Journal of Environmental Management 332 (2023) 117308

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Improving the sustainability of heterogeneous Fenton-based methods for micropollutant abatement by electrochemical coupling

Julio J. Conde [*,1], Santiago Abelleira [1], Sofia Estévez, Jorge González-Rodríguez, Gumersindo Feijoo, Maria Teresa Moreira

CRETUS, Department of Chemical Engineering, Universidade de Santiago de Compostela, 15782, Santiago de Compostela, Spain

ARTICLE INFO

Keywords:
LCA
Advanced oxidation
AOP
PPCPs
Electrochemistry

ABSTRACT

Advanced oxidation processes such as Fenton reaction-based processes have attracted great interest in recent years as a promising alternative for the removal of persistent pollutants in wastewater. The use of nanocatalysts in advanced oxidation processes overcomes the limitations of homogeneous Fenton processes, where acidic pH values are required, and a large amount of sludge is generated after treatment. Aiming at maximizing the catalytic potential of the process, different configurations include coupling photocatalysis or electrochemistry to Fenton reactions. This manuscript presents a comparative environmental and economic analysis of different heterogeneous Fenton-based process using magnetic nanoparticles: Fenton, photo-Fenton, electro-Fenton and photoelectron-Fenton. These alternatives encompass not only different reaction conditions but also varying degradation kinetics, which control the treatment capability in each specific case. It is not only important to determine the technological feasibility of the proposal based on the removal performance of the target compounds, but also to identify the environmental profile of each configuration. In this regard, the Life Cycle Assessment methodology was applied considering a combination of primary and secondary data from process modeling. Moreover, and aiming towards the future large-scale implementation of the technology, an economic analysis of each configuration was also performed to provide a better understanding about the costs associated to the operation of Fenton-based wastewater treatments.

1. Introduction

The effective management and removal of micropollutants is one of the major challenges in wastewater treatment. Unlike macropollutants (such as nitrogen, phosphorus, organic matter, or suspended solids), these compounds are found in very low concentrations and present, in many cases, such low degradability properties that their reduction in conventional wastewater treatment plants is hindered (Suárez et al., 2008; Margot et al., 2015). Numerous studies since the 1990s have revealed that, despite their low concentrations, micropollutants have adverse effects on ecosystems and human health (Geissen et al., 2015). Tertiary treatment technologies for micropollutant abatement have been widely studied in recent decades but there is not a clear candidate for widespread implementation in treatment plants (Burch et al., 2019). An asymmetric development is reported among the available technologies, as some have already been installed on a large scale (ozonation, ultraviolet, adsorption on activated carbon or membrane processes), while others are still on the edge of implementation, such as Fenton processes, photocatalysis or electrochemical techniques (de Boer et al., 2022).

The homogeneous Fenton process for wastewater treatment has shown relevant advantages over other advanced oxidation processes (AOPs), being a suitable and affordable way to degrade organic molecules in aqueous media. For instance, Fenton reagents are cheap, easy to handle and store, and the reaction is conducted at ambient temperature and pressure (Pignatello et al., 2006). Fenton-based processes generate hydroxyl radicals through the so-called Fenton reaction, in which Fe^{2+} ions catalyze the degradation of hydrogen peroxide. Once hydroxyl radicals are produced, Fenton reaction propagates producing other type of reactive oxygen species, such as hydroperoxyl or superoxide radicals. In parallel with the production of oxidant species, the regeneration of Fe^{2+} ions also occur through reactions with hydrogen peroxide and the

---

* Corresponding author.
E-mail address: julio.conde@usc.es (J.J. Conde).

[1] Both authors contributed equally to this paper.

https://doi.org/10.1016/j.jenvman.2023.117308
Received 19 September 2022; Received in revised form 1 January 2023; Accepted 13 January 2023

generated radicals at much lower reaction rates (Brillas et al., 2009).

The most prominent drawbacks associated with the homogeneous Fenton process are the requirement of acidic pH to avoid iron precipitation and the generation of large amounts of ferric sludge. Both conditions require additional treatment prior to water discharge, resulting in significant consumption of chemicals to adjust the pH of the water matrix. Heterogeneous catalysts, in contrast, can circumvent the stringent pH requirements as well as sludge generation, but reaction kinetics are significantly affected causing a reduction of the degradation efficiencies (Xavier et al., 2015). The use of nanostructured catalysts is an alternative ensuring the enhancement of the catalytic area and potentially, fostering the reaction kinetics. To this effect, the use of iron oxides with magnetic properties boosts the recovery and reuse capacity of the catalyst by using magnets that can retain the nanoparticles within the reaction medium (Moldes-Diz et al., 2018).

The Fenton process has been widely used in combination with photocatalytic methods to improve the removal efficiency, giving rise to the so-called **photo-Fenton (PF)** processes. It has been demonstrated that light irradiation with wavelengths below 580 nm enhances catalyst regeneration by reducing spent Fe^{3+} to Fe^{2+}. Photo-assisted methods increase the efficiency of Fenton-based reactions both in terms of degradation rate and chemical consumption, as hydrogen peroxide use in the regeneration of Fe^{2+} is reduced and an additional hydroxyl radical is generated (Pignatello et al., 2006). The popularization and cost reduction of LED lamps in the last decade have reduced the electrical consumption in comparison with conventional lamps, while maintaining similar degradation efficiencies (de Souza et al., 2021).

Aiming to reduce the consumption of chemicals, **electro-Fenton (EF)** has been proposed for the in-situ electrogeneration of hydrogen peroxide coupled to the Fenton process. This configuration simplifies the operation for chemical storage and handling, allowing precise chemical dosing with the control of the current applied to the electrochemical system. The production of H_2O_2 is based on the incomplete reduction of oxygen and is performed using either gas diffusion cathodes or submerged cathodes, using carbon woven/felt electrodes, which requires a continuous supply of air to the electrode surface to ensure excess oxygen. Although the introduction of electrochemistry was intended to generate hydrogen peroxide, the reaction kinetics at pH values close to neutrality were improved compared to regular Fenton methods (Liu et al., 2018), opening the possibility to circumvent the strict pH requirements of the standard Fenton reaction to obtain competitive degradation rates. The enhancement of the degradation kinetics is attributed to the regeneration of spent catalyst on the carbon-based cathodes (Sirés et al., 2007). As a disadvantage, electro-Fenton methods require a threshold conductivity of the aqueous matrix, so the use of supporting electrolytes is necessary for the operation of electrochemical systems to avoid potential losses and thus excessive energy consumption.

Electro-Fenton methods can also be enhanced in several ways. One of the mostly used is the introduction of light, which is known as **photoelectro-Fenton (PEF)**. PEF combines the benefits of light-assisted and electro-assisted Fenton, improving the efficiency of the degradation and mineralization of organic micropollutants (Brillas, 2020). Additionally, as an anodic reaction is required to close the circuit, it is possible to couple the Fenton process with electrochemical oxidation instead of using a counter electrode that merely promotes water electrolytic decomposition. For instance, the use of BDD (Boron-Doped Diamond), known for their high overpotential for oxygen evolution reaction, promote the formation of additional hydroxyl radicals to improve micropollutant degradation (Meijide et al., 2021).

The application of the Life Cycle Assessment (LCA) methodology as a tool for the environmental diagnosis within the wastewater sector aims to harmonize the technical aspects of treatment technologies with their associated environmental impacts. In this way, it is possible to develop engineered optimized advancements fulfilling minimum requirements and providing improved environmental outcomes. Although there is extensive literature addressing the technical aspects of Fenton-based processes, only a total of 15 relevant papers (See Table S1) framed within the topics of Fenton-based methods and LCA have been found, based on a previous bibliographic analysis performed by the authors (de Boer et al., 2022). It is relevant to note that half of the published papers are based on primary data from laboratory-scale experiments, where the LCA methodology provides information on the hotspots of the technologies from the early stages of research (Hetherington et al., 2014), revisiting the original conception that this type of study should be carried out for well-established technologies and products for which a large amount of process data is available. The analyzed studies on Fenton-based processes, conclude that the environmental profile is indirectly dependent on fundamental aspects such as the reaction kinetics, pH or the dosage of hydrogen peroxide. However, according to the literature review presented in the Supporting Information, there is only one study suggesting that photo-Fenton configuration seems to have less impact than other alternatives, such as regular or electrochemical assisted Fenton (Serra et al., 2011). Thus, there is a lack of systematic environmental analyses comparing the different available Fenton-based configurations to highlight their weaknesses and hotspots.

The objective of this work is the benchmarking, considering environmental and economic aspects, of four Fenton-based configurations for the degradation of organic micropollutants: Fenton, photo-Fenton, electro-Fenton and photoelectro-Fenton at acidic and circumneutral pH. Each configuration, at different pH values, will be associated to specific chemical and electricity requirements which will constitute the background of the environmental and economic indicators, turning out into alternations of the environmental and economic profiles. Therefore, once the main hotspots are identified, it is important to transfer that information back to the experimental work and rethink under what conditions we can improve each alternative. It is then when the cycle analysis makes sense, since based on the results we can reevaluate new conditions for each alternative.

2. Materials and methods

2.1. Goal and scope definition

One of the objectives of the LCA is the search for environmentally favorable solutions. Therefore, a benchmarking between Fenton-based (Fenton, photo-Fenton, electro-Fenton and photoelectro-Fenton at acidic (optimum) and circumneutral pH) configurations aiming to degrade organic micropollutants has been proposed for assessment. The comparison will be performed under the consideration that all the alternatives would be able to remove at least 75% of the carbamazepine found in the wastewater of a 100 L batch reactor. The functional unit (FU) was defined accordingly.

Although other four micropollutants (estrone, estradiol, ethinylestradiol and bisphenol A) were tested in laboratory scale experiments, carbamazepine was chosen for this LCA study based on its recalcitrant characteristics, since a 75% implies that the other target compounds were reduced by more than 80%. Besides, the reduction target of 75% was considered as an efficient value since it guarantees reasonable reaction times, shown in Fig. S1 in the Supplementary Information. Subsequently, process modeling was carried out to obtain inventory data for a 100 L sequential batch reactor, considered to be the most appropriate for comparison of similar Fenton-based configurations with different degradation kinetics.

The analysis was developed according to ISO standards 14040 and 14044 with an attributional approach and under the framework of cradle-to-gate system boundaries with a zero-burden assumption for the secondary wastewater treatment effluent (ISO, 2006a, 2006b). All the differences between each treatment alternative studied are presented in Fig. 1, along with their system boundaries. Inputs from nature and the technosphere are distinguished, as well as background and foreground subsystems. The background processes include all inventory data that

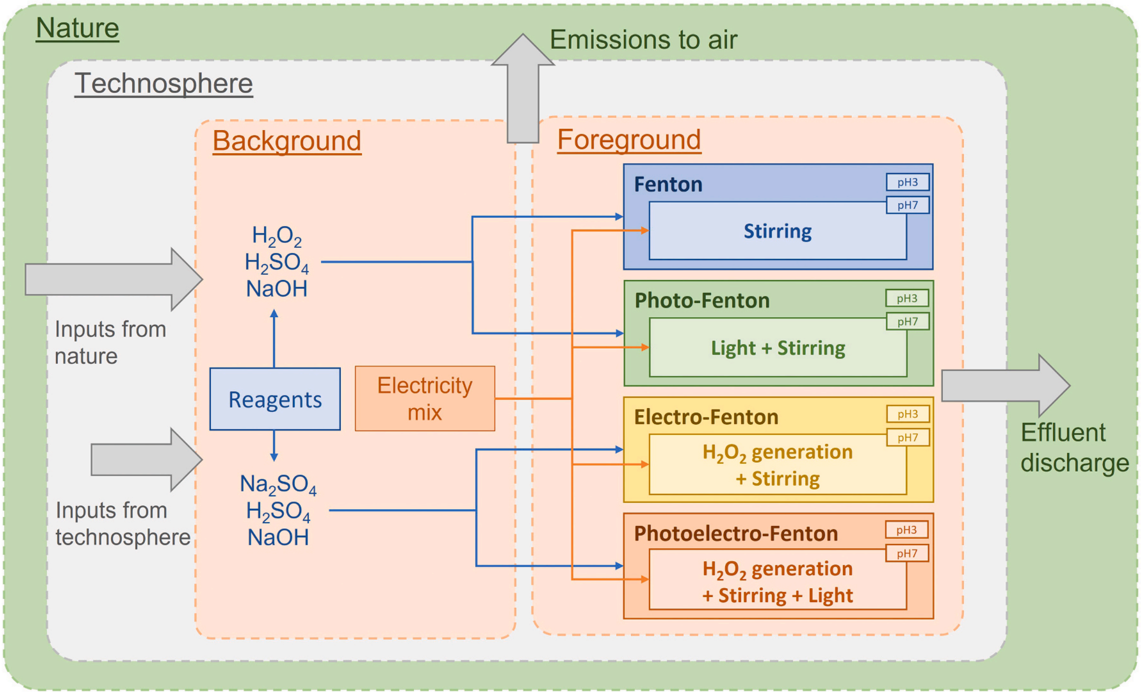

Fig. 1. Scope and system boundaries of the analyzed scenarios.

have been obtained through the ecoinvent 3.8 database (Wernet et al., 2016). Some examples are the sodium hydroxide and sulfuric acid used for acidification or conductivity enhancement and the electricity consumed for agitation and light supply. The environmental impacts from the electrogenerated hydrogen peroxide are directly associated to those from the operation of the alternative since the production is in situ (it is part of the foreground subsystem).

The main assumptions considered regarding the selected system boundaries and data source are presented below.

- The environmental impacts associated to the production of the magnetic nanoparticles (MNP) only addresses the chemical consumption to synthesize them (see Table S3).
- The micropollutants are assumed to be completely mineralized to CO_2, which was estimated using theoretical TOC values calculated from the removal rate of each micropollutant.
- Apart from direct gaseous emissions, there could also be aqueous compounds giving rise to an environmental impact. They can be present in the aqueous matrix as inorganic ions from the dissociation of the added reagents, but their low concentration results in a negligible impact. The excess of H_20_2, due to its short half-life in water bodies, should not cause any environmental impact either (Ueki et al., 2020). Therefore, and given that all of them represent less than the 5% of all impacts of the system, the cut-off criteria were included. Similar assumptions were considered in other studies. An example could be the research performed by Serra et al. (2011).
- The average European electricity mix of the ecoinvent database was set for all Fenton alternatives.
- The analysis has focused in the determination of the hotspots from the operational phase and thus, the infrastructure/construction were left out of the system boundaries.

2.2. Inventory analysis

The degradation of the micropollutants was studied at laboratory scale for the above-mentioned four configurations using a nanostructured magnetite-based catalyst (See Fig. S2 for simplified schematics of each configuration). Moreover, as the acidification to operate at pH optimum values and the subsequent neutralization were regarded as one of the main hotspots on the technique, each of the configurations was evaluated at the optimum operational pH (pH 3) and circumneutral pH. The operational parameters for the different configurations were selected on the basis of the optimum results found in the experimental research published by González-Rodríguez et al. (2021) and González-Rodríguez et al. (2022) for Fenton and photo-Fenton processes, respectively. For further details, one may check Table S4 in the Supplementary Information.

Magnetite nanoparticles coated with polyacrylic acid and immobilized on a mesoporous silica matrix support (Fe_3O_4@PAA/SBA15) were selected for this study as they are proven to improve the efficiency of heterogeneous Fenton reactions for the removal of dyes and endocrine disrupting compounds (E1, E2 and EE2), achieving removal efficiencies greater than 90%. The performance of Fe_3O_4@PAA/SBA15 was shown to be appropriate for use in batch reactors, minimizing catalyst losses, with a recovery after 5 subsequent batch cycles of 84%, and reduction of micropollutant degradation of less than 5% in consecutive cycles (González-Rodríguez et al., 2021). Fe_3O_4@PAA/SBA15 also manifest an excellent performance when used in photo-Fenton treatments with LED light, showing excellent kinetic degradation values for five different pharmaceutical micropollutants (González-Rodríguez et al., 2022).

The experimental kinetic constants, expressed as the average value of duplicate experiments, along with the corresponding coefficients of determination for linear adjustment are shown in Table 1. Regular Fenton experiments at circumneutral pH revealed negligible values of micropollutant degradation after 120 min, which points out a very small degradation constant for this alternative. The application of LED light increases the degradation constants by one order of magnitude which falls within the same range for electro-Fenton processes. From these results, the operation of Fenton and photo-Fenton processes out of the optimum values at circumneutral pH values, dramatically affect the degradation rate of the organic micropollutants. However, in the electrochemical-assisted alternatives, the reduction of the degradation constants at circumneutral pH is not so severe compared to acid media constants, as they remain in the same order of magnitude.

The parameters of the scale-up process have been estimated from the operational data acquired from the laboratory scale experiments. The

Table 1
Experimental kinetic constants of the different Fenton-based configurations at pH 3 and circumneutral pH.

	pH 3		Neutral pH		pH 3		Neutral pH	
	k/h^{-1}	R^2	k/h^{-1}	R^2	k/h^{-1}	R^2	k/h^{-1}	R^2
	Fenton[a]				**Photo-Fenton**			
BPA	0.31	0.993	–	–	3.24	0.968	0.12	0.937
CBZ	0.24	0.992	–	–	1.79	0.030	0.24	0.892
E1	0.40	0.993	–	–	2.67	0.962	0.34	0.956
E2	0.28	0.958	–	–	3.16	0.972	0.33	0.960
EE2	0.46	0.950	–	–	2.27	0.986	0.20	0.946
	Electro-Fenton				**Photoelectro-Fenton**			
BPA	6.17	0.992	2.14	0.945	6.68	0.992	3.50	0.966
CBZ	2.61	0.999	1.27	0.970	3.88	0.988	1.91	0.981
E1	6.58	1.000	2.17	0.900	8.73	0.997	4.01	0.952
E2	5.83	0.998	2.00	0.895	6.97	0.997	3.05	0.984
EE2	5.61	1.000	2.32	0.882	7.51	0.999	3.10	0.950

[a] Neutral Fenton experiments showed negligible degradation for the target micropollutants.

sequential batch reactor (SBR) with a magnetic separation system patented in the research group (Moldes-Diz et al., 2018) was considered for the scale-up, as it was proven reliable when using MNPs. The SBR was designed to work in four discrete steps: feed, reaction, catalyst recovery and discharge. One may check Fig. S3 in Supplementary Information for a simplified scheme of the cycle steps. The abatement of micropollutants in batches may facilitate the comparison of the different Fenton-based alternatives given that the degradation kinetics changes between them for the same reactor design. A diversity of degradation kinetics results in different reaction times, while keeping constant for all scenarios emptying and filling times. In consequence the batch length differences between Fenton-like configurations are directly dependent on the reaction duration.

Prior and afterwards the SBR, and only for pH 3 operation, goes the acidification and neutralization stage. Chemicals such as sodium hydroxide and sulfuric acid are feed to the influents and effluents of the reactor. Additionally, non-electrochemical alternatives had an external hydrogen peroxide input. Fig. 2 presents a general block diagram of the operational sequence, including the extra stages for the processes under pH 3 conditions (shaded in blue), electrochemical-assisted (shaded in yellow) and light-assisted processes (shaded in green).

The following assumptions were taken when scaling-up the laboratory processes to a 100 L sequential batch reactor.

- The Sequential Batch Reactor design volume was estimated considering a 10% oversizing compared to its operating volume. Then, its diameter was set in 50.5 cm and the liquid level with flat bottom in 50.3 cm.
- The reaction duration was established for the degradation goal (75%) predefined for CBZ (Table S5 highlights the reaction times and degradation rates of the different configurations). Besides, and considering a pseudo-first order kinetics, the reaction system at laboratory scale was assumed to behave comparably for the modelled scale-up process.
- The electricity consumption required for stirring was determined using a turbine impeller at 350 rpm (16.5 cm diameter and 17.1 cm width) and rectangular buffers (16.8 × 5.0 cm), which ensure turbulent flow. Considering water properties at ambient temperature, the power of the stirrer was 83.4 W. Additionally, 35% of friction losses as well as an engine efficiency of 70% were contemplated, thus making the necessary power estimation 160.9 W.
- The electricity demand during the periods of feeding, separation and discharge of the SBR was labeled as "other operations". Feeding and discharge were estimated using a pump with a flow rate of 0.4 L s^{-1} and a power of 38 W while the separation had a steady rate for stirring of 10 min (recorded to be enough for the magnetic separation of the particle).
- Light supply is calculated from the external surface of the reactor. The outer area of the SBR is approximately 50 times the one measured for the laboratory vessel, so a conversion factor of 50 will be applied to determine the light demand.
- The reagent concentration was maintained in the operating systems and thus, the mass/volume of added chemicals was directly proportional to the scale.
- Catalyst losses were defined in agreement to the results achieved from the laboratory scale batch experiments of González-Rodríguez et al. (2021), reporting 16% of catalyst losses after 5 consecutive cycles for a regular Fenton process using Fe_3O_4@PAA/SBA15.
- The potential drops between electrodes at laboratory and pilot scale were identical, as electrode materials and conductivity of the water matrix did not change. The applied current will be calculated to produce the same rate of hydrogen peroxide while maintaining

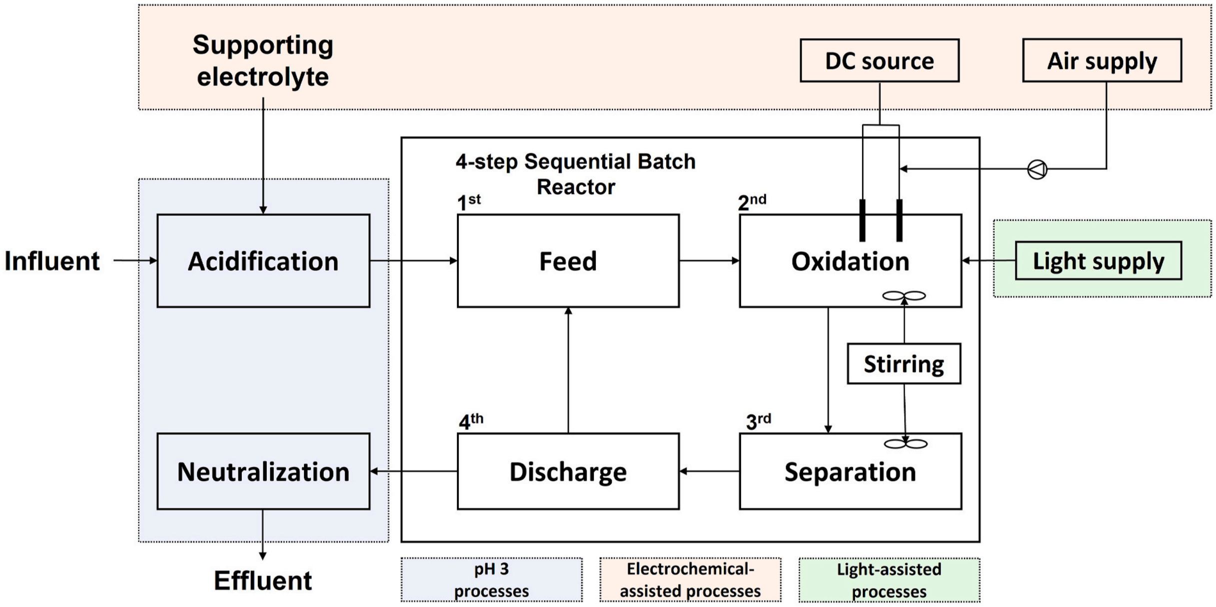

Fig. 2. Simplified scheme of the process scale-up for the different analyzed configurations.

constants current density and electroactive area per unit of volume of treated water.

- An air supply consumption of 32.6 W is estimated by modeling a fan that delivers a flow of 2 L s^{-1} with an impeller diameter of 30 mm and no pressure losses. The employed efficiencies were taken of the Standard 205-10 by AMCA (Air Movement and Control Association).

2.3. Life cycle impact assessment method

The environmental analysis is based on the application of ReCiPe 2016 v1.1 Midpoint (H/H) and Endpoint (H/H) methods, using SimaPro 9.3 software (Huijbregts et al., 2017). Two criteria have been followed for the selection of the impact categories. In the first place, the sector in which the scenarios under assessment are involved. Global warming, acidification and eutrophication are some of the categories that received more attention for wastewater treatment followed by toxicity and ozone layer depletion (Corominas et al., 2013). Secondly, the nature of the LCA: comparative analysis of advanced treatment processes. Therefore, some of the mostly used impact categories compiled in the LCA state-of-the-art for Fenton-based technologies have also been considered (see Table S2). The selected impact categories were global warming (GW), stratospheric ozone depletion (OD), freshwater eutrophication (FE), marine eutrophication (ME), freshwater ecotoxicity (FET), human toxicity – cancer (HCT), non-cancer human toxicity (HNT), mineral resource scarcity (MRS), fossil resource scarcity (FRS) and water consumption (WC). Moreover, ReCiPe 2016 can also report a single environmental damage score, based on three endpoint categories (human health, ecosystem quality and resource scarcity) for each of the scenarios and thus facilitate benchmarking of the different configurations.

2.4. Economic assessment

Although LCA promotes a safe environment for nature and humans, the truth is that its standalone analysis does not necessarily pushes a technology within the market. It is not an overstatement to claim that many customers with a deep environmental awareness will not choose a technology with an astronomic price difference with others widely implemented unless subsidies are provided (Wu and Zhang, 2022). Therefore, the Life Cycle Inventory (LCI) of the LCA has also be directly used to the determination of the costs associated to the performance of the Fenton-based processes between each other. As already proposed for LCA, investment related to infrastructure (construction, personnel, maintenance, or land purchase costs) will be out of the boundaries of the analysis. The focal point would be the operation limited to a sequential batch reactor of 100 L.

On the other hand, the economic assessment has only accounted for internal costs since the environmental external costs would have not provided complementary outcomes to the already elicited by the LCA. Energy/chemical contribution has been identified which aims at the techno-economic viability of the alternatives before the leap to full scale applications.

3. Results and discussion

3.1. Life Cycle Inventory

The input and output process flows are collected in Table 2. All the data is shown for the scale-up operation of the studied configurations, modelled from laboratory scale experiments according to the assumptions described on **Section 2.2**.

3.2. Life Cycle Assessment

A benchmarking of the four Fenton-based configurations was performed using the ReCiPe Endpoint method, since the assessment provides a single dimensionless value. Endpoint single score results are calculated by the aggregation of damage categories (human health, ecosystems and scarcity of natural resources) when normalized and weighted. Fig. 3 depicts the total environmental damage, both in mPt and in relative contribution, of each configuration and the profile was subdivided by type of consumable or subsystem. Table S6, found in the Supplementary Information, provides the detailed outcomes from Fig. 3.

In agreement with this damage analysis, photo-Fenton at pH 3 is that the most favorable alternative (8.21 mPt) followed by the two electrochemical-assisted configurations (EF and PEF) at circumneutral pH (11.79 and 11.84 mPt, respectively). Unlike photo-Fenton, both electro-Fenton and photoelectro-Fenton at circumneutral pH present a lower impact than their acidic counterpart due to their improved kinetic constants far from the optimum operational pH. EF and PEF at neutral pH have displayed similar score, as the impact attenuation achieved by the reduction of reaction time in PEF configuration is not enough to compensate for the additional impacts of light supply. Thus, it can be concluded that photoelectro-Fenton does not present a clear environmental advantage over electro-Fenton.

The most obvious hotspot in electrochemical-assisted configurations is the addition of the supporting electrolyte, having the same impact in all configurations, 7.91 mPt, as the same amount of Na_2SO_4 is used to increase aqueous matrix conductivity. Although the supporting electrolyte is added to reduce potential drops due to solution resistance and thus minimize electricity consumption, it is accounting for more than 50% of the total score of electrochemical-assisted configurations. Stirring is another important contribution to the total impact, especially in

Table 2
Life cycle inventory of the analyzed Fenton-based alternatives for a 100 L sequential batch reactor.

	Fenton	Photo-Fenton		Electro-Fenton		Photoelectro-Fenton	
	pH 3	pH 3	Neutral	pH 3	Neutral	pH 3	Neutral
Inputs from technosphere							
Chemicals/g							
Catalyst loss	0.64	0.64	0.64	0.64	0.64	0.64	0.64
H_2O_2	20.0	20.0	20.0	–	–	–	–
H_2SO_4	237.1	237.1	–	237.1	–	237.1	–
NaOH	193.4	193.4	–	193.4	–	193.4	–
Na_2SO_4	–	–	–	710.2	710.2	710.2	710.2
Electricity consumption/W h							
Stirring	929.2	124.3	929.2	100.0	208.8	58.3	112.5
Light supply	–	61.8	462.1	–	–	29.0	55.9
H_2O_2 generation	–	–	–	117.1	244.4	68.3	131.7
Air supply	–	–	–	20.3	42.4	11.8	22.8
Other operations	32.1	32.1	32.1	32.1	32.1	32.1	32.1
Outputs to nature							
Theoretical air emissions/mg							
CO_2	367.0	372.6	317.6	399.5	380.3	388.9	383.5

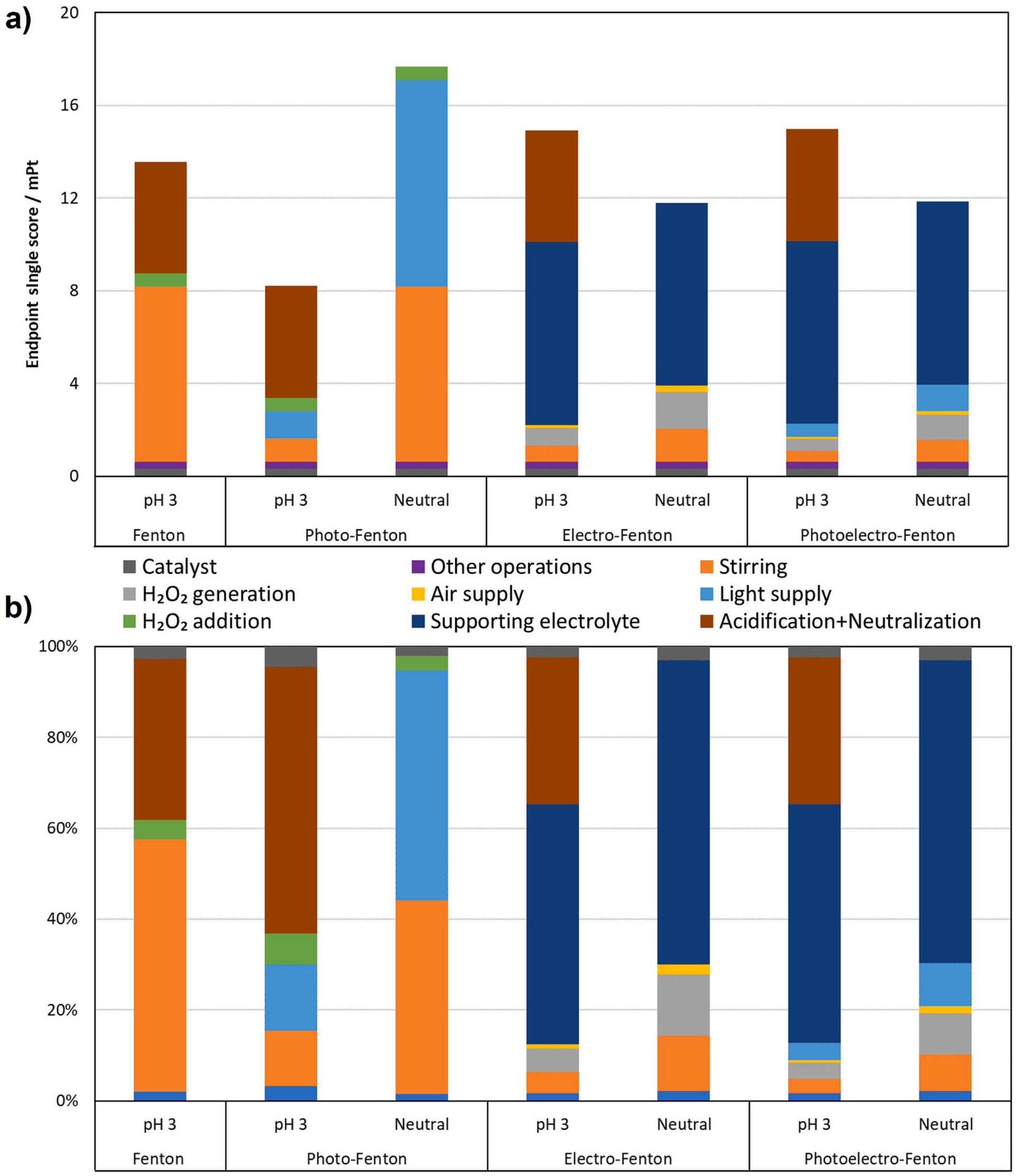

Fig. 3. Environmental single score damage (a) and the relative contribution of each subsystem (b) for the analyzed Fenton-based alternatives.

the processes with the lowest degradation constants, accounting for the 56% in acid Fenton and 43% in neutral photo-Fenton configurations. Accordingly, neutral PF configuration presents the worst environmental damage score (17.68 mPt). The light supply is also clearly disadvantageous in combination with processes with low degradation constants such as neutral PF. This result agrees with the only LCA study that consider operation at acidic and circumneutral pHs in homogeneous solar photo-Fenton configuration, concluding that neutral SPF is the worst performing configuration for 12 of 15 considered impact categories (Gallego-Schmid et al., 2019). However, it should be noted that the main hotspot in their study was caused by complexing agent addition to avoid the precipitation of iron ions.

Chemical consumption, namely by acidification-neutralization at pH 3 alternatives and the addition of supporting electrolyte in electrochemical-assisted configurations, is also a main contributor to the score of the different configurations, ranging from 32 to 67% of the total impact. Surprisingly, in the methods that require the addition of hydrogen peroxide (F and PF), the impact of H_2O_2 is minimal, ranging between 3 and 7% of the total single score impact of each configuration, contradicting previous published analyses (Foteinis et al., 2018). Moreover, the impacts associated to in-situ H_2O_2 production (Na_2SO_4 + electricity) convey higher environmental impacts than the direct addition of H_2O_2.

The results of midpoint characterization of the different Fenton-based configurations for the selected impact categories are compiled in Table S7 of the Supplementary Information. In Fig. S4, the relative comparison of the results is presented for the four configurations with the lower environmental damage single score values to facilitate the visualization of the results. The comparison is performed by assigning a value of 100% to the worst performing value in each category. Regular Fenton at pH 3, as expected, is the least favorable configuration in 8 of 10 impact categories, in line with the results obtained for the endpoint single score in the previous section. On the other hand, acid photo-Fenton is the most favorable in 9 of the 10 selected impact categories, which shows that it is the optimal configuration from the point of view of environmental impacts. A deeper analysis of the impacts in each of the categories considering the different subsystem contributions is depicted in Fig. 4 for photo-Fenton at pH 3 and photoelectro-Fenton at

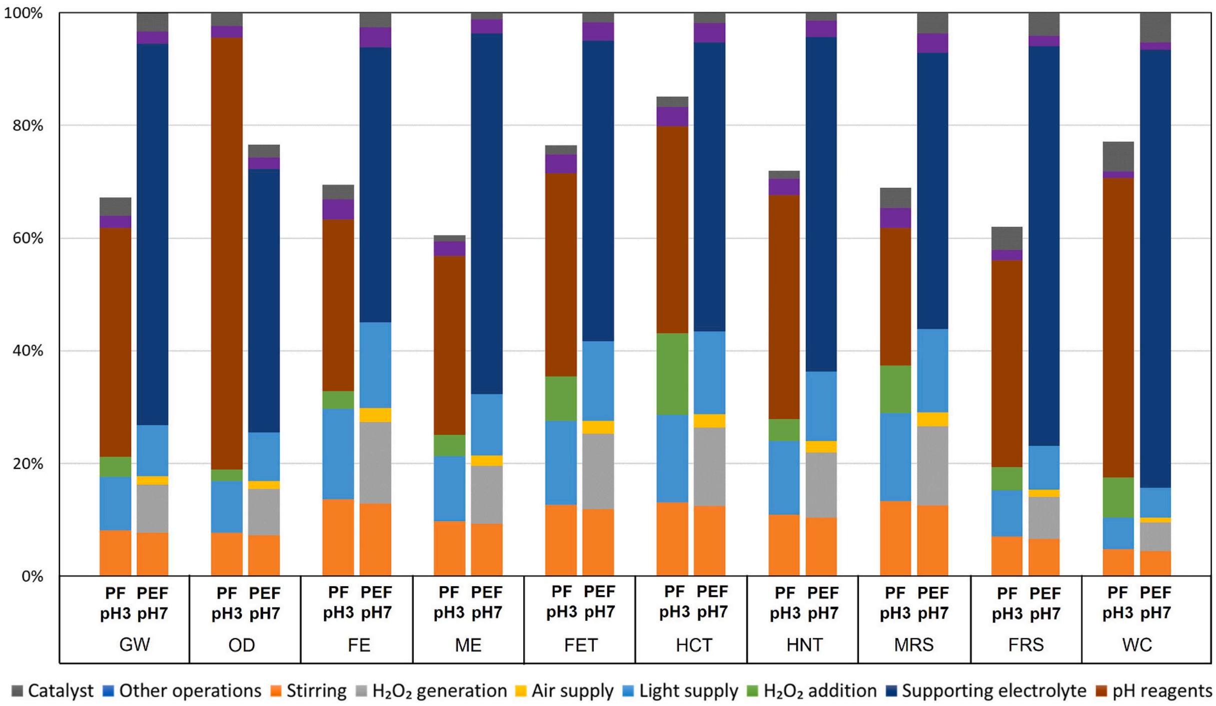

Fig. 4. Deconvoluted contributions of the midpoint characterization of acid photo-Fenton and neutral photoelectro-Fenton. Impact categories: global warming (GW), stratospheric ozone depletion (OD), freshwater eutrophication (FE), marine eutrophication (ME), freshwater ecotoxicity (FET), human toxicity – cancer (HCT), non-cancer human toxicity (HNT), mineral resource scarcity (MRS), fossil resource scarcity (FRS) and water consumption (WC).

circumneutral pH.

The use of chemical reagents is a major contributor to the analyzed categories, due to the impact of pH modification for acid PF and the supporting electrolyte for neutral PEF. However, the impact of chemicals in PEF configuration appears to have more impact in most of the categories when compared to PF. For instance, the impact produced by the sum of hydrogen peroxide, sulfuric acid and sodium hydroxide in PF (50% of GW) is less than the impact produced by the supporting electrolyte alone in PEF (75% of GW). Only in ozone layer deterioration category, the impact of the H_2O_2 production accounts for a greater impact in the case of the photo-Fenton configuration. This is mainly due to the emission of CFC-10 into the atmosphere during the production of H_2O_2, which alone is responsible for 66% of all PF impacts in this category. While the pH modification cannot be avoided for the photo-Fenton configuration, as the reaction kinetics dramatically diminish with higher pH values (González-Rodríguez et al., 2022), the amount of supporting electrolyte could be further optimized in the process.

Even though chemicals present a greater impact than energy consumption in all the analyzed categories, especially in water consumption (88% in PEF and 89% in PF), this trend is reversed in other categories such as FE, FET and HCT, with values about 40% of the total impact attributed from electricity consumption. This effect is caused by atmospheric emissions thermoelectrical plants, such as fine particles, sulfur and nitrogen oxides. The impacts associated to energy consumption for PEF are greater than the impacts for PF configuration. Although the PF configuration present a slower degradation kinetics, illumination and agitation contributions are slightly higher when compared to PEF configuration, however PEF is also consuming energy during hydrogen peroxide generation. Unexpectedly, the impact associated to in-situ production of hydrogen peroxide is greater than its industrial production in all the categories but HCT and WC.

3.2.1. *Sensibility analysis*

The previous section showed that the most important environmental impacts in electrochemical assisted Fenton configuration are caused by the addition of supporting electrolyte. It should be noted that the required amount of Na_2SO_4 has not been optimized during laboratory experimentation. The use of a concentration of 0.05 M was set so the electrical resistance of the reaction medium is not a limitation to the electrochemical reaction, as the potential will depend on the applied current and the resistance of the electrolytic system. However, not only the conductivity of the medium could be optimized to reduce the ohmic losses of the electrolyte but the design of the electrochemical setup.

As the optimum conductivity value is unknown for this specific system, the most straightforward solution to reduce the quantity of supporting electrolyte by maintaining a constant electrolyte resistance is the reduction of the interelectrode distance. The interelectrode distance in the laboratory scale experiment was set at 1.5 cm due to the design of the beaker. Assuming 5 mm as an appropriate distance between the anode and the cathode, a direct calculation evidence that the concentration of Na_2SO_4 could be reduced to 0.013 M, corresponding to 185 g of Na_2SO_4 per batch of the 100 L reactor. Considering that the amount of electrolyte could be reduced in constructive features in the scale-up process, Fig. S5 presents the environmental single score damage of the studied configurations with the optimized quantity of supporting electrolyte.

The optimized electrolyte concentration dramatically reduces its associated impact from a score of 7.91 mPt (0.05 M) to 2.06 mPt (0.013 M). Consequently, single score impacts of the electro-Fenton and photoelectro-Fenton configurations have been reduced to 5.97 and 6.01 mPt, respectively. Thus, it is demonstrated that electrochemical assisted Fenton configurations can ameliorate the environmental single score of acid photo-Fenton by more than 30% if a careful design of the electrochemical system is considered. Even though Serra et al. (2011) have concluded in a previous work that solar photoelectro-Fenton processes had a greater environmental impact than non-electrochemical methods due to the impact of electrical consumption of the electrodes, it is demonstrated that the inclusion of configurations at neutral pH result in a kinetic improvement of the electro-Fenton and photoelectro-Fenton processes that considerably reduces the overall impact of the process.

Further insights on the influence of the supporting electrolyte concentration can be obtained from the plots of Fig. 5, in which the single

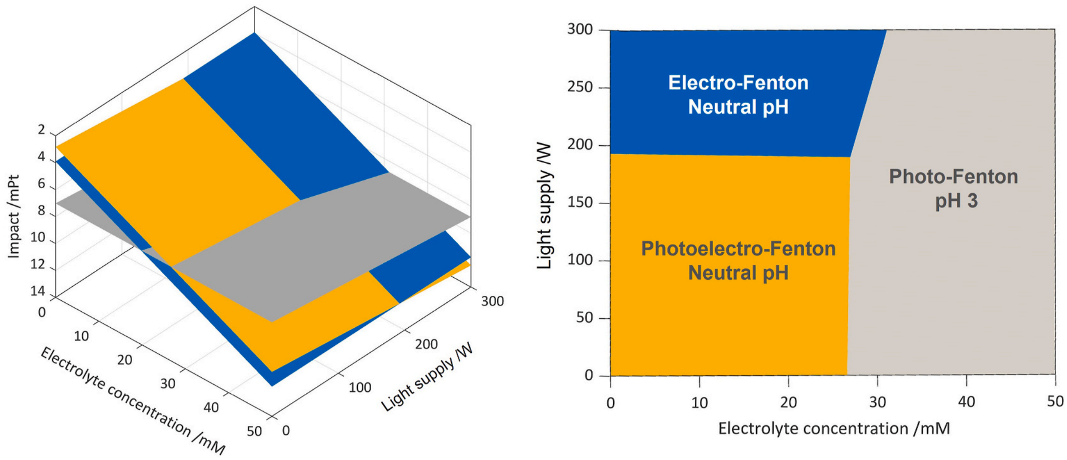

Fig. 5. Plot of the single score impact of neutral EF, neutral PEF and acid PF as a function of electrolyte concentration and light supply (a) with the correspoding domains of lower single score impact for each configuration (b).

score impact of neutral EF, neutral PEF and acid PF as a function of electrolyte concentration is depicted. Additionally, as the light supply is a key parameter for two of the three configurations with best environmental profile it has been considered as a relevant variable for the sensitivity analysis. For the sensitivity analysis of light supply, it will be assumed that the variation of incident light does not affect the degradation kinetics of the system. Thus, Fig. 5a depicts a 3D plot of the single score impact values of the methods, in different ranges of light supply consumption (0–300 W) and supporting electrolyte concentration (0–0.05 M), as well as a 2D plot defining the configurations in which single score impact is lower for the analyzed parameters.

The results clearly show that supporting electrolyte concentration is critical for the environmental viability of electrochemical assisted Fenton configurations. Above the 0.025–0.030 M range, electrochemical methods present a worse environmental profile than acid PF. However, it should be considered that lab-scale experiments were performed with distilled water, but in the case of wastewater, the matrix will have some base conductivity that will reduce the required concentration of electrolyte, and thus reduce the associated environmental impacts. Regarding the consumption of LED lamps, the effect on the impact is not as important as the electrolyte concentration, but it shows that above consumptions of 200 W, EF present lower impacts than PEF. However, as it can be seen in the 3D plot, the effect of LED consumption on the single score impact values is not as relevant as the concentration of supporting electrolyte.

3.3. Economic analysis

The operational costs of the different Fenton-based configurations have been studied using the Life Cycle Inventory of the 100 L sequential batch reactor and considering the same functional unit. However, the concentration of electrolyte was reduced to 0.013 M as discussed in the sensibility analysis, as it represents a more rational operational value considering a practical application of the process. Reagent costs have been calculated after a literature review (See Table S8), in which market prices for the compounds used the different configurations were considered for the calculation of an average price to estimate the operation costs. For the electricity cost, Eurostat biannual electricity price for non-household consumers in 2021 for the European Union has been used (EU-27, 0.1053 € kWh^{-1}). The detailed operational costs of each of the analyzed Fenton configurations are collected in Table S9.

The cost of chemicals is clearly dependant on the working pH of the configurations, resulting in costs ranging from 1.17 to 1.06 € m^{-3} for pH 3 operation. Neutral pH methods, on the other hand, present much lower costs, between 0.22 and 0.33 € m^{-3}. Electrical consumption of regular Fenton at pH 3 and photo-Fenton at neutral pH stands out among the rest, as low degradation kinetics translate into high electrical costs, mainly due to the consumption of stirring. A graphical comparison of the operational costs is depicted in Fig. 6. Considering these results, both neutral electro-Fenton and photoelectron-Fenton methods are the most cost-effective options among all the analyzed configurations.

The electricity consumption of Fenton at pH 3 and the neutral photo-Fenton stands out compared to the rest, similarly to the environmental analysis. In fact, the neutral photo-Fenton configuration is the process with the highest cost per cubic meter, despite having the lowest chemical consumption (13% of the total costs). The slow degradation kinetics result in high electricity usage, due to stirring (39%) and illumination (48%). Electrochemical assisted methods and photo-Fenton at pH 3 have remarkably similar operation costs, ranging between 1.27 and 1.28 € m^{-3}. In these configurations, the costs are tied to the modification of the pH, mainly because of the cost of the sodium hydroxide (above 50% of the total costs). The neutral electro-Fenton and photoelectro-Fenton methods have the lowest operating costs with 0.66 and 0.67 € m^{-3}, respectively. However, it should be noted that the operation with the 0.05 M Na_2SO_4, as it appears on the LCI before the sensibility analysis, will increase in 0.63 € m^{-3} the cost of the electrochemical assisted methods. This effect shows once again the importance of optimizing supporting electrolyte concentration, as considering the Na_2SO_4 concentration used in lab-scale experiments would equalize the costs with photo-Fenton at pH 3 configuration.

The obtained operational costs of Fenton-based methods are in the range of previously reported economic analyses. Cabrera Reina et al. (2018) studied the operational costs of solar photo-Fenton with homogenous catalyst at acid pH obtaining cost in the range of 0.69 and 1.31 € m^{-3} for a raceway pond reactor. However, they did not include stirring costs in a previous homogenization step, which according to this paper is a major contributor to the total costs. Sánchez Pérez et al. (2020) further evaluated the economic performance of solar raceway pond reactors including operation at neutral pH, obtaining much lower operation costs (0.25 € m^{-3} at pH 3 and 0.56 € m^{-3} at pH 7). The cost increase of photo-Fenton at neutral pH contradicts the conclusions of this paper, as the main contributor to the cost is not the energy consumption but the use of an iron complexing agent to avoid iron precipitation. Neutralization costs were also reduced due to the usage of a packed column of calcium carbonate instead of the addition of sodium hydroxide. In a subsequent study (Miralles-Cuevas et al., 2016), the operational costs of the SPF were compared to a stablished advanced oxidation process such as ozonation, concluding that ozonation has lower costs (0.64 € m^{-3}) compared to the SPF process (0.92 € m^{-3}) due to lower chemical consumption. However, other authors have reached

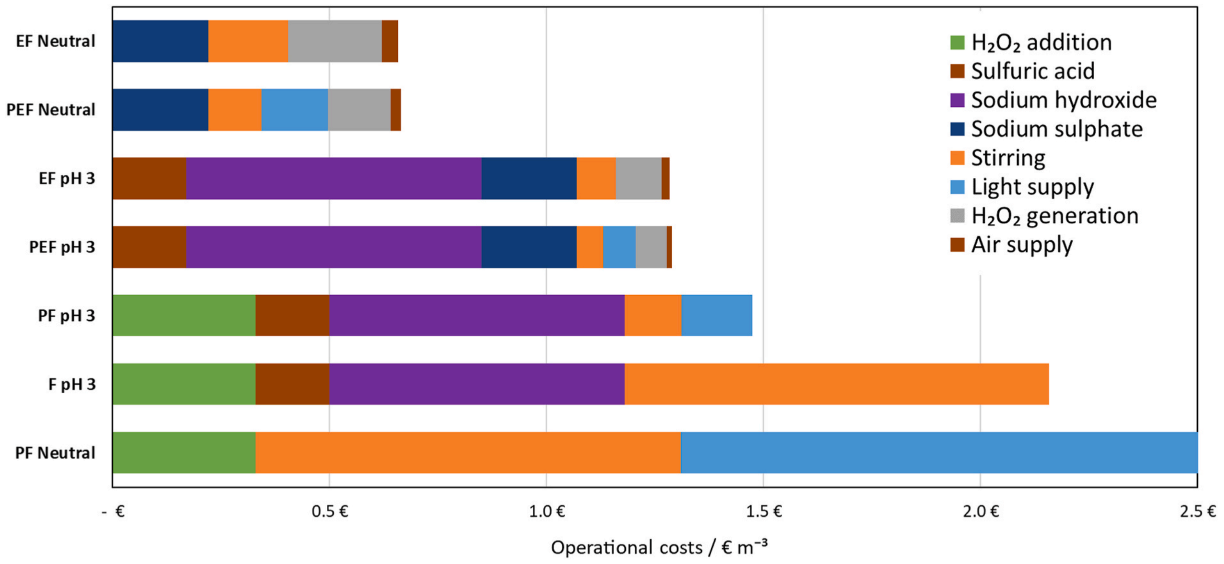

Fig. 6. Comparison of the operational costs of Fenton-based configurations for a 100 L sequential batch reactor.

opposite conclusions, reporting that the operational costs ozonation is higher than SPF process, mainly to the oxygen and electricity consumption required to generate the ozone (Prieto-Rodríguez et al., 2013). These results show that operational costs can vary considerably depending on the focus and scope of the analysis, therefore results should only be compared if the scale, reactor type, composition of the influent and the removal efficiency of the target micropollutants are similar.

4. Conclusions and future directions

Environmental impacts of different Fenton-based configurations (regular Fenton, photo-Fenton, electro-Fenton and photoelectro-Fenton) considering their operational pH have been analyzed by means of Life Cycle Assessment, aiming to find the most environmentally favorable option for the elimination of micropollutants. This work points out that the most promising configurations are electro-Fenton and photoelectro-Fenton configurations at circumneutral pH, presenting single score impacts of 5.97 and 6.01 mPt, respectively, considering an optimized supporting electrolyte concentration.

As it was initially hypothesized, the pH of the reaction medium is a key factor in the environmental benchmarking, as Fenton-based methods exhibit faster degradation kinetics at acidic pH. As a downside, working at acidic pH implies high chemical consumption for acidification and neutralization. This is where electrochemical assisted methods shine, as the reduction of kinetic constants at circumneutral pH are less pronounced than regular Fenton and photo-Fenton. Even though chemical consumption in acidic pH operation is critical, based on the values obtained from the laboratory scale experiments, the best configuration in terms of environmental impacts is photo-Fenton at pH 3. However, it can be concluded from the environmental evaluation that the optimization of the electrolyte concentration is crucial for the viability of the electrochemical assisted, as laboratory experiments were performed using an overestimated concentration of supporting electrolyte. During the sensitivity analysis, it has been concluded that the concentration of the supporting electrolyte can be optimized by minimizing the ohmic losses in the aqueous matrix with the design of the electrode system. The use of a more adequate concentration value considerably changes the initial results so electro-Fenton and photoelectro-Fenton configurations at neutral pH present the least environmental impact. The subsequent economic benchmarking was performed by using the optimized supporting electrolyte concentration, pointing out that neutral electro-Fenton and photoelectro-Fenton configurations present the lowest operating costs (0.66 and 0.67 € m^{-3}, respectively), similarly to the environmental benchmarking.

The benchmarking analysis may also result in the following recommendations for further research and the implementation of Fenton-based technologies for micropollutant abatement:

Process design: Sequential batch reactor was selected as the most appropriate configuration for heterogenous Fenton treatments with magnetic nanocatalysts. However, batch operation in the SBR is strongly dependent on stirring electrical consumption and thus on the degradation kinetics of the configurations, so other reactor types might have less penalization for slower degradation kinetics. As for the operations related to reagent addition, other authors also showed that neutralization costs were also reduced by packed column of calcium carbonate instead of sodium hydroxide (Sánchez Pérez et al., 2020), as it is a reagent with higher cost and environmental impact.

Operating conditions: The optimal operating conditions of electrochemical assisted methods should be further explored to optimize the reaction kinetics. Using pH above the optimum in Fenton (González-Rodríguez et al., 2021) and photo-Fenton (González-Rodríguez et al., 2022) configurations was previously demonstrated to be highly detrimental for degradation kinetics, however, the effect on reaction kinetics using pH values between 3 and 7 for electrochemical assisted methods was not considered and could lead to an improvement of both environmental and economic profiles.

Catalyst: Despite all the benefits to the cyclability and reusability in Fenton-based treatments demonstrated by Fe_3O_4@PAA/SBA15 MNPs, it has been previously demonstrated that its lab-scale production is not environmentally recommended when compared to other MNPs (Feijoo et al., 2019). Research efforts should be put in enhancing the synthetic route of MNPs to reduce its environmental impact in a hypothetic scale-up of the process, as well as finding more environmentally sustainable MNPs with similar cyclability and reusability characteristics.

Light supply: The effect of light supply on micropollutant abatement should be further investigated, namely, by optimizing the nature and spatial distribution of the light sources. This work has been performed by using commercial white light LED lamps, which showed significant improvement in reaction kinetics. However, the use of blue light LED (in the range of 400–420 nm) could further improve the effect on micropollutant abatement. Optimization of irradiance could also play an important role, as it was demonstrated in the sensibility analysis. In addition, the use of solar irradiance should be considered as environmental and cost-effective solution, but its use would require the use of certain types of reactors, such as parabolic collector or raceway ponds reactors.

Credit author statement

J.J.C.: Investigation, Methodology, Writing – original draft preparation, Conceptualization, Supervision; S.A.: Investigation, Methodology, Writing – review & editing; S.E. and J.G.-R.: Methodology, Writing – review & editing; G.F.: Conceptualization; M.T.M.: Writing – review & editing, Conceptualization, Supervision. All authors have read and agreed to the published version of the manuscript.

Funding

This research was supported by HP-NANOBIO (PID2019-111163RB-I00), funded by Agencia Estatal de Investigación (AEI), and SPOTLIGHT (PDC2021-121540-I00) projects, funded by Agencia Estatal de Investigación (AEI) and European Union NextGenerationEU/PRTR.

Declaration of competing 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.

Data availability

Data will be made available on request.

Acknowledgements

J.J.C. acknowledges Xunta de Galicia financial support through a postdoctoral fellowship (Grant reference ED481B-2021/015). S.E. and J. G.-R. predoctoral fellowships were funded by Agencia Estatal de Investigación (AEI) and by "ESF Investing in your future" (Grant references PRE2020-092074 and FPU19/004612, respectively). The authors belong to the Galician Competitive Research Group (GRC) ED432C-2021/37.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2023.117308.

References

Brillas, E., 2020. A review on the photoelectro-Fenton process as efficient electrochemical advanced oxidation for wastewater remediation. Treatment with UV light, sunlight, and coupling with conventional and other photo-assisted advanced technologies. Chemosphere 250, 126198. https://doi.org/10.1016/j.chemosphere.2020.126198.

Brillas, E., Sirés, I., Oturan, M.A., 2009. Electro-fenton process and related electrochemical technologies based on fenton's reaction chemistry. Chem. Rev. 109, 6570–6631. https://doi.org/10.1021/cr900136g.

Burch, K.D., Han, B., Pichtel, J., Zubkov, T., 2019. Removal efficiency of commonly prescribed antibiotics via tertiary wastewater treatment. Environ. Sci. Pollut. Res. 26, 6301–6310. https://doi.org/10.1007/s11356-019-04170-w.

Cabrera Reina, A., Miralles Cuevas, S., Cornejo Ponce, L., 2018. The combined effect of irradiance and iron concentration on photo-Fenton treatment cost. AIP Conf. Proc. 2033, 160002 https://doi.org/10.1063/1.5067161.

Corominas, Ll, Foley, J., Guest, J.S., Hospido, A., Larsen, H.F., Morera, S., Shaw, A., 2013. Life cycle assessment applied to wastewater treatment: state of the art. Water Res. 47, 5480–5492. https://doi.org/10.1016/j.watres.2013.06.049.

de Boer, S., González-Rodríguez, J., Conde, J.J., Moreira, M.T., 2022. Benchmarking tertiary water treatments for the removal of micropollutants and pathogens based on operational and sustainability criteria. J. Water Process Eng. 46, 102587 https://doi.org/10.1016/j.jwpe.2022.102587.

de Souza, Z.S.B., Silva, M.P., Fraga, T.J.M., Motta Sobrinho, M.A., 2021. A comparative study of photo-Fenton process assisted by natural sunlight, UV-A, or visible LED light irradiation for degradation of real textile wastewater: factorial designs, kinetics, cost assessment, and phytotoxicity studies. Environ. Sci. Pollut. Res. 28, 23912–23928. https://doi.org/10.1007/s11356-020-12106-y.

Feijoo, S., González-Rodríguez, J., Fernández, L., Vázquez-Vázquez, C., Feijoo, G., Moreira, M.T., 2019. Fenton and photo-fenton nanocatalysts revisited from the perspective of life cycle assessment. Catalysts 10, 23. https://doi.org/10.3390/catal10010023.

Foteinis, S., Monteagudo, J.M., Durán, A., Chatzisymeon, E., 2018. Environmental sustainability of the solar photo-Fenton process for wastewater treatment and pharmaceuticals mineralization at semi-industrial scale. Sci. Total Environ. 612, 605–612. https://doi.org/10.1016/j.scitotenv.2017.08.277.

Gallego-Schmid, A., Tarpani, R.R.Z., Miralles-Cuevas, S., Cabrera-Reina, A., Malato, S., Azapagic, A., 2019. Environmental assessment of solar photo-Fenton processes in combination with nanofiltration for the removal of micro-contaminants from real wastewaters. Sci. Total Environ. 650, 2210–2220. https://doi.org/10.1016/j.scitotenv.2018.09.361.

Geissen, V., Mol, H., Klumpp, E., Umlauf, G., Nadal, M., van der Ploeg, M., van de Zee, S. E.A.T.M., Ritsema, C.J., 2015. Emerging pollutants in the environment: a challenge for water resource management. Int. Soil Water Conserv. Res. 3, 57–65. https://doi.org/10.1016/j.iswcr.2015.03.002.

González-Rodríguez, J., Conde, J.J., Vargas-Osorio, Z., Vázquez-Vázquez, C., Piñeiro, Y., Rivas, J., Feijoo, G., Moreira, M.T., 2022. LED-driven photo-Fenton process for OMP removal by nanostructured magnetite anchored in mesoporous silica. SSRN 4179210. doi:10.2139/ssrn.4179210.

González-Rodríguez, J., Gamallo, M., Conde, J.J., Vargas-Osorio, Z., Vázquez-Vázquez, C., Piñeiro, Y., Rivas, J., Feijoo, G., Moreira, M.T., 2021. Exploiting the potential of supported magnetic nanomaterials as fenton-like catalysts for environmental applications. Nanomaterials 11, 2902. https://doi.org/10.3390/nano11112902.

Huijbregts, M.A.J., Steinmann, Z.J.N., Elshout, P.M.F., Stam, G., Verones, F., Vieira, M., Zijp, M., Hollander, A., van Zelm, R., 2017. ReCiPe2016: a harmonised life cycle impact assessment method at midpoint and endpoint level. Int. J. Life Cycle Assess. 22, 138–147. https://doi.org/10.1007/s11367-016-1246-y.

Hetherington, A.C., Borrion, A.L., Griffiths, O.G., McManus, M.C., 2014. Use of LCA as a development tool within early research: challenges and issues across different sectors. Int. J. Life Cycle Assess. 19, 130–143. https://doi.org/10.1007/s11367-013-0627-8.

ISO, 2006a. ISO 14040: Environmental Management — Life Cycle Assessment — Principles and Framework. International Organization Standardization.

ISO, 2006b. ISO 14044: Life Cycle Assessment — Requirements and Guidelines. International Organization Standardization.

Liu, D., Zhang, H., Wei, Y., Liu, B., Lin, Y., Li, G., Zhang, F., 2018. Enhanced degradation of ibuprofen by heterogeneous electro-Fenton at circumneutral pH. Chemosphere 209, 998–1006. https://doi.org/10.1016/j.chemosphere.2018.06.164.

Margot, J., Rossi, L., Barry, D.A., Holliger, C., 2015. A review of the fate of micropollutants in wastewater treatment plants. WIREs Water 2, 457–487. https://doi.org/10.1002/wat2.1090.

Meijide, J., Dunlop, P.S.M., Pazos, M., Sanromán, M.A., 2021. Heterogeneous electro-fenton as "green" technology for pharmaceutical removal: a review. Catalysts 11, 85. https://doi.org/10.3390/catal11010085.

Miralles-Cuevas, S., Oller, I., Agüera, A., Pérez, J.A.S., Sánchez-Moreno, R., Malato, S., 2016. Is the combination of nanofiltration membranes and AOPs for removing microcontaminants cost effective in real municipal wastewater effluents? Environ. Sci. Water Res. Technol. 2, 511–520. https://doi.org/10.1039/C6EW00001K.

Moldes-Diz, Y., Eibes, G., Vázquez-Vázquez, C., Fondado, A., Mira, J., Feijoo, G., Lema, J. M., Moreira, M.T., 2018. A novel enzyme catalysis reactor based on superparamagnetic nanoparticles for biotechnological applications. J. Environ. Chem. Eng. 6, 5950–5960. https://doi.org/10.1016/j.jece.2018.09.014.

Pignatello, J.J., Oliveros, E., MacKay, A., 2006. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. Crit. Rev. Environ. Sci. Technol. 36, 1–84. https://doi.org/10.1080/10643380500326564.

Prieto-Rodríguez, L., Oller, I., Klamerth, N., Agüera, A., Rodríguez, E.M., Malato, S., 2013. Application of solar AOPs and ozonation for elimination of micropollutants in municipal wastewater treatment plant effluents. Water Res. 47, 1521–1528. https://doi.org/10.1016/j.watres.2012.11.002.

Sánchez Pérez, J.A., Arzate, S., Soriano-Molina, P., García Sánchez, J.L., Casas López, J. L., Plaza-Bolaños, P., 2020. Neutral or acidic pH for the removal of contaminants of emerging concern in wastewater by solar photo-Fenton? A techno-economic assessment of continuous raceway pond reactors. Sci. Total Environ. 736, 139681 https://doi.org/10.1016/j.scitotenv.2020.139681.

Serra, A., Domènech, X., Brillas, E., Peral, J., 2011. Life cycle assessment of solar photo-Fenton and solar photoelectro-Fenton processes used for the degradation of aqueous α-methylphenylglycine. J Env. Monit. 13, 167–174. https://doi.org/10.1039/C0EM00552E.

Sirés, I., Garrido, J.A., Rodríguez, R.M., Brillas, E., Oturan, N., Oturan, M.A., 2007. Catalytic behavior of the Fe^{3+}/Fe^{2+} system in the electro-Fenton degradation of the antimicrobial chlorophene. Appl. Catal. B Environ. 72, 382–394. https://doi.org/10.1016/j.apcatb.2006.11.016.

Suárez, S., Carballa, M., Omil, F., Lema, J.M., 2008. How are pharmaceutical and personal care products (PPCPs) removed from urban wastewaters? Rev. Environ. Sci. Biotechnol. 7, 125–138. https://doi.org/10.1007/s11157-008-9130-2.

Ueki, R., Imaizumi, Y., Iwamoto, Y., Sakugawa, H., Takeda, K., 2020. Factors controlling the degradation of hydrogen peroxide in river water, and the role of riverbed sand. Sci. Total Environ. 716, 136971 https://doi.org/10.1016/j.scitotenv.2020.136971.

Wernet, G., Bauer, C., Steubing, B., Reinhard, J., Moreno-Ruiz, E., Weidema, B., 2016. The ecoinvent database version 3 (part I): overview and methodology. Int. J. Life Cycle Assess. 21, 1218–1230. https://doi.org/10.1007/s11367-016-1087-8.

Wu, Y., Zhang, Y., 2022. The Impact of Environmental Technology and Environmental Policy Strictness on China's Green Growth and Analysis of Development Methods. J Environ Public Health. https://doi.org/10.1155/2022/1052824. Article ID 1052824.

Xavier, S., Gandhimathi, R., Nidheesh, P.V., Ramesh, S.T., 2015. Comparison of homogeneous and heterogeneous Fenton processes for the removal of reactive dye Magenta MB from aqueous solution. Desalination Water Treat. 53, 109–118. https://doi.org/10.1080/19443994.2013.844083.