

Recent Developments in Emerging Contaminants Determination and Treatment Technologies

Mohammed J. K. Bashir ^{1,*}  and Amin Mojiri ² 

¹ Department of Environmental Engineering, Faculty of Engineering and Green Technology (FEGT), Universiti Tunku Abdul Rahman, Kampar 31900, Perak, Malaysia

² Department of Civil and Environmental Engineering, Graduate School of Advanced Science and Technology, Higashihiroshima 739-8725, Japan

* Correspondence: jkbashir@utar.edu.my; Tel.: +60-5-4688888 (ext. 4559); Fax: +60-5-4667449

1. Introduction

The most fundamental need, which all people must have to maintain their life, is access to clean water. However, because of human activities such as farming, industry, the manufacture of cosmetics and other products, and the running of healthcare facilities, dangerous chemicals have found their way into our water systems, thus worsening the current problem of freshwater availability [1]. Contaminants such as endocrine-disrupting compounds (EDCs), personal care products (PCPs), pharmaceuticals, pesticides, polycyclic aromatic hydrocarbons (PAHs), engineered nanomaterials, micro/nanoplastics, and polychlorinated dibenzodioxins/furans have been progressively recognized in aqueous bodies over the past decade [2]. These substances are collectively referred to as emerging contaminants (ECs) because no comprehensive guidelines or toxicological data exist for them. Owing to their low concentrations and high solubility, these poisons are difficult to eliminate and can be harmful to nearby ecosystems, wildlife, and humans. Antibiotics, for instance, can breed bacteria that are resistant to them, harming both people and the environment permanently.

The water consumption, usage patterns, sewer conditions, population density, land use, and environmental persistence all affect the concentrations of these ECs in the aquatic environment. Before now, the majority of these pollutants were either unknown, unidentified, or incorrectly classified as toxins with potential environmental risks [3–5]. It is still unclear what will happen to them in designed systems, water/wastewater treatment facilities, and the environment in general. The majority of these contaminants are bioactive, bio-accumulative, abundant, and last a long time in the environment. Even though the concentration of these ECs is relatively low (ranging from ng/L to µg/L), continuous exposure to them can cause a substantial detrimental impact on environmental sustainability and human health.

In-depth studies have recently concentrated on creating effective techniques that may efficiently identify or eliminate these pollutants from wastewater while recovering any beneficial compounds present in surface water, groundwater, and wastewater.

However, there is little accessible information on the majority of these emerging pollutants, and the vast majority are still uncontrolled [4,5]. In addition, it is yet unknown how much of an environmental and health impact these emerging pollutants entail. Advances in analytical chemistry, technology, and engineering have made it possible to identify specific ECs in the environment [5]. To detect and quantify ECs in the environment, further research in this area is required.

Accordingly, this article is intended to highlight recent research and researchers' efforts to discuss novel methods for the determination, risk evaluation, and remediation of ECs.



Citation: Bashir, M.J.K.; Mojiri, A. Recent Developments in Emerging Contaminants Determination and Treatment Technologies. *Separations* **2022**, *9*, 434. <https://doi.org/10.3390/separations9120434>

Received: 10 November 2022

Accepted: 8 December 2022

Published: 13 December 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

2. Determination and Treatment Challenges of EMCs

In this section, we go over a number of research papers that cover the most recent ways of identifying, assessing, and treating ECs using cutting-edge procedures and equipment. In chemical analysis, especially in the area of trace-levels residue analysis the stability of the analytes is a crucial factor. The analyses of water have been improved recently as a result of developments in analytical technology and separation sciences. Unfortunately, one of the most important problems with water analysis in this context is the stability of compounds from sampling stations to laboratory techniques [6]. In their study, Barreca et al. [6] investigated the stability of drugs, pesticides, and antibiotics using a simple method that applied mass-spectrometric detection for analytical reasons. The stability of chemicals was examined throughout the development and validation of the method to identify the ideal conditions for sampling, extraction, and analysis. They concluded that the analytes Clotrimazole, Miconazole, Ipconazole, Famoxadone, and Metaflumizone are not stable in aqueous solution if not appropriately treated, even after a short period of time following sample preparation or sampling. Even 168 h after sampling, all the analytes on the watchlist of compounds remain stable in aqueous solutions when at least 25% ACN is added [6].

Vera et al. [7] investigated the occurrence of selected known or suspected endocrine-disrupting pesticides in Portuguese surface waters using SPME-GC-IT/MS. The trace detection of 20 known or suspected endocrine-disrupting pesticides, using a multiresidue analytical approach based on a solid-phase microextraction (SPME) followed by gas chromatography-ion trap mass spectrometry (GC-IT/MS), was carried out. The simultaneous determination of 20 important pesticides was first optimized using the proposed analytical approach, SPME-GC-IT/MS. The methodology for identifying the target components in water samples performed well in terms of analytical validation and met the requirements set forth by European analytical standards.

Eight organochlorine pesticides (α -, β -HCHs, lindane, HCB, o,p'-DDT, p,p'-DDE, p,p'-DDD, α -endosulfan), cypermethrin, and vinclozolin are the most often found pesticides out of the 20 substances tested (13 organochlorine, 1 organophosphorus, 2 dicarboximide, and 4 pyrethroid [7]).

Several analytical techniques have been developed to extract residual pesticides from agricultural water; samples of agricultural water are commonly prepared using liquid–liquid, solid-phase, and solid–liquid extraction techniques. The use of huge amounts of organic solvents, ineffective clean-up techniques, and lengthy processing durations are some drawbacks of these approaches. QuEChERS (quick, easy, cheap, effective, rugged, and safe) was established as an alternative extraction method to overcome these issues [8]. Song et al. [8] used the QuEChERS method to analyze multi-residue pesticides in agricultural water by using a combined-sorbent-based clean-up procedure. During sample analysis, multi-residue pesticides were identified and quantified using the described approach. The findings imply that the QuEChERS approach, which combines ENVI-Carb and another sorbent, can be used to effectively analyze multiple residues of pesticides in agricultural water [8].

Hrouzková and Szarka [9] studied a modified QuEChERS Procedure for the isolation of pesticide residues from textile samples followed by GC–MS determination. They highlighted that despite the fine processing of cotton fibers, pesticide residues could still be found in textile goods. However, limited attempts have been made to ascertain the concentrations of these dangerous substances in the finished textile goods [9]. It is evident that textile goods may, in fact, contribute to the presence of pesticides and ECs in water sources.

Lee et al. [10] investigated the presence of pesticides and veterinary pharmaceuticals in environmental water samples using UHPLC–Quadrupole–Orbitrap HRMS combined with online solid-phase extraction. For 41 targeted chemicals in water samples, a method for simultaneous analysis was established. The quantitation and detection limits for the technique were 1.02–5.47 and 0.32–1.72 ng/L, respectively. Excellent technique repeatability

and decreased experimental error were both displayed by the online solid-phase extraction system.

Spirulina and chlorella are two common types of microalgae used as supplements. Both can grow up naturally in a variety of bodies of water. They are primarily produced in countries with subpar water quality and occasionally no water legislation, which might act as a vector for the entry of micropollutants into the food chain. Thus, Martín-Girela et al. [11] performed a simultaneous assessment of 31 developing contaminants in commercial microalgae—including pharmaceutical and personal care products, hormones, flame retardants, and biocides—that are frequently identified as micropollutants in freshwater. The approach was tested on a variety of foods containing microalgae supplements, and the findings showed that the examined chemicals were below the limits of detection [11]. Nevertheless, due to the growing usage of reclaimed waters and manure, which can introduce ECs into the food chain, their method could be utilized to evaluate the safety of microalgae supplements.

Issues concerning exposure to perfluoroalkyl and polyfluoroalkyl substances (PFASs) and potential risks generated with a focus on PFAS occurrence and transformation in various media, characterization and treatment technologies were addressed by Abunada et al. [5]. The complexity and difficulty of regulating PFAS chemicals were discussed because of the arising uncertainty and lack of epidemiological evidence encountered. The effect of numerous scientific, technical, and societal elements affected the diversity in PFAS regulatory levels around the world. One of the main causes of this difference is the variable toxicological and the inadequate characterization of PFAS exposure rate. Technical complexity is increased by the absence of established standards for analysing PFAS in surface water, groundwater, wastewater, or solids. Although it is acknowledged that PFASs may provide health concerns in a variety of media, research on the relationship between PFAS exposure levels and risk significance is still in its infancy [5].

Several studies have been conducted recently to better understand the performance of various technologies in treating ECs. Conventional water/wastewater treatment procedures do not entirely and consistently eliminate ECs. Due to the characteristics of ECs, such as their high solubility, surfactant qualities, and thermal stability, a number of well-known and standard treatment procedures, such as air stripping, and thermal treatment, are inefficient in treating ECs. The adsorption procedure, among other physical and chemical treatment methods, has undergone extensive testing and has proven to be an efficient way to remove ECs from water. It is clear that as surface area rose, the adsorption capacity and efficacy of the adsorption process both improved. However, during the adsorption process, the pollutant will move from the liquid phase to solid waste, which will require hazardous waste management. Fouling is the key issue and restriction with RO and nanofiltration membranes. However, before it is discharged, the created brine water needs to undergo additional treatment. Advanced oxidation techniques hold great promise for removing ECs from water. AOPs recently demonstrated good removal efficiency when employed at a laboratory scale. For example, Ochir et al. [12] investigated the oxidative treatment of five different pesticides—alachlor (ALA), carbendazim (CAR), diuron (DIU), pyrimethanil (PYR), and tebuconazole (TEB). This was carried out by comparing the relative reactivities of the pesticides as a function of three different oxidative treatment processes—chlorine (HOCl), ozone (O_3), and ozone/hydrogen peroxide. They found that the oxidative treatment techniques had a significant impact on the removal efficiency of the chosen pesticides. Treatments with HOCl, O_3 , and O_3/H_2O_2 were quite effective in removing CAR (>80%) and PYR (>99%), but not at all effective in reducing TEB (20%). HOCl (81%) was shown to be more efficient than O_3 (24%) and O_3/H_2O_2 (49%), in the case of DIU. The elimination efficiencies of ALA were O_3/H_2O_2 (49%), O_3 (20%), and HOCl (8.5%) in that order. The degradation of pesticides was affected differently by the oxidative treatment processes when the pH of the solution was raised from 5.0 to 9.0. In addition, the presence of humic acid, NH_4^+ , and NO_2 in rainwater dramatically reduced pesticide breakdown [12].

However, the discharge of ECs is still unregulated because there is no strict law in place and not enough toxicological information on these ECs. These issues led to the creation of temporary aqueous guidelines. Local discharge regulations are generally focused on conventional measures, such as total suspended solids (TSS), chemical oxygen demand (COD), and biochemical oxygen demand (BOD), in the majority of countries. The US Environmental Protection Agency, the European Union, the World Health Organization (USEPA), and numerous other international regulatory bodies have also released a list of toxins along with their authorized discharge limits. The significance of treating these ECs before releasing them into the environment is demonstrated by all of these new laws.

3. Conclusions

A significant hazard to human life has been created by the intensive and widespread nature of enterprises that release large amounts of ECs into the environment. The chance of unknown ECs leak, fate, transit, and exposure by numerous companies are making the job of policymakers more challenging. The incidence, transformation, degradation pathways, and potential treatment of ECs need to be better understood, even though their pathway is still not entirely known. Unfortunately, because of their low concentrations and great solubility, EC poisons can harm both people and wildlife, as well as local ecosystems, and they are challenging to remove. Additionally, due to an absence of stringent legislation and insufficient toxicological data on these ECs, this release remains unregulated. In addition, it is yet unknown how much of an environmental and health impact these emerging pollutants entail. Advances in analytical chemistry, technology, and engineering have made it possible to identify specific ECs in the environment. To detect and count environmental ECs, more research in this field is required.

Author Contributions: Writing—original draft preparation, M.J.K.B.; writing—review and editing, A.M. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Jaffari, Z.H.; Abuabdou, S.M.A.; Ng, D.Q.; Bashir, M.J.K. Insight into two-dimensional MXenes for environmental applications: Recent progress, challenges, and prospects. *FlatChem* **2021**, *28*, 100256. [\[CrossRef\]](#)
2. Cong, Y.; Wang, W.; Chen, X.; Lv, S.-W. A dandelion-like NiCo₂O₄ microsphere with superior catalytic activity as the mediator of persulfate activation for high-efficiency degradation of emerging contaminants. *J. Environ. Chem. Eng.* **2022**, *10*, 106920. [\[CrossRef\]](#)
3. Wang, J.; Wang, S. Activation of persulfate (PS) and peroxydisulfate (PMS) and application for the degradation of emerging contaminants. *Chem. Eng. J.* **2018**, *334*, 1502–1517. [\[CrossRef\]](#)
4. Pereira, L.C.; de Souza, A.O.; Franco Bernardes, M.F.; Pazin, M.; Tasso, M.J.; Pereira, P.H.; Dorta, D.J. A perspective on the potential risks of emerging contaminants to human and environmental health. *Environ. Sci. Pollut. Res. Int.* **2015**, *22*, 13800–13823. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Abunada, Z.; Alazaiza, M.Y.D.; Bashir, M.J.K. An Overview of Per- and Polyfluoroalkyl Substances (PFAS) in the environment: Source, fate, risk and regulations. *Water* **2020**, *12*, 3590. [\[CrossRef\]](#)
6. Barreca, S.; Forni, C.; Colzani, L.; Clerici, L.; Daverio, D.; Dellavedova, P. Study on the stability of antibiotics, pesticides and drugs in water by using a straightforward procedure applying HPLC-mass spectrometric determination for analytical purposes. *Separations* **2021**, *8*, 179. [\[CrossRef\]](#)
7. Vera, J.; Fernandes, V.C.; Correia-Sá, L.; Mansilha, C.; Delerue-Matos, C.; Domingues, V.F. Occurrence of selected known or suspected endocrine-disrupting pesticides in portuguese surface waters using SPME-GC-IT/MS. *Separations* **2021**, *8*, 81. [\[CrossRef\]](#)
8. Song, N.-E.; Jung, Y.S.; Choi, J.Y.; Koo, M.; Choi, H.-K.; Seo, D.-H.; Lim, T.-G.; Nam, T.G. Development and application of a multi-residue method to determine pesticides in agricultural water using QuEChERS extraction and LC-MS/MS analysis. *Separations* **2020**, *7*, 52. [\[CrossRef\]](#)
9. Hrouzková, S.; Szarka, A. Development of a modified QuEChERS Procedure for the isolation of pesticide residues from textile samples, followed by GC-MS determination. *Separations* **2021**, *8*, 106. [\[CrossRef\]](#)
10. Lee, H.-J.; Kim, C.; Ryu, H.-D.; Chung, E.G.; Shin, D.; Lee, J.K. Simultaneous determination of pesticides and veterinary pharmaceuticals in environmental water samples by UHPLC-Quadrupole-Orbitrap HRMS combined with on-Line Solid-Phase Extraction. *Separations* **2020**, *7*, 14. [\[CrossRef\]](#)

11. Martín-Girela, I.; Albero, B.; Tiwari, B.K.; Miguel, E.; Aznar, R. Screening of contaminants of emerging concern in microalgae food supplements. *Separations* **2020**, *7*, 28. [[CrossRef](#)]
12. Ochir, D.; Lee, Y.; Shin, J.; Kim, S.; Kwak, J.; Chon, K. Oxidative treatments of pesticides in rainwater runoff by HOCl, O₃, and O₃/H₂O₂: Effects of pH, humic acids and inorganic matters. *Separations* **2021**, *8*, 101. [[CrossRef](#)]