Light-Based Removal of Emerging Contaminants

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Contaminants of emerging concern (CECs) are currently an unregulated class of contaminants with increasing global presence and awareness. However, the management of CECs in water bodies is particularly challenging due to the difficulty in detection and their recalcitrant degradation by conventional means. Light-based oxidation processes are viable options for such application. Light-driven oxidation processes use light as an irradiation source to generate oxidative species for the degradation of emerging contaminants. The key few technologies available are discussed in the review article: photo/Fenton, photocatalysis, photolysis, UV/Ozone. Herein, a cost–benefit analysis on various light-based processes was conducted to access the suitability for CECs degradation. It was found that the UV/Ozone process might not be suitable due to the complication with pH adjustments and limited light wavelength. It was found that EEO values were in this sequence: UV only > UV/combination > photocatalyst > UV/O3 > UV/Fenton > solar/Fenton. The solar/Fenton process has the least computed EEO < 5 kWh m−3 and great potential for further development. Newer innovations such as solar/catalyst can also be explored with potentially lower EEO values. Light-based processes could also be used to detect CECs in surface water. Hence forming the 2 pronged approach for CEC management.

emerging contaminants | environmental pollutant management | light-driven technology

1. Introduction

Due to growing concern about the potential harm to the aquatic ecosystem and human health, a growing emphasis has been placed on the research of cost-effective treatment technology for contaminants of emerging concern (CECs). CECs are currently unregulated in most countries, with their treatment options not well documented [1]. The global prevalence of CECs in surface waters, groundwaters, and municipal wastewaters has resulted in a tightening of standards for emerging contaminants [2]. Despite guidelines set by local authorities, the occurrence of unregulated discharge often occurs due to a lack of strong legislation and ecotoxicity data on CECs [3]. CECs are resilient to the conventional biological treatment processes or have slow kinetics for biodegradation [4]. Uncontrolled release of CECs into water environments causes problems like environmental persistence, ecotoxicity, and potential harm to human health. Current detection methods of CECs also suffer from few limitations, such as prohibitive cost, time-consuming detection means, and low throughput. Rapid industry changes also make the treatment and regulation of CECs particularly challenging. For instance, Ahearn et al. [5] found that the replaced substance (GenX), for the recently regulated perfluorooctanoic acid (PFOA), had a more detrimental

environmental impact. Hence, there is a pressing need for the treatment and management of CECs to keep up with global trends.

Light-driven advanced oxidation processes (AOPs) are a viable solution for the overall management of CECs, due to their high efficiency in degrading a wide spectrum of organics. The drastic decrease in the cost of UV-light emitting diode (LED) with a single peak emission wavelength has also allowed for more precise and cheaper UV-based detection of compounds [6]. Furthermore, the occurrence of CECs in secondary effluents with characteristically low turbidity and high UV transmittance >35–65% [7], makes light-based treatment particularly attractive.

Despite the multiple advantages of light-based systems, there is a lack of review for the light-based treatment and management of CECs. Hence, this review aims to provide an updated overview of the occurrence, treatment and management of CECs, using light-based technology. This review discusses a two-pronged approach for the treatment and management of CECs, highlighting recent applications within the last 3 years. Lastly, a cost–benefit analysis is done on the various light-based technology for greater insights into their potential development. Future directions for the light-driven process have also been suggested.

2. Overview of Light-Driven Processes

Due to the global occurrence of CECs in various waters and the difficulty in detection of these compounds, there is a pressing need for the overall treatment and detection of CECs. Herein, a two-pronged approach is proposed for the treatment and management of CECs (**Figure 1**). Light-based treatment can be categorized into UV/oxidant, UV/ozone, photo-Fenton, and photocatalysis, with each having a range of UV wavelength and factors affecting its operation, which is discussed below, whereas the detection methods discussed involve rapid and alternative methods for the detection of CECs in wastewater.

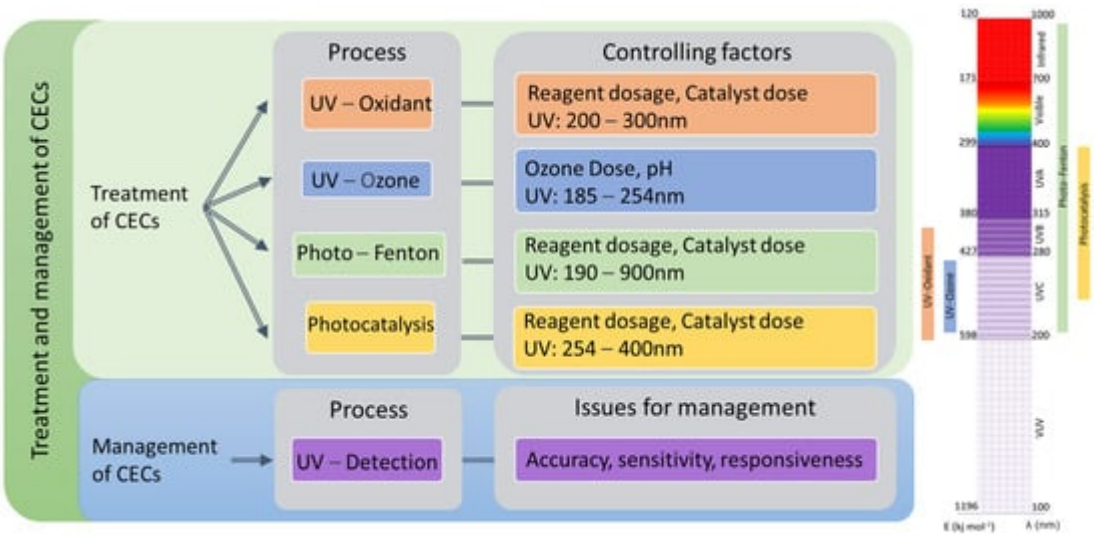

Figure 1. Overview of the treatment and management of CECs.

2.1. Mechanism of Light-Driven Processes

Light-driven processes involve two main reactions: (1) direct photolysis and (2) generation of highly reactive oxidative substrates, such as hydroxyl (•OH), chlorine (•Cl), sulfate (SO_4•$^-$), and hydroperoxyl radicals (HO_2•), by catalytically converting water or oxidants for the degradation of wastewater. Direct photolysis occurs when the light energy used (E_λ) is more than the associated bond energy of the contaminants [8]. The energy supplied by the light processes could be approximated to a specific wavelength, whereas radicals react directly with CECs and degrade them. The key reaction mechanisms and graphical illustration of the mechanisms are summarised in **Figure 2**. Detailed discussion on the mechanism could be found within the review article listed

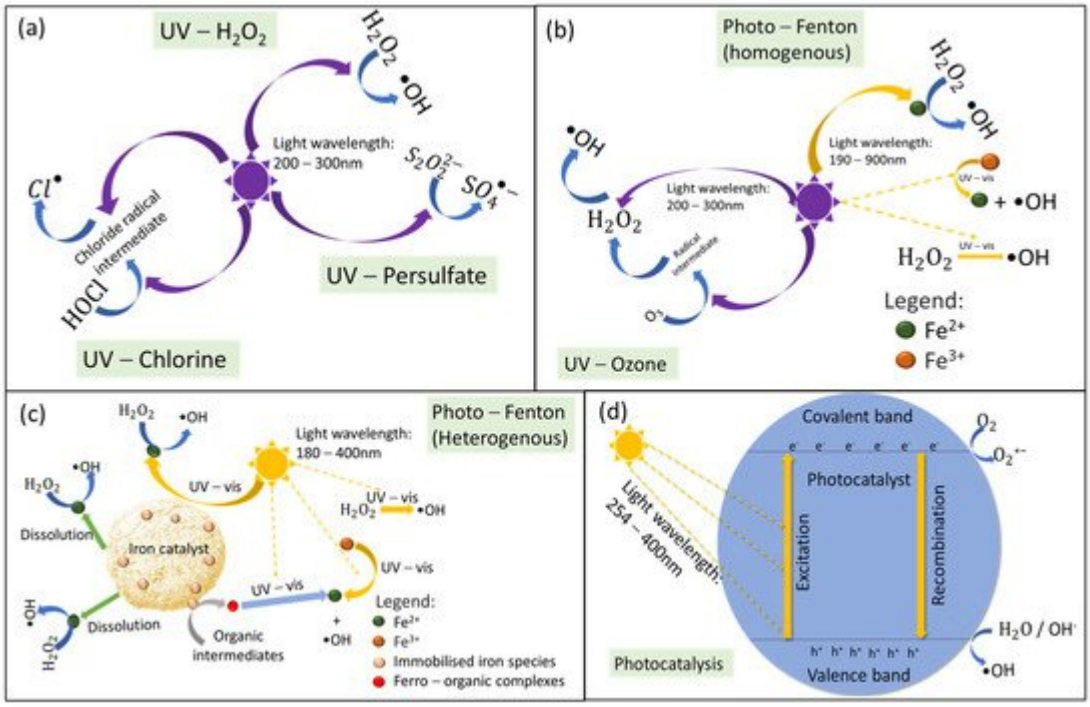

Figure 2. Graphical illustration of the reaction mechanisms for various light-driven processes: UV/oxidant (**a**), UV/ozone and photo-Fenton (homogenous) (**b**), photo-Fenton (heterogenous) (**c**), photocatalyst (**d**).

3. Cost–Benefit Analysis of Light-Driven AOPs on the Treatment of CECs

Simulated treatment costs of various light-driven processes are studied and evaluated using a matrix E_{EO} value developed by Bolton et al. [9] (**Figure 3**). Optimized conditions from the articles reviewed would be set as the operation condition for the computation of the E_{EO} values. Detailed computation of the E_{EO} values can be found in the Supplementary S4.

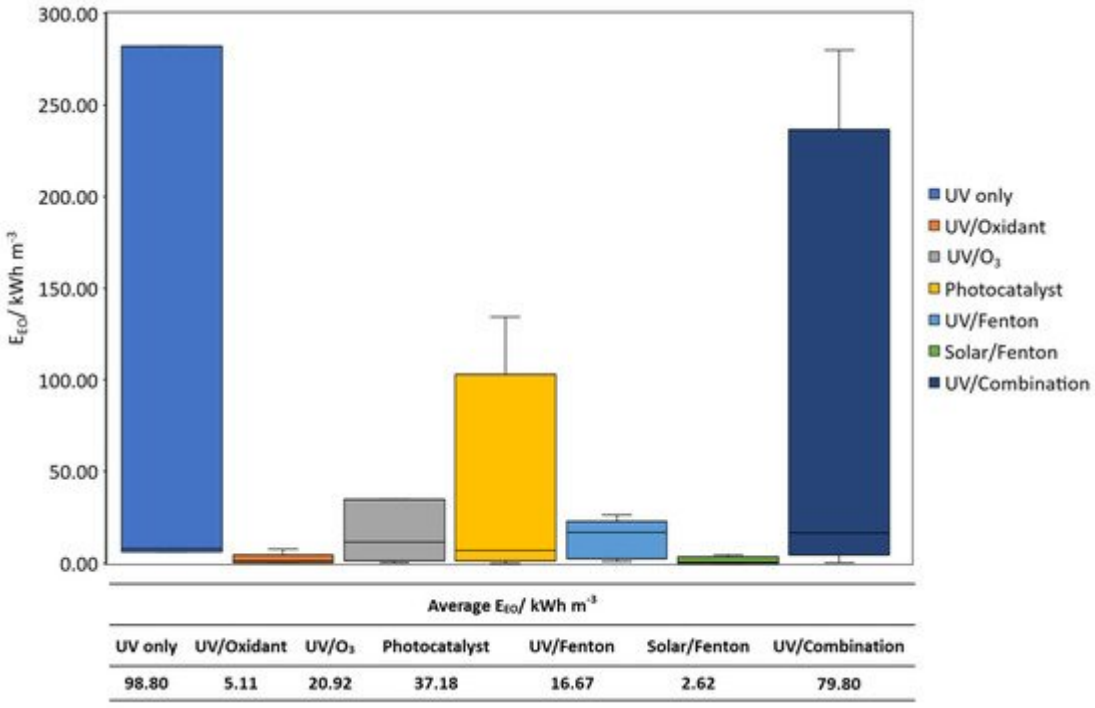

Figure 3. Average E_{EO} values of reviewed light-driven AOPs (note: A range of E_{EO} values were shown in the figure as error bars, while the bar graphs showed the average E_{EO} values).

It can be seen that the average E_{EO} values are in this sequence: UV only > UV/combination > photocatalyst > UV/O_3 > UV/Fenton > solar/Fenton. The average E_{EO} of the systems computed is 98.8, 5.11, 20.92, 37.18, 16.67, 2.62, and 76.80 kWh m^{-3} for UV only, UV/oxidant, UV/O_3, photocatalyst, UV/Fenton, solar/Fenton, and UV/combination, respectively. UV and UV/oxidant strength and selectivity of oxidants result in certain CECs having better degradation than others [10], hence resulting in a varied computation. It was also noted that for selected studies relatively low initial concentration (<0.01 mg/L) of CECs used in the study for UV/oxidant, compared to other processes also likely contributed to the low E_{EO} values. Whereas the UV/O_3 process requires both an energy-intensive UV lamp and ozone generator, it could have resulted in high operational costs. However, since it can achieve high degradation efficiencies of contaminants [11], the average E_{EO} values are not as high. For photocatalysis, articles presented in this study were lab-scaled reactors, resulting in a wide range of E_{EO} values, ranging from 0.000038 kWh m^{-3} for a simple treatment of 1 mg/L of tris-(2-chloroisopropyl) phosphate to treating pesticides-containing wastewater with a COD of 1130 mg/L at 233 kWh m^{-3}. A similar AOP treatment setup might yield different E_{EO} values based on the degradation performance of the contaminant. For example, UV/H_2O_2 in the degradation for domestic wastewater treatment (0.22 kWh m^{-3}) [12] is much lower than synthetic pharmaceutical wastewater treatment (322 kWh m^{-3}) [13]. The photocatalyst presented relatively higher average E_{EO} values. However, the higher values presented are due to the use of blacklight UV lamps [14]. Excluding the values computed with the blacklight UV lamps, the photocatalyst has a relatively low average E_{EO} value of 4.77 kWh m^{-3}. In the UV/combination list, the E_{EO} values ranged from 0.32395–280 kWh m^{-3}, as the combined process may be even more costly as more chemicals or operational costs from the additional equipment associated with the respective combined processes. Higher treatment efficiencies can result in lower treatment time and drive down the E_{EO} as reported by Sgroi et. al. in the treatment of micro-pollutants found in tertiary wastewater effluent [15],

whereas UV/Fenton had a relatively high E_{EO} value due to the relatively poorer degradation performance. Solar/Fenton overall had a lower E_{EO} value due to its low energy requirement, yet good degradation performance of CECs.

To circumvent the high cost associated with the operation of UV lamps, there has been growing interest in the use of solar-powered processes with a lower E_{EO} value. Solar/Fenton presents low E_{EO} values across various wastewater treatment applications: The average E_{EO} value of solar/Fenton is also much lower than UV/Fenton at 2.62 and 16.67 kWh m^{-3}, respectively. Furthermore, operating the solar/Fenton process at a pilot-scale did not significantly increase the E_{EO} values (4.39 kWh m^{-3}), as reported by Expósito et al. [16]. This shows that the solar/Fenton process has potential for scale-up operations and more studies can be done on this aspect for the overall management of CECs. While the computation of E_{EO} might not be a fair comparison when the degradation nature of CECs is so vastly different, it provides a good indication of the potential cost for the degradation of such wastewater. UV and UV/Oxidant processes are also not as effective for hard to degrade compounds such as perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), and bisphenol A (BPA), whereas solar/Fenton and UV/catalysis show great potential due to their generally low E_{EO} values. Besides, solar/catalyst also has the potential to be further developed with potentially lower E_{EO} values than UV/catalysis processes. However, due to limited research on solar/catalyst, a reliable E_{EO} value could not be obtained as a comparison.

Further analysis of the other cost-benefits of each process could be found in the article

4. Light-based detection methods of CECs

A cheaper alternative for the detection of CECs is through the use of light-based spectroscopy. Light-driven detection techniques have been widely proven to be useful in characterizing natural organic matter (NOM) in natural water, drinking water and wastewater. Adsorption of light measures the ‘missing’ wavelength of light that is shone on the water sample. Light-driven detection is based on the absorption of light by organic compounds which results in the excitation of the electrons from the ground state to a higher energy state. The energy difference of each ground state and excitation state pair corresponds to an absorption band. Compounds that contain aromatic rings and double bonds can absorb energy in the form of ultraviolet light to excite the electrons to higher anti-bonding molecular orbitals. UV absorbance, especially at 254 nm is one of the most widely used surrogate parameters to quantify NOM reactivity. Previous studies also found that ●OH radicals tend to react with large molecules with various reaction sites, aromatic compounds, electron-rich organic moieties. Hence, UV254 nm or UV280 nm could be used as indicators to predict the removal of CECs from UV/H_2O_2. Newer forms of chemiluminescence use enzyme-linked immunosorbent assays (ELISA) and time-resolved fluoroimmunoassays to detect CECs with a high degree of accuracy. Whereas for the excitation and emission type, a known light source is shone on the sample and the measured signals would be the excitation wavelength vs. emission wavelength vs. fluorescence intensity. The EEM could be used to discriminate different groups of NOM based on the difference in light emission and excitation of fluorophores. NOMs with certain molecular structures are reported to have fluorescent properties in a wide range of excitation/ emission wavelengths. Lastly, the physicochemical signal detection relies on the physio-chemical reaction to light onto the sample and is highly dependent on the

compounds being monitored. Infrared spectroscopy was also explored to detect a low concentration of CECs. Recently, various core-shell nanostructures have been widely developed to enhance the surface-enhanced Raman scattering (SERS) techniques for the detection of pesticides. Newer methodology like Surface plasmon resonance (SPR) was also demonstrated to have the potential for CEC detection.

Detailed examples of the newer innovation for ligh-based CECs could be found in the article listed.

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