Electrochemical Treatment of Wastewater by ElectroFenton, Photo-ElectroFenton, Pressurized-ElectroFenton and Pressurized Photo ElectroFenton: A First Comparison of these Innovative Routes

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In the last few years increasing attention has been devoted to the utilization of electroFenton (EF) and EF based technologies for the treatment of wastewater polluted by recalcitrant organics. It has been shown that the performances of EF can be strongly improved using ultraviolet (UV) irradiation, e.g., by the photo-electroFenton (PEF) method, or pressurized air or oxygen, e.g., by the pressurized-electroFenton (PrEF) one. Although several studies were carried out on the degradation of many organic pollutants using EF, PEF or PrEF, a systematic comparison between PEF and PrEF was never reported as well as the possibility to couple the irradiation with pressurized air. In this study the performances of EF, PEF and PrEF were systematically compared using synthetic solutions of three model organic substrates (e.g., formic acid, oxalic acid and Acid Orange 7). In addition, the pressurized-photo-electroFenton (PrPEF) process was proposed for the first time.

1. Introduction

In the last decades, several researchers have studied innovative routes for the effective remediation of wastewater contaminated by organic pollutants resistant to conventional biological processes.[1–7] The aim of these studies was to develop a process characterized by high removals of organics, no generation of toxic by-products, low cost, use of environmentally friendly reagents, mild operative conditions, large flexibility and stability of adopted electro-catalysts.[1–7] Some electrochemical processes, such as direct anodic oxidation,[1–5] oxidation by electro-generated active chlorine[1,2,6] and electro-Fenton (EF),[1,2,7] are characterized by very promising performances in terms of high removals of organics, use of an environmentally friendly reagent, such as electrons, and mild conditions, such as room temperature and pressure close the atmospheric one. However, these routes suffer from some drawbacks that are limiting their use on an applicative scale. As an example, the direct anodic oxidation is very effective at boron doped diamond anodes (BDD) that are, however, characterized by quite high costs,[1] while indirect oxidation by electro-generated active chlorine can give rise to the formation of various toxic chlorinated by-products.[6]

EF process is considered up to now one of the most promising routes.[7] It is based on the use of carbonaceous cathodes for *in-situ i*) electro-generation of H_2O_2 via $2e^-$ oxygen reduction (eq. (1)) and *ii*) electro-regeneration of the Fe^{2+} catalyst (eq. (3)), which allows to convert H_2O_2 in HO· according to Fenton reaction (eq. (2)).

$$O_2 + 2e^- + 2H^+ = H_2O_2 \quad (1)$$

$$H_2O_2 + Fe^{2+} \rightarrow HO\cdot + Fe^{3+}\ HO^- \quad (2)$$

$$Fe^{3+} + e^- = Fe^{2+} \quad (3)$$

EF presents various advantages including *i*) relatively low costs with respect to other electrochemical processes, *ii*) unlike the Fenton process, on-site generation of H_2O_2 and fast regeneration of Fe^{2+} and *iii*) low amounts of sludge production. However, it presents some relevant drawbacks such as *i*) the low solubility of O_2 in water that leads to slow generations of H_2O_2 and low removals of organics, *ii*) for conventional homogeneous iron catalysts, the need to work at low pH to avoid the precipitation of iron, and *iii*) the formation of quite resistant complexes between iron catalysts and carboxylic acids generated by the oxidation of aromatic compounds.[7,8] Moreover, some parasitic reactions can convert H_2O_2 in water and/or O_2 (eqs. (4–8)) or HO· in weaker oxidants (eqs. (9–12)), reducing the efficacy of the method.[9]

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad (4)$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (5)$$

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

$$Fe^{3+} + H_2O_2 \leftrightarrows [Fe^{III}(HO_2)]^{2+} + H^+ \quad (7)$$

$$[Fe^{III}(HO_2)]^{2+} \rightarrow Fe^{2+} + O_2^{\bullet -} + H^+ \quad (8)$$

$$H_2O_2 + HO\cdot \rightarrow H_2O + HO_2^{\bullet} \quad (9)$$

$$HO_2^{\bullet} + HO\cdot \rightarrow H_2O + O_2 \quad (10)$$

$$O_2^{\bullet -} + HO\cdot \rightarrow OH^- + O_2 \quad (11)$$

$$2\ HO\cdot \rightarrow H_2O_2 \quad (12)$$

In previous works, it was shown that various approaches can be attempted to solve or minimize such problems. Various kinds of heterogeneous catalysts have been tested in order to increase the working pH.[10–15] The problem of the low solubility of O_2 in water can be minimized using innovative cathodes,[1,7,16–18] such as gas diffusion electrodes (GDEs) or modified carbon felts (MCF), or advanced cells, such as jet-[19] or microfluidic ones.[8,20] In addition, pressurized air can be effectively used in EF (PrEF) to enhance the O_2 solubility in water, and, as a consequence, the generation of H_2O_2 (by eq. (2)) and the removal of organics.[13,15,21–25] It was shown that the utilization of PrEF for the treatment of some organics give even higher removals than the direct oxidation at BDD.[15,23] As an example, in the case of the treatment of aqueous solutions of 8-hydroxyquinoline-5-sulfonic acid, the increase of the pressure up to 10 bars enhanced significantly the removal of the organic and of TOC; however, a further enhancement of the pressure up to 12 bars gave lower removals, probably due to a self-scavenging effect.[15,26] In fact, hydroxyl radicals may be scavenged by excess H_2O_2 according to eq. (9) and the formed $HO_2\bullet$ has a lower oxidation potential than HO·.[15] Another interesting approach consists in the utilisation of photo-electro-catalytic methods[27,28] and, in particular, in the combination of EF and ultraviolet (UV) irradiation, e.g. the photo-electroFenton method (PEF), which involves: *i*) production of greater amount of HO· by photo reduction of $Fe(OH)^{2+}$ (eq. (13)) and homolysis of H_2O_2 (eq.(14)) and *ii*) photodecarboxylation of Fe(III)-carboxylate species according to the general reaction (15).[7,16,29–33]

$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + HO\cdot \quad (13)$$

$$H_2O_2 + hv \rightarrow 2HO\cdot \quad (14)$$

$$Fe(OOCR)^{2+} + hv \rightarrow Fe^{2+} + \cdot R + CO_2 \quad (15)$$

As an example, oxalic acid forms complexes such as $Fe(C_2O_4)^+$, $Fe(C_2O_4)_2^-$ and $Fe(C_2O_4)_3^-$ that absorb photons from 250 to 580 nm and whose photodecarboxylation follows eq. (16) by passing through an excitation state undergoing a ligand-metal charge transfer:[7]

$$2Fe(C_2O_4)_n^{(3-2n)} + hv \rightarrow 2Fe^{2+} + (2n-1)C_2O_4^{2-} + 2CO_2 \quad (16)$$

Recently, it was also shown that the consumption of energy for EF can be strongly reduced using wastewater with biodegradable organics in the anodic compartment by microbial fuel or electrolysis cells even if with very long treatment times[34,35] or using salinity gradients by reverse electrodialysis (RED) or assisted RED.[36,37]

Although several studies were carried out for the degradation of many organics using EF, PEF or PrEF, a systematic comparison between PEF and PrEF was never reported as well as the possibility to couple the PEF with the PrEF in one process. Hence, the scope of the present study was to compare the performances of electro-Fenton (EF), photo-electro-Fenton (PEF) and pressurized-electro-Fenton (PrEF) processes as well as to develop for the first time the pressurized-photo-electro-Fenton (PrPEF) process. Three organics widely investigated in literature and characterized by relatively high resistance to electrochemical processes, such as formic acid (FA), oxalic acid (OA) and Acid Orange 7 (AO7), were chosen as model pollutants.

2. Results and Discussion

2.1. ElectroFenton Treatment of Aqueous Solutions of Formic Acid, Oxalic Acid and Acid Orange 7

First, the removal of FA, OA and AO7 by EF was investigated. According to the literature, the electro-generation of H_2O_2 and EF can benefit from the use of quite low current densities (12.5–50 $A\,m^{-2}$).[22,38,39] Hence, first experiments were performed at 25 $A\,m^{-2}$ in an undivided cell equipped with a carbon felt cathode, a Ti/IrO_2-Ta_2O_5 anode and an aqueous solution containing the model organic pollutant, Na_2SO_4 as supporting electrolyte and $FeSO_4$ as catalyst. For all the investigated cases, according to the literature, EF treatment allowed to achieve a reduction of the concentrations of the organics. Ti/IrO_2-Ta_2O_5 anode was chosen since it gives a very small contribution to the mineralization of adopted organics,[4,20] thus allowing to focus on the performances of EF process. In the case of FA, which is directly oxidized to CO_2, a relatively high abatement of the concentration of ~59% was achieved after 8 h (Figure 1). The process is characterized by a relatively low current efficiency (CE) (~25%) and a moderate energetic consumption (433 $kWh\,g_{TOC}^{-1}$) due mainly to the occurrence of parasitic reactions such as H_2 evolution (eq. (17)) and cathodic reduction of H_2O_2 to water (eq. (18)). In particular, the H_2 evolution is favoured with respect to the H_2O_2 formation (eq. (1)) due to the low solubility of O_2 in water at atmospheric pressure (ca. 0.8 $mg\,L^{-1}$ in contact with air at atmospheric pressure and 25 °C).

$$2\ H^+ + 2\ e^- \rightarrow H_2 \quad (17)$$

$$H_2O_2 + 2\ H^+ + 2\ e^- \rightarrow 2\ H_2O \quad (18)$$

In the case of OA, slight lower abatements and CE were obtained (abatement and CE of ~48 and ~20% after 8 h,

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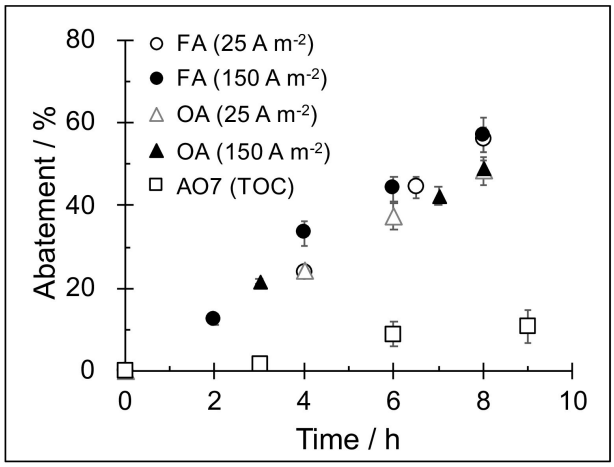

Figure 1. Removal of formic acid (FA) and oxalic acid (OA) (%) and of TOC (for the solution of AO7) vs. time by EF. Electrolyses were performed using a carbon felt cathode and a Ti/IrO_2-Ta_2O_5 anode with a water solution of FA or OA (10 mM) at 25 A m^{-2} or 150 A m^{-2} or AO7 (0.43 mM) at 150 A m^{-2}. The water solutions contained also Na_2SO_4 (50 mM), H_2SO_4 (pH 3) and $FeSO_4$ (0.5 mM).

respectively), because of the higher resistance of this compound with respect to FA. In fact, the kinetic constant of the reaction between hydroxyl radicals and organics was reported to present a value close to 10^7 and 10^8–10^9 $M^{-1}s^{-1}$ for OA and FA, respectively.[40]

It was found in previous research that an increase of the current density can allow to accelerate the removal of organics even if with lower current efficiencies.[41] Hence, to try to accelerate the remediation process, some electrolyses were repeated at higher current densities for the aqueous solutions of FA and OA. However, as shown in Figure 1, the increase of the current did not result in a significant acceleration of the abatement. Moreover, a drastic decrease of the CE and an increase of the energetic consumption were observed. As an example, for FA the increase of the current density from 25 to 150 A m^{-2} resulted in a decrease of CE from 25 to 4% and in an enhancement of energetic consumptions from 433 to 3980 kWh g_{TOC}^{-1}. Similarly, for OA the increase of the current density from 25 to 150 A m^{-2} resulted in a decrease of CE from 20 to 3.3% and in an enhancement of the energetic consumptions from 620 to 6200 kWh g_{TOC}^{-1}. These results are mainly due to the low solubility of O_2 when water is in contact with air at atmospheric pressure, that induces a slow mass transfer of O_2 to the cathode surface. This imposes slow kinetics for the generation of H_2O_2 and, as a consequence, slow removals of the organics. In particular, under the adopted operative conditions, the process is expected to be under the kinetic control of the mass transfer of O_2 to the cathode surface which is not affected by the current density. Conversely, high current densities are expected to enhance the working potential and, as a consequence, the H_2 evolution (eq. (17)) and the cathodic decomposition of H_2O_2 (eq. (18)),[20] causing the decrease of the CE.

In the case of AO7, a very fast and total removal of the colour was achieved but coupled with a very slow abatement of the TOC that was close to 11% after 9 h (Figure 1). Indeed, it has been previously shown that EF is the least effective electrochemical process (compared with direct anodic oxidation at BDD or indirect oxidation by electro-generated active chlorine) for the removal of AO7 because of the formation of recalcitrant by-products.[42] According to the literature, the main relevant by-products are hydroquinone, oxalic and maleic acids which remain in the solution for very long times during EF process.[19,42]

2.2. Photo-electroFenton

Many authors have shown that the combination of EF and ultraviolet (UV) irradiation (e.g., the photo-electroFenton method, PEF) enhances the removal of various organics such as phenol,[29] dyes,[43] 4-chloro-o-cresol,[44] aniline,[45] etc. Also, in our study, it was found that the utilization of ultraviolet (UV) irradiation allows to increase the removal of adopted organics. In the case of FA, the utilization of PEF instead of EF allowed to drastically enhance the abatement of the organic concentration (Figure 2A). As an example, after 8 h a removal of 57 and 82% was achieved by EF and PEF, respectively, with a similar cell potential. Indeed, as previously discussed in the literature, the irradiation produces a greater amount of HO· by photo reduction of $Fe(OH)^{2+}$ (eq. (13)) and homolysis of H_2O_2 (eq. (14)) and, in addition, it favours the oxidation of the quite resistant complexes between carboxylic acids and iron catalysts (eq. (15)).

In the case of aqueous solutions of AO7, an even more strong effect of irradiation was observed (Figure 2B). The removal of TOC after 9 h increased from approximately 11 to 41% with an enhancement of the CE from about 2 to 5% while the energetic consumption due to the electrolysis decreased from 2345 to 1187 kWh g_{TOC}^{-1}. Conversely, in the case of OA, a more limited effect of irradiation was observed, probably due to the high resistance of this compound to the oxidation by HO·. At both 25 and 150 A m^{-2}, the use of the irradiation gave a slight enhancement of the abatement from 48 to ~53–54% after 8 h. A clearer effect of the irradiation was observed prolonging the electrolyses performed at 25 A m^{-2} up to 24 h. In this case, at the end of these long electrolyses the removal of OA was close to 71 and 87% for EF and PEF processes, respectively (Figure 2C).

2.3. Pressurized-electroFenton and Comparison with PEF

It has been previously shown that the utilization of pressurized air or O_2 can enhance drastically the removal of organics.[13,19–25] Here, the effect of the pressure on EF process was investigated for the three model organic compounds using pressurized air in the range 1–5 bars. In the case of AO7, a very strong effect of the pressure was observed. The removal of TOC after 8 h increased from approximately 10 to 48% when the air pressure

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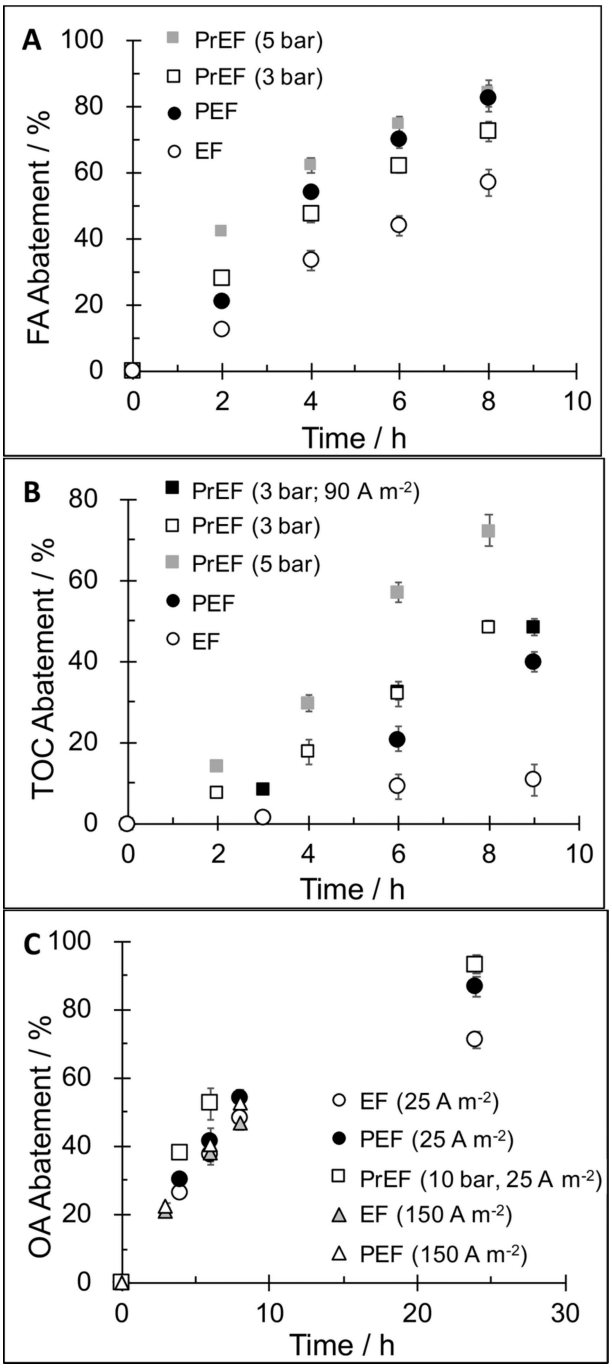

Figure 2. Removal of FA (2A), OA (2C) and of TOC for the solution of AO7 (2B) vs. time by EF, PEF and PrEF (at 3 and 5 bars) at 150 (or 25 or 90 when indicated) A m^{-2} at carbon felt cathode. Water solutions contained FA or OA (10 mM) or AO7 (0.43 mM), Na_2SO_4 (50 mM), H_2SO_4 (pH 3) and $FeSO_4$ (0.5 mM).

was increased from 1 to 3 bars (Figure 2B). Hence, the energetic consumption decreased from 2345 to 446 kWh g_{TOC}^{-1}. As previously mentioned in the literature, the good performances of PrEF are mainly due to the increase of the solubility of O_2 in water with the air pressure. Higher pressure of air enhances the generation of H_2O_2 (eq. (1)) with respect to the H_2 evolution (eq. (17)), thus favouring the formation of HO· (eq. (2)).[20]

According to the literature,[12,19–24] PrEF process is strongly affected by time passed, pressure and current density. For this reason, some PrEF experiments were repeated for an aqueous solution of AO7 for a longer time (15 h) or at a different current density (90 vs. 150 A m^{-2}) or at higher pressures (5 bars) with the following results:

- for the longer experiment performed at 3 bars, after 15 h, the removal increased up to 85% (data not shown) with a small decrease of the CE from 6.1 to 5.7%;
- for experiments performed at 90 A m^{-2} instead of 150 A m^{-2}, just a very small decrease of the abatements of the TOC was achieved for the same time passed (Figure 2B) but with a lower amount of charge, a smaller cell potential (from 3.8 to 3.0 V) and a higher CE (8.7 vs. 6.5%), as a result of a lower impact of parasitic processes; as a consequence, the energetic consumption decreased from 445 to 226 kWh g_{TOC}^{-1};
- the increase of pressure from 3 to 5 bars enhanced the removal achieved after 8 h from 48 to 72% (Figure 2B) with an increase of the CE from 6.1 to 9.1%, as a result of the higher solubility of O_2. As a consequence, the energy consumption decreased from 445 to 286 kwh g_{TOC}^{-1}.

The effect of air pressure was evaluated also for FA and OA. First the electrolyses were performed at 150 A m^{-2} and 1, 3 and 5 bars for aqueous solution of FA. As shown in Figure 2A, the adoption of PrEF at a quite small air pressure (3 bars) strongly accelerated the abatement of FA. The abatement after 8 h increased from 57 to 72% enhancing the pressure from 1 to 3 bars with an enhancement of CE from 4 to 5%. A further enhancement of the pressure up to 5 bars increased the final abatement of FA to 84% (Figure 2A) and the CE to 6%. In order to further enhance the figures of merit of the process, some experiments were repeated at both *i*) higher pressure (10 bars) in order to enhance the solubility of O_2 and the removal of TOC and *ii*) lower current density (25 A m^{-2}) to reduce the impact of parasitic process, and *iii*) for longer times. In these conditions, a removal of FA of 24 and 43% was achieved after 4 h at 1 and 10 bars, respectively. After 24 h, the removal of FA reached 80 and 93% at 1 and 10 bars, respectively, with a CE of 13% for the pressurized process.

In the case of the more resistant organic, i.e., OA, the process was performed at a relatively high pressure of 10 bars. As shown in Figure 2C, also in this case the adoption of pressurized air allowed to accelerate the organic removal; indeed, after 6 h the removal of OA increased from 37 to 52% and after 24 h from 71 to more than 90%.

As discussed in the introduction, the performances of PEF and PrEF were never compared before. In the following a first comparison of such routes is reported. As shown in Figure 2, both PEF and PrEF significantly enhance the removals of FA and OA and of TOC for the aqueous solution of AO7. In particular, for aqueous solutions of FA, very high and similar removals were achieved for PEF and PrEF performed at 5 bars (Figure 2A). Similarly, for OA, PEF and PrEF (at 10 bars) gave after 24 h very high and similar removals of ~87 and ~93% (Figure 2C), respectively. On the other hand, in the case of the aqueous solutions of AO7, better results were achieved with PrEF at both

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3 and 5 bars with respect to PEF (Figure 2B). In order to compare the performances of these processes, the cost of these two approaches should be also taken in considerations. In the case of PEF, the use of the lamp is expected to enhance significantly the capital and operative costs with respect to EF. As an example, according to Priambodo et al.,[46] the cost of electricity increased for PEF with respect to EF of about 28%. Mousset et al. reported that the use of PEF instead of EF increases the overall costs dramatically (more than 3 times).[38] Conversely, in the case of PrEF it has been reported that, for pressures up to 15–20 bars, a very small increase of both operative and capital costs (lower than 10%) is given by the use of PrEF instead of EF. In particular, for pressures of 6 bars, the energetic consumptions due to the compression were reported to be lower than the gain of electric energy arisen by the higher current efficiency achieved with PrEF with respect to EF.[22] Hence, on overall PrEF is expected to give similar performances of PEF but with lower capital and operative costs.

2.4. Pressurized Photo-electroFenton

In spite of the fact that both PrEF and PEF were previously investigated in detail, a coupled approach was never reported. For this reason, a pressurized photo-electroFenton process (PrPEF) was investigated here for the first time using a pressurized cell equipped with two low pressure mercury vapor UV-C lamps. First experiments were performed with an aqueous solution of FA at quite different operating conditions: *i*) 150 A m^{-2} at 3 and 5 bars (Figure 3A and 3B) and *ii*) 25 A m^{-2} at 10 bars (Figure 3C and 3D). As shown in Figure 3A, high abatement of FA close to 90% was achieved by PrPEF at 3 bars at the end of the electrolysis. Moreover, the removal of FA accelerated upon enhancing the pressure because of the higher solubility of O_2; after 4 h, it was close to 65 and 90% at 3 and 5 bars, respectively. In addition, PrPEF at 5 bars allowed to achieve an almost total removal of FA (~98%) after 8 h. It is possible to conclude that the coupled adoption of pressurized air and irradiation allows to strongly improve the performances of EF process for the removal of FA. These results are probably

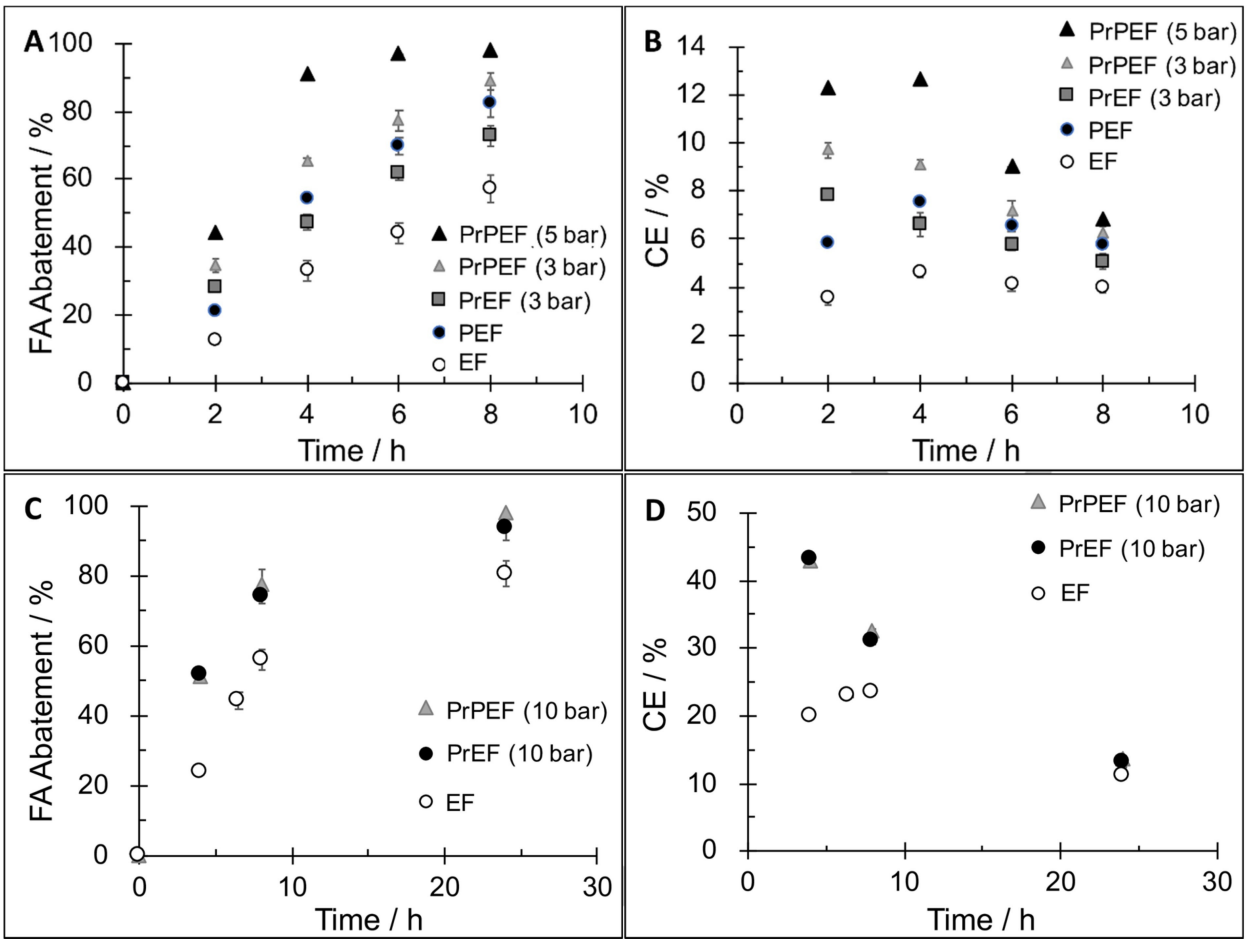

Figure 3. Removal of formic acid (3A, 3C) and current efficiency (3B, 3D) vs. time for the treatment of a water solution of FA (initial concentration 10 mM) by PrPEF. Experiments performed at carbon felt cathode at 150 (3A, 3B) and 25 A m^{-2} (3C, 3D). Results obtained with EF, PEF and PrEF under the same operative conditions were reported for the sake of comparison. The water solution contained also Na_2SO_4 (50 mM), H_2SO_4 (pH 3) and $FeSO_4$ (0.5 mM).

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due to the fact that in PrPEF the removal of organics benefits simultaneously from the faster generation of H_2O_2 due to the higher solubility of O_2 (eq. (1)) achieved using pressurised air and from the positive effects of the UV-C irradiation on the generation of HO· by reactions (13) and (14) and on the photodecarboxylation of Fe(III)-carboxylate species (eq. (15)).

It is worth to mention that, as shown in Figure 3A and 3B, the use of PrPEF allowed to enhance the removal of FA and the CE with respect to both PEF and PrEF methods. As an example, after 8 h the PrPEF at 3 bars gave a removal of FA of ~90% while PEF and PrPEF gave an abatement of ~82 and 72%, respectively.

Figure 3C reports the removal of FA achieved at low current density (25 A m^{-2}) by PrPEF at 10 bars. The removals of FA obtained by EF and PrEF method vs. time were also reported for the sake of comparison. In this case, experiments were prolonged up to 24 h to have a significant amount of charge passed. It can be clearly observed that the PrPEF at 10 bars allowed to increase drastically the removals of FA and the CE (Figure 3D) with respect to EF. However, the use of the lamp gave just a small increase of the FA removal (97 vs. 93% after 24 h for PrPEF and PrEF, respectively) with respect to PrEF due to the very good performances of the process achieved at these relatively high pressures also in the absence of irradiation.

The PrPEF process was evaluated also in the case of aqueous solutions of AO7 and OA. In the case of AO7, the PrPEF at a quite low pressure of 2 bars gave significant higher abatements with respect to the other investigated processes (Figure 4A). Indeed, PrPEF at 2 bars after 8 h gave an abatement of TOC of ~46% while EF, PrEF (at 2 bars) and PEF gave an abatement of 10, 19 and 40%, respectively (Figure 4A). The increase of the pressure to 3 bars allowed to enhance the removal of TOC at both PrPEF and PrEF that gave, however, quite similar results (~49%); thus, showing that under these adopted operative conditions the use of the lamp was not useful.

In the case of the very resistant OA molecule, a quite different picture was obtained. For this organic molecule, the utilization of both pressure and irradiation allowed to drastically accelerate the removal of the organic with respect to both EF, PEF and PrPEF. As shown in Figure 4B, after 6 h, PrPEF (at 10 bars) allowed to remove about 75% of OA while EF, PEF and PrEF (at 10 bars) gave an abatement of 37, 41 and 52%. Similarly, after 6 h, PrPEF presented a CE close to 42% while EF, PEF and PrEF a CE of 20, 23 and 29%.

Figure 5 reports the removals of FA and OA vs. time achieved by EF and PrPEF under the same operative conditions. As previously discussed, EF gave for FA a faster and higher removal with respect to OA, probably due to the fact that FA reacts in a faster way with HO· with respect to OA. However, it is worth to mention that the use of PrPEF allowed to accelerate the removal of both these compounds and give very similar and high abatements of these two acids.

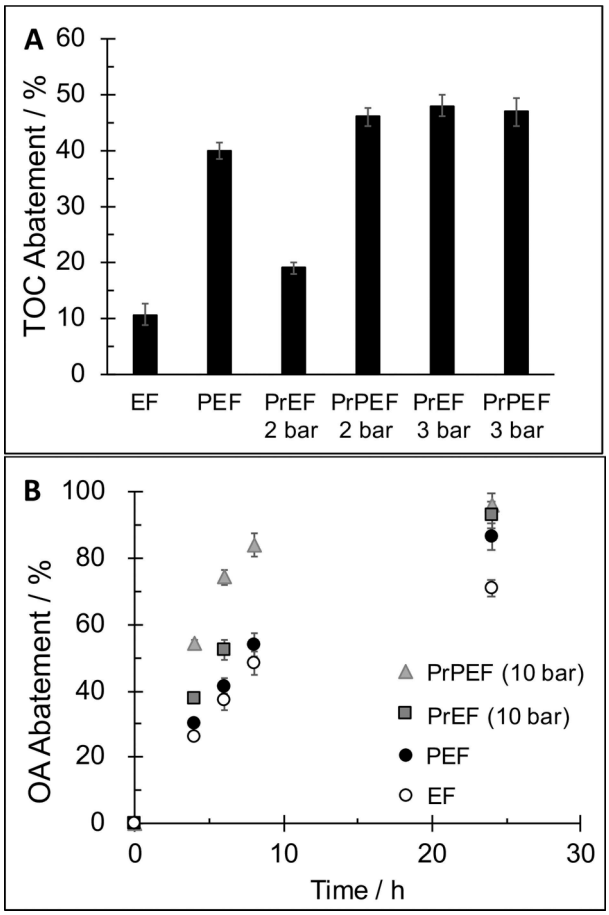

Figure 4. Treatment of water solutions of AO7 (initial concentration 0.43 mM) and OA (initial concentration 10 mM) by PrPEF. Figure 4A reports the removal of TOC achieved by PrPEF after 8 h at 2 and 3 bars and 150 A m^{-2}. The abatement achieved by EF, PEF and PrEF was also reported for comparison. Figure 4B reports the abatement of OA vs. time passed for EF, PEF, PrEF and PrPEF at 10 bars and 25 A m^{-2}. Water solution of Na_2SO_4 (50 mM), $FeSO_4$ (0.5 mM) and H_2SO_4 (pH 3) and a carbon felt cathode were used.

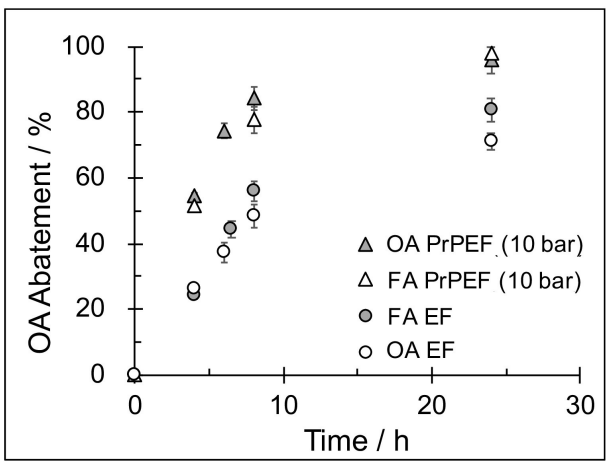

Figure 5. Comparison between the treatment of OA and FA (initial concentration 10 mM) by EF and PrPEF (at 10 bars) at 25 A m^{-2}. Water solutions of Na_2SO_4 (50 mM), $FeSO_4$ (0.5 mM) and H_2SO_4 (pH 3) and carbon felt cathode were used.

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3. Conclusions

In this study the performances of photo-electroFenton (PEF) and pressurized-electroFenton (PrEF) were compared for the first time. It was shown that both PEF and PrEF strongly accelerate the treatment of the three adopted model organic substrates (e.g., formic acid (FA), oxalic acid (OA) and Acid Orange 7 (AO7)) with respect to EF. Similar performances are achieved by PEF and PrEF by a proper selection of the pressure for the removal of OA and FA. However, in the case of AO7, better results were achieved with PrEF at both 3 and 5 bars with respect to PEF. Moreover, PrEF at relatively low pressures is expected to present lower costs with respect to PEF.

In addition, a pressurized-photo-electroFenton (PrPEF) process was proposed for the first time by coupling the use of irradiation and pressurized air. It was shown that PrPEF improves the performances of EF process in terms of higher and faster removals of organics and TOC and higher current efficiencies. Moreover, for both OA and FA, PrPEF gave faster abatements with respect to PEF and PrEF. In the case of AO7, the PrPEF at a quite low pressure of 2 bars gave significant higher abatements with respect to the other investigated processes but at 3 bars PrPEF and PrEF gave quite similar results; thus, showing that, under the adopted operative conditions, the use of the lamp was not useful.

In conclusion, PrPEF can be considered as a new and powerful approach to remove very resistant organics without the use of expensive anodes and cathodes. However, further investigations will be necessary in the future to better asses the perspectives of this new approach, also involving the evaluation of solar irradiation in order to reduce the costs of the process.

Experimental Section

Electrolyses

Electrolyses were performed in an undivided high-pressure AISI 316 stainless steel cell (Figure 6). The system was characterized by a stainless-steel body with a coaxial cylindrical geometry. A borosilicate-glass beaker was sited inside the body to confine the electrolyte. Two low-pressure mercury vapor lamp of 11 W were used to light up the electrolyte through the use of two quartz windows (total area of 0.8 cm^2) placed in the side wall of the stainless-steel body. The head of the cell was equipped with a gas inlet, a vent, two electrical connections for the electrodes and a dip tube that allow to extract liquid samples during the experiment. The electrodes were immersed in the electrolyte inside the beaker with an inter-electrode gap of 2.5 cm and a stirring bar at 400 rpm. A manometer was used to control the operating pressure. Air (Alphagaz™ 1, Air Liquide 99.999%) was used to fill the reactor till the desired operative pressure.

The anode was Ti/IrO_2-Ta_2O_5 with a total front wet area of 3.9 cm^2 whereas the cathode was carbon felt (Carbon Lorraine, France) with a wet area of 3.2 cm^2 faced to the anode. The volume of solution was 50 mL. The electrolyses were performed with amperostatic alimentation (Amel 2053 potentiostat/galvanostat) at room temperature. Most of the experiments were repeated at least twice, giving rise to a good reproducibility of results (±4%).

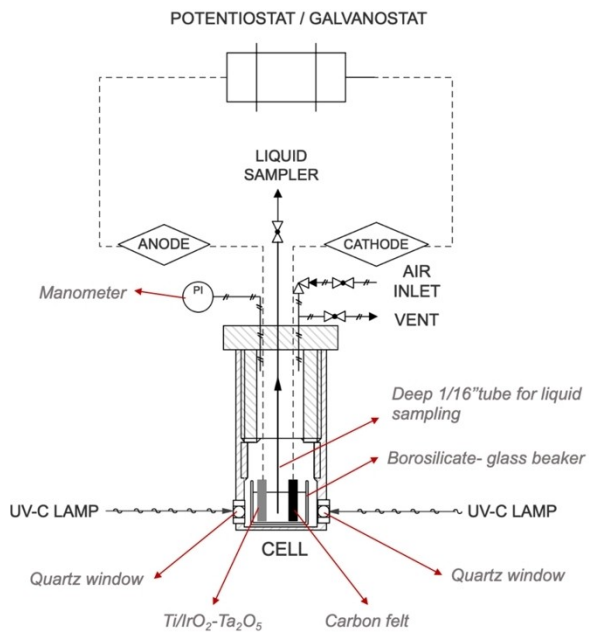

Figure 6. High-pressure AISI 316 stainless steel cell.

Reagents and Analyses

Water CHROMASOLV™ Plus, (Honeywell Rieden-de Haen™, for HPLC) was used as solvent. Acid Orange 7 (Sigma-Aldrich), oxalic acid (Merk Schuchardt OHG, anhydrous for synthesis) or formic acid (Sigma-Aldrich, 98–100% purity) were selected as model pollutants. Na_2SO_4 50 mM (ACS Reagent, ≥99%) was used as supporting electrolyte to enhance the conductivity of the solution. H_2SO_4 (Sigma-Aldrich) was used to achieve a pH of 3 and $FeSO_4$ (AnalaR NORMAPUR, VWR chemicals) 0.5 mM as catalyst.

The degradation of AO7 was followed by the evaluation of the total organic carbon (TOC) of the electrolyte. TOC was analyzed by a TOC-L CSH/CSN analyzer Shimadzu. The abatement (e.g., the conversion) of the total organic carbon (TOC Abatement) and the current efficiency for the removal of the TOC (CE_{TOC}) were defined by eqs. (19) and (20), respectively.

$$\text{TOC Abatement} = (\Delta\text{TOC})_t/\text{TOC}^\circ \tag{19}$$

$$CE_{TOC} = \text{nFV C}^\circ\ (\text{TOC Abatement})/\text{I t} \tag{20}$$

where (ΔTOC)t is the decay of the TOC ($mg_{carbon}\ L^{-1}$), TOC° and C° the initial concentrations of the TOC ($mg_{carbon}\ L^{-1}$) and of the organic pollutant (mol L^{-1}) inside the electrochemical cell, respectively, n is the number of electrons exchanged for the oxidation of the organic pollutant to carbon dioxide (84 for the AO7), F the Faraday constant (96487 C mol^{-1}), I the applied current intensity and t the electrolysis time and V the volume of the solution.

The concentration of formic and oxalic acids was evaluated by HPLC using an Agilent 1260 fitted with a Rezex ROA-Organic Acid column (Phenomenex) at 20 C° and coupled with a UV detector working at 210 nm. A water solution 0.005 N of H_2SO_4 (Sigma-Aldrich) was eluted at 0.5 mL min^{-1} as the mobile phase. Calibration curve were obtained by using the pure standards of formic and oxalic acids. The abatement and the CE of the organic acids were estimated by eqs. (21) and (22):

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$$\text{Abatement organic acid} = (C^{\circ} - C_t)/C^{\circ} \quad (21)$$

$$CE_{\text{organic acid}} = n\ F\ V\ C^{\circ}\ (\text{Abatement organic acid})/I\ t \quad (22)$$

where n is 2 for both formic and oxalic acids.

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Conflict of Interest

The authors declare no conflict of interest.

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[1] C. A. Martínez-Huitle, M. A. Rodrigo, I. Sirés, O. Scialdone, *Chem. Rev.* **2015**, *115*, 13362–13407.
[2] C. A. Martínez-Huitle, O. Scialdone, M. A. Rodrigo, in *Electrochemical water and wastewater treatment. Elsevier*, **2018**.
[3] C. A. Martìnez-Huitle, M. Panizza, *Curr. Opin. Electrochem.* **2018**, *11*, 62–71.
[4] O. Scialdone, *Electrochim. Acta* **2009**, *54*, 6140–6147.
[5] Y. He, H. Lin, Z. Guo, W. Zhan, H. Li, W. Huang, *Sep. Purif. Technol.* **2019**, *212*, 802–821.
[6] O. Scialdone, F. Proietto, A. Galia, *Curr. Opin. Electrochem.* **2021**, *27*, 100682.
[7] E. Brillas, I. Sirés, M. A. Oturan, *Chem. Rev.* **2009**, *109*, 6570–6631.
[8] O. Scialdone, A. Galia, S. Sabatino, *Electrochem. Commun.* **2013**, *26*, 45–47.
[9] E. Brillas, *Chemosphere* **2020**, *250*, 126198.
[10] S. Ammar, M. A. Oturan, L. Labiadh, A. Guersalli, R. Abdelhedi, N. Oturan, E. Brillas, *Water Res.* **2015**, *74*, 77–87.
[11] N. Barhoumi, L. Labiadh, M. A. Oturan, N. Oturan, A. Gadri, S. Ammar, E. Brillas, *Chemosphere* **2015**, *141*, 250–257.
[12] A. H. Ltaïef, A. D'Angelo, S. Ammar, A. Gadri, A. Galia, O. Scialdone, *J. Electroanal. Chem.* **2017**, *796*, 1–8.
[13] A. H. Ltaïef, S. Sabatino, F. Proietto, S. Ammar, A. Gadri, A. Galia, O. Scialdone, *Chemosphere* **2018**, *202*, 111–118.
[14] M. Zhou, M. A. Oturan, I. Sirés. in *Electro-Fenton Process*, *Springer*, **2018**.
[15] N. Hamdi, F. Proietto, H. B. Amor, A. Galia, R. Inguanta, S. Ammar, A. Gadri, O. Scialdone, *ChemElectroChem* **2020**, *7*, 2457–2465.
[16] S. O. Ganiyu, M. Zhou, C. A. Martínez-Huitle, *Appl. Catal. B* **2018**, *235*, 103–129.
[17] A. Da Pozzo, E. Petrucci, C. Merli, *J. Appl. Electrochem.* **2008**, *38*, 997.
[18] M. Panizza, G. Cerisola, *Water Res.* **2009**, *43*, 339–344.
[19] J. F. Pérez, J. Llanos, C. Sáez, C. López, P. Cañizares, M. A. Rodrigo, *Electrochem. Commun.* **2016**, *71*, 65–68.
[20] O. Scialdone, A. Galia, S. Sabatino, *Appl. Catal. B* **2014**, *148–149*, 473–483.
[21] J. F. Pérez, A. Galia, M. A. Rodrigo, J. Llanos, S. Sabatino, C. Sáez, B. Schiavo, O. Scialdone, *Electrochim. Acta* **2017**, *248*, 169–177.
[22] O. Scialdone, A. Galia, C. Gattuso, S. Sabatino, B. Schiavo, *Electrochim. Acta* **2015**, *182*, 775–780.
[23] J. F. Pérez, A. Galia, M. A. Rodrigo, J. Llanos, C. Sáez, O. Scialdone, *Electrochim. Acta* **2018**, *273*, 447–453.
[24] N. Klidi, F. Proietto, F. Vicari, A. Galia, S. Ammar, A. Gadri, O. Scialdone, *J. Electroanal. Chem.* **2019**, *841*, 166–171.
[25] J. F. Pérez, J. Llanos, C. Sàez, C. Lòpez, P. Cañizares, M. A. Rodrigo, *J. Cleaner Prod.* **2019**, *211*, 1259–1267.
[26] A. Da Pozzo, P. Ferrantelli, C. Merli, E. Petrucci, *J. Appl. Electrochem.* **2005**, *35*, 391–398.
[27] P. Li, T. Zhang, M. A. Mushtaq, S. Wu, X. Xiang, D. Yan, *Chem. Rec.* **2021**, *21*, 841–857.
[28] R. Gao, D. Yan, *Adv. Energy Mater.* **2020**, *10*, 1900954.
[29] A. Babuponnusami, K. Muthukumar, *Chem. Eng. J.* **2012**, *183*, 1–9.
[30] W. P. Ting, M. C. Lu, Y. H. Huang, *J. Hazard. Mater.* **2008**, *156*, 421–427.
[31] C. Flox, S. Ammar, C. Arias, E. Brillas, A. V. V. Zavala, R. Abdelhedi, *Appl. Catal. B* **2006**, *67*, 93–104.
[32] D. P. Garcia, R. V. Medrano, M. H. Esparza, *Sol. Energy* **2009**, *83*, 306–315.
[33] D. Clematis, M. Panizza, *Chemosphere* **2021**, *270*, 129480.
[34] C. H. Feng, F. B. Li, H. J. Mai, *Environ. Sci. Technol.* **2010**, *44*, 1875–1880.
[35] G. Riccobono, G. Pastorella, F. Vicari, A. D'Angelo, A. Galia, P. Quatrini, O. Scialdone, *J. Electroanal. Chem.* **2017**, *799*, 293–298.
[36] P. Ma, X. Hao, F. Proietto, A. Galia, O. Scialdone, *Electrochim. Acta* **2020**, *354*, 136733.
[37] P. Ma, X. Hao, A. Galia, O. Scialdone, *Chemosphere* **2020**, *248*, 125994.
[38] E. Mousset, W. H. Loh, W. S. Lim, L. Jarry, Z. Wang, O. Lefebvre, *Water Res.* **2021**, *200*, 117234.
[39] P. Ma, H. Ma, A. Galia, S. Sabatino, O. Scialdone, *Sep. Purif. Technol.* **2019**, *208*, 116–122.
[40] M. Leon, G. E. A. Dorfman, in *Reactivity of the hydroxyl radical in aqueous solutions*, First Edition, **1973**.
[41] M. Panizza, G. Cerisola, *Water Res.* **2009**, *43*, 339–344.
[42] G. T. Chi, Z. K. Nagy, K. D. Huddersman, *Prog. React. Kinet.* **2011**, *36*, 189–214.
[43] C. Espinoza, J. Romero, L. Villegas, L. Cornejo-Ponce, R. Salazar, *J. Hazard. Mater.* **2016**, *319*, 24–33.
[44] S. Irmak, H. I. Yavuz, O. Erbatur, *Appl. Catal. B* **2006**, *63*, 243–248.
[45] E Expósito, C. M. Sánchez-Sánchez, V. Montiel, *J. Electrochem. Soc.* **2007**, *154*, E116.
[46] R. Priambodo, Y. J. Shih, Y. J. Huang, Y. H. Huang, *Sustain. Environ. Res.* **2011**, *21*, 389–393.

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