorvastatin, bezafibrate, clindamycin, sulfamethazine, and 4-aminoantipyrine. Additional hybrid systems founded on activated sludge pursued by UF or activated sludge pursued by gamma radiation are cost-effective for eliminating some EDCs, pesticides, and analgesic pharmaceuticals. Combined setups employing ultrafiltration, activated carbon pursued by the ultrasound process may be a better technology to deal with a large variety of ECs; however, they may not be cost-effective.

## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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## **Abbreviations**

AOPs	Advanced oxidation processes
ECs	Emerging contaminants
EDCs	Endocrine disruption chemicals
MBR	Membrane bioreactor
MF	Microfiltration
NF	Nanofiltration
PCPs	Personal care products
RO	Reverse osmosis
UF	Ultrafiltration
WWTP	Wastewater treatment plants