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Challenges and opportunities

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Abstract

Combination of electro-Fenton (EF) process with other advanced oxidation processes (AOPs) is found very much effective for water and wastewater treatment. The combined processes including sono-EF (SEF), photo-EF (PEF), electro-peroxone, ferrate-EF and EF combined with persulfate oxidation allow enhancing the mineralization efficiency of treatment as well as reducing operational cost and toxicity of treated wastewater. Even though, there are several advantages in combined processes, they also present some disadvantages such as increased side reactions, increased energy requirement etc., which are challenges to overcome.

Keywords: Electro-Fenton; Advanced oxidation processes; Combined process; Hydroxyl radical.

1. Introduction

Even though electro-Fenton (EF) process has several advantages like its capability to generate hydrogen peroxide in-situ, higher mineralization efficiency, enhanced ferrous ion regeneration capacity and lesser catalyst requirement; the disadvantages like longer time requirement for complete mineralization of pollutants, scaling up issues, passivation of electrodes etc. made a barrier for its real field implementation [1–6]. Another drawback of EF process is related to the acidic pH (pH 3) requirement for its effective performance. A few heterogeneous catalyst was found much effective even in neutral pH [7]. However, electrolytic generation of hydrogen peroxide at neutral pH is a challenging task, as proton is needed for the two-electron reduction of oxygen and subsequent generation of hydrogen peroxide. Therefore, in general, higher mineralization rates in EF process are achievable at acidic conditions and neutralization of EF treated effluent is needed for further treatment or its discharge.

Several modified versions of EF process like photo-Fenton, peroxicoagulation, and anodic-Fenton were tested to solve the issues associated with EF process [2,8–10]. However, the drawbacks of EF process are marginally solved by these modified processes. Another method to improve the performance of the EF process is to combine it with other advanced oxidation processes (AOPs). Thus, the process efficiency can be improved in terms of pollutant degradation kinetics, mineralization efficiency, biodegradability enhancement, toxicity reduction etc. Passivation of electrodes can be reduced by combing with sonochemical processes [11].

The present article, analyse the performance of EF process in combination with other AOPs. Performance enhancement is detailed along with advantages and disadvantages of combined systems.

2. Coupling EF process with different AOPs

Implementation of the EF process requires [4,12]:

- suitable cathode material for H_2O_2 formation and Fe^{3+} reduction to Fe^{2+} ;
- a homogeneous (dissolved in the bulk) or heterogeneous (solid) iron source ;
- pH adjustment, particularly for homogeneous EF (optimal pH is 3) ;
- current supply.

Several combinations have then been investigated for promoting the removal of organic compounds. The idea is based on the establishment of suitable operating conditions for the implementation of another AOP in the same reactor. The objective is to increase the production of oxidant species (to enhance degradation/mineralization efficiency) or reduce energy consumption (to enhance cost effectiveness) in such a hybrid reactor.

The choice of the anode material offers a first opportunity. For example, non-active materials such as BDD or TiO_x materials allow for production of large amounts of hydroxyl radicals from water oxidation at the anode surface [13–15]. Using porous anode materials in flow-through configuration also provides solutions for improving mass transport conditions [16].

Addition of suitable chemical reagents gives the opportunity to enhance the formation of oxidant species. Ferrate (Fe^{VI}), a powerful oxidant, was recently used as an iron source (instead of conventional Fe^{II} or Fe^{III}) for the EF process (EF-Fe^{VI}) [17]. Addition of sulfite or persulfate and subsequent electrochemical activation is another way to generate oxidant species such as $SO_4^{\bullet-}$, $SO_3^{\bullet-}$ and $^{\bullet}OH$ [18–20]. Sulfite is able to accelerate the regeneration of Fe^{2+} [21]. Introduction of O_3 also improves the oxidation of organic compounds through the electro-peroxone process via reaction of O_3 with H_2O_2 [22].

Using irradiations from artificial or solar light allow for implementation of various processes linked to the EF processes. The (solar) photo-EF (PEF) process is based on the use of UV irradiations for promoting the formation of $^{\bullet}OH$ and the regeneration of Fe^{2+} through (i) rupture of the metal-carboxylate ligand bond, (ii) photodecarboxylation of Fe(III)-oxalate complexes, (iii) photoreduction of $Fe(OH)^{2+}$ and (iv) photolytic rupture of H_2O_2 [9,23]. Addition of a photocatalyst (e.g. TiO_2) has been investigated for implementation of the photocatalytic EF(EF-PC) process [9,24]. Development of photo-anodes by coating a semiconductor photocatalyst on a conductive support allows for implementing the photoelectrocatalytic EF (EF-PEC) process [9,25,26], which is the focus of a great attention over the last few years [27].

Ultrasound irradiation is another way to improve the EF process (SEF) efficiency, owing to (i) formation of additional $^{\bullet}OH$ from water by cavitation, (ii) faster regeneration of Fe^{2+} from Fe-O_2H^{2+} and (iii) mass transport enhancement [28–30].

3. Performance of EF process coupled with other AOPs

Coupling between the EF process and other AOPs always can enhance degradation/ mineralization efficiency, reduce solution toxicity and operational cost compared to EF alone due to the enhanced generation of oxidants (mainly •OH), which accelerate the degradation and mineralization of the contaminants and reduce treatment time [3,4,10,31]. For example, the apparent rate constant (k_{app}) for the degradation of erythrosine B dye at 20 mA cm^{-2} was reported to be 0.2461, 0.5222 and 0.4539 min^{-1} for EF, PEF (100 W) and SPEF (570 W m^{-2}) after 2 h of treatment [32]. Degradation rate of 0.076 and 0.322 min^{-1} and total organic carbon (TOC) removal of 37% and 65% were observed for EF alone and SPEF, respectively, during treatment of 50 mg L^{-1} of amoxicillin at 150 mA cm^{-2} [33]. UVA-PEF treatment of bezafibrate showed higher degradation (92%) compared to visible-light PEF (55%) and EF (42%) owing to higher absorbance of Fe catalyst within UV region [34]. EF-sulfite showed enhanced degradation of anthracene, achieving 85.9% degradation compared to 75.3% obtained in EF alone [18] and carbamazepine, 100% compared to 83.7% observed in EF alone [19]. Enhanced degradation was observed during EF-persulfate treatment of cefotaxime (100%) [35], and diclofenac (96.3%) [20]. PEC-EF always perform better than either photocatalysis or EF alone [36,37]. The k_{app} for the degradation of amaranth were 0.157, 0.171 and 0.211 h^{-1} for PEC, EF and PEC-EF respectively [38]. The degradation kinetics of triphenyltin chloride was observed to follow the sequence PEC-EF (0.274 min^{-1}) > PEF (0.219 min^{-1}) > PEC (0.011 min^{-1}) [25].

The effluents treated by coupled processes PEF, SPEF, PEC-EF and EF-persulfate always have reduced toxicity compared to EF treatment alone because of the enhanced degradation and mineralization of pollutants by the coupled technologies. For example, EF-persulfate treated fruit processing wastewater exposed to Daphnia magna showed increased EC_{50} (48 h) from 17% (5.8 TU) to 20.4% (4.9 TU) for EF compared to 28.9% (3.5 TU) obtained with EF-persulfate at 50 mA cm^{-2} [39].

Coupled EF-sulfite/persulfate requires does not require additional energy to EF other than chemical cost. Lower energy consumption was always observed for PEF, SPEF PEC-EF compared to EF, but the operating cost of PEF and PEC-EF is always higher owing to the cost and energy consumption of the lamps. The energy consumption during treatment of acid blue 29 by EF and SPEF were 257 and 57 kWh (kg TOC)$^{-1}$, respectively [40], whereas the PEF treatment of brown HT dye using UVA lamp with wavelength of 365 nm (75 mW cm^{-2}) requires 225 kWh (kg COD)$^{-1}$, thus, not much suitable for large-scale applications, even the process has significant additional dye removal efficiency than EF, electrochemical oxidation and ozonation [41]. SPEF has lower energy/cost requirement because of abundant and availability of sunlight as natural energy source.

4. Advantages of coupling EF with other AOPs

The combination between EF and other AOPs can bring interesting synergies and therefore provides some advantages. It can enhance the treatment efficiency of wastewater treatment by increasing the number of $^{\bullet}$OH active sites within the reactor, and can generate other strong radicals ($SO_4^{\bullet-}$, $Cl^{\bullet}$, etc.) that contribute additional removal of organic pollutant [9,42]. Moreover, an increase of regeneration rate of Fe(II) from photoreduction of Fe(III) in SPEF has been established [23,43], which not only permit to increase the $^{\bullet}$OH production, but also allows reducing the amount of sludge generation and the associated management cost [44,45]. Furthermore, the flexibility of electrochemical systems [46] allows combining EF with AOPs in single hybrid reactor [24,43], which decrease the footprint and promote synergies of reactions. The fact that the working electrode is the cathode in EF process [47], the anode can also favor reactions according to their properties [48]. For instance, using transparent anode which allows the passage of UV radiation go through the material and interact both with anode surface and bulk solution following photoelectrocatalysis mechanisms [24,49].

In the meantime, such coupling could modify operating and capital costs; therefore, a cost feasibility study is required when comparing these combinations in order to determine the optimal cost-effective conditions [44]. A significant rise of cost with the coupling could represent drawbacks, which are discussed in the following section.

5. Disadvantages of EF coupled with AOPs: Side reactions and non-radical pathways

During the coupling of EF with other AOPs, the excess of certain chemicals entails side reactions consuming the oxidant species in detriment of pollutant degradation. Such undesired effects are exacerbated when several chemicals/oxidant promoters are combined in the same reactor. The main side reactions affecting EF efficiency are related to the excess of Fe^{2+} and/or H_2O_2 consuming $^{\bullet}OH$ according to Eqs. 1 and 2, respectively. Additionally, high current densities are known to affect the degradation/mineralization efficiency due to further H_2O_2 reduction to H_2O (Eq. 3) and the evolution of H_2 (Eq. 4) [4]. When EF is combined with anodic oxidation (EF-AO) using non-active anodes (BDD, TiO_x…), the degradation efficiency is also decreased at high current densities due to O_2 evolution entailed by recombination of surface $^{\bullet}OH$ (Eq. 5), and H_2O_2 anodic decomposition (Eq. 6) [50,51]. In the case of the combined EF-sulfite and EF-persulfate processes, the excess of H_2O_2 can consume $^{\bullet}OH$ and $SO_4^{\bullet-}$ (Eq. 1 and 7, respectively), decreasing the degradation efficiency [18,19]. Excessive amounts of SO_3^{2-} in EF-sulfite can also be detrimental for $^{\bullet}OH$ availability (Eq. 8). In the case of the EF-persulfate process, the excess of $S_2O_8^{2-}$ can entail waste reactions as well, reducing the amount of oxidants available for pollutant degradation. Such reactions include the consumption of $SO_4^{\bullet-}$ by $S_2O_8^{2-}$ (Eq. 9) and the recombination of $SO_4^{\bullet-}$ (Eq. 10) once such radicals are formed by Fe^{2+} activation of $S_2O_8^{2-}$ (Eq. 11). The surplus of Fe^{2+} also reduces the amount of $SO_4^{\bullet-}$ according to the waste reaction of Eq. 12 [20]. Accordingly, the experimental conditions of combined approaches must

be carefully optimized to obtain the highest degradation/mineralization efficiencies avoiding parasitic reactions. Advantages and disadvantages of various EF coupled with AOPs are provided in Table 1.

$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + O_2^{\bullet-} + H^+$ (1)

$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^-$ (2)

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ (3)

$2H^+ + 2e^- \rightarrow H_2$ (4)

$2BDD({}^{\bullet}OH) \rightarrow 2BDD + O_2 + 2H^+ + 2e^-$ (5)

$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ (6)

$H_2O_2 + SO_4^{\bullet-} \rightarrow HO_2^{\bullet} + SO_4^{2-} + H^+$ (7)

$SO_3^{2-} + {}^{\bullet}OH \rightarrow SO_3^{\bullet-} + OH^-$ (8)

$S_2O_8^{2-} + SO_4^{\bullet-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet-}$ (9)

$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-}$ (10)

$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\bullet-}$ (11)

$SO_4^{\bullet-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-}$ (12)

Regeneration of catalyst is a major concern in all the AOPs. The catalyst used in AOPs may affect the efficiency of subsequent process or it may be a threat to the environment, if it is discharged. Hence, recovery and reusability of catalyst used in all AOPs is a critical parameter for its practical application.

6. Conclusions

Combination of EF process with other AOPs is an effective way of pollutant removal in terms of oxidative degradation/mineralization efficiency, biodegradability enhancement and toxicity reduction. Even though, the combined system has several advantages, a few disadvantages such as improvements in the rate of side reactions, increase in the process cost (in a few systems), and promotion of non-radical pathways (in a few systems) etc., constitute the challenges. Overall, the combined systems provide better results than individual AOPs. However, more studies in higher scales are needed for understanding the real issues before their implementation in the real field.

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Table 1: Main combined EF-AOPs: Main reactions, advantages and challenges

Combined process	Main reactions	Advantages	Challenges	Refs.
EF-Anodic oxidation (EF-AO)	Cathode: $H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + Fe^{3+} + OH^-$ $Fe^{3+} + e^- \rightarrow Fe^{2+}$ Anode: $M + H_2O \rightarrow M({}^{\bullet}OH) + H^+ + e^-$ Bulk solution: $H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + Fe^{3+} + OH^-$	- Production of ${}^{\bullet}OH$ at the cathodic and anodic sides for enhanced pollutant degradation and higher mineralization current efficiency. - High mineralization yields.	- High cost of BDD, the most powerful material for AO. - Lack of powerful anodes for AO available in the market, others than BDD. - Formation of ClO_3^- and ClO_4^- at the anode	[50]
EF-Ferrate (EF-Fe^{VI})	Cathode: $H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + Fe^{3+} + OH^-$ $Fe^{3+} + e^- \rightarrow Fe^{2+}$ Bulk: Fe^{VI}–mediated oxidation and formation of reduced form of Fe $H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + Fe^{3+} + OH^-$	- Pre-oxidation of organic compounds using Fe^{VI} as iron source - Reuse of reduced forms of Fe^{VI} for EF process - Lower treatment time (faster degradation)	- Cost of Fe^{VI}	[15]

EF-Sulfite	Cathode: $H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + Fe^{3+} + OH^-$ $Fe^{3+} + e^- \rightarrow Fe^{2+}$ Anode: $SO_3^{2-} \rightarrow SO_3^{\bullet-} + e^-$ Bulk solution: $H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + Fe^{3+} + OH^-$ $Fe^{3+} + SO_3^{2-} \rightarrow SO_3^{\bullet-} + Fe^{2+}$ $SO_3^{\bullet-} + O_2 \rightarrow SO_5^{\bullet-}$ $SO_5^{\bullet-} + HSO_3^- \rightarrow HSO_5^- + SO_3^{\bullet-}$ $Fe^{2+} + HSO_5^- \rightarrow Fe^{3+} + SO_4^{\bullet-}$ $SO_5^{\bullet-} + SO_3^{2-} \rightarrow SO_5^{2-} + SO_3^{\bullet-}$ $SO_5^{\bullet-} + SO_3^{2-} \rightarrow SO_4^{\bullet-} + SO_4^{2-}$ $SO_5^{\bullet-} + SO_5^{\bullet-} \rightarrow 2SO_4^{\bullet-} + O_2$	- Production of $SO_4^{\bullet-}$ to enhance pollutant degradation. - Wide pH range of operation. - SO_3^{2-} is inexpensive and nontoxic. - SO_3^{2-} is transformed into SO_4^{2-} after treatment.	- Side reactions decreasing efficiency when high SO_3^{2-} doses are used. - Higher concentration of SO_4^{2-} after treatment (that can require post-treatment in certain cases)	[18,19]
EF-Persulfate	Cathode: $H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + Fe^{3+} + OH^-$ $Fe^{3+} + e^- \rightarrow Fe^{2+}$ $S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{\bullet-}$	- Selective $SO_4^{\bullet-}$ are produced to enhance pollutant degradation. - Possibility to operate the system at wider pH values.	- Occurrence of several undesired reactions reducing the efficiency,	[20]

	Bulk solution: $H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + Fe^{3+} + OH^-$ $S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\bullet-}$ Anode : $SO_4^{2-} \rightarrow SO_4^{\bullet-} + e^-$ $SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-}$ $S_2O_8^{2-} + {}^{\bullet}OH \rightarrow SO_4^{\bullet-} + HSO_4^- + 0.5\ O_2$ Non-radical activation of $S_2O_8^{2-}$	- Possibility to form persulfate from SO_4^{2-} at suitable anode material - High availability of persulfate salts.	especially in real wastewater matrices. - Cost of persulfate salts. - Higher concentration of SO_4^{2-} after treatment (that can require a post-treatment in certain cases)	
Photoelectro-Fenton – Photoelectrocatalysis (PEF - PEC)	Cathode: $H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + Fe^{3+} + OH^-$ $Fe^{3+} + e^- \rightarrow Fe^{2+}$ Photoanode: semiconductor + $h\nu \rightarrow e_{CB}^- + h_{VB}^+$ $h_{VB}^+ + RX \rightarrow RX^{\bullet+}$ $h_{VB}^+ + H_2O \rightarrow {}^{\bullet}OH + H^+$	- Enhanced regeneration of Fe^{2+} - Production of ${}^{\bullet}OH$ at the cathodic and anodic sides for enhanced degradation/mineralization current efficiency (PEC). - High mineralization rates due to multiple electrochemical and photochemical reactions.	- Photoanodes are not commercially available (PEC). - Need for development of efficient and scalable photoanodes (PEC). - Need for visible-light-active photoanodes (PEC).	[25,52]

	Bulk solution: $H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + Fe^{3+} + OH^-$ $[Fe(OH)]^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH$ $Fe(OOCR)^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + {}^{\bullet}OH$ $H_2O_2 + h\nu \rightarrow 2{}^{\bullet}OH$	- The external potential reduces h_{VB}^+/e_{CB}^- recombination for higher degradation efficiency (PEC). - No need for separation of the photocatalyst since it is supported in a conductive material forming the photoanode (PEC). - Possibility to use solar light with solar active photoanodes (PEC).	- Need for development of large-scale photoreactors. - Intermittent solar irradiation / cost of artificial light irradiation	