

# Effective removal and mineralization of 8-hydroxyquinoline-5-sulfonic acid by pressurized-electro-Fenton-like process with Ni-Cu-Al layered double hydroxide

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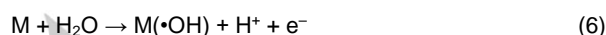
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**Abstract:** Ni-Cu-Al layered double hydroxide (Ni-Cu-Al LDH) was proposed as electro-Fenton-like catalyst for 8-hydroxyquinoline-5-sulfonic acid (8-HQS) removal in water. The properties of prepared catalysts were characterized by X-ray, SEM and EDAX analyses. The effect of numerous operative parameters on the removal of 8-HQS and TOC was studied. Very high removals of both 8-HQS and TOC (87 and 79%, respectively) were obtained using a pressurized electro-Fenton like process (PrEFL-LDH) at P = 10 bars, using a Ti/IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> anode for 6 hours. The process presented good performances in a large range of pH (3-10) and gave better removals of 8-HQS and TOC with respect to that achieved by both *i*) EF catalysed by homogeneous (FeSO<sub>4</sub>) or natural heterogeneous catalysts (pyrite and chalcopyrite) and *ii*) anodic oxidation at Boron Doped Diamond anode. Ni-Cu-Al LDH retained its catalytic activity after four cycles. Moreover, the carboxylic acid intermediates were identified and analyzed by HPLC.



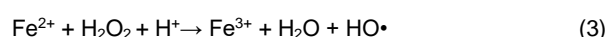
Furthermore, the anode (M) can generate hydroxyl radicals (reaction (6)) that contribute to the mineralization of organics in undivided cells.



However, the EF performances are usually limited by *i*) the low solubility of oxygen in water that leads to a low generation of hydrogen peroxide and slow removals of organics and *ii*) for conventional homogeneous catalysts, the necessity to work at acidic pH in order to avoid the precipitation of the iron catalyst and sludge accumulation after neutralization [4,5]. In previous works, it was shown that various approaches can be attempted to try to solve such problems. The problem of the low solubility of oxygen in water can be minimized using innovative cathodes, including gas diffusion electrodes (GDEs) [2-4] and modified carbon felts (MCF) [2,3] or advanced cells, such as jet-cells [6], micro fluidic cells [5,7] and pressurized reactors [8-10]. Moreover, various heterogeneous catalysts have been tested in order to increase the working pH, including: cheap natural catalysts, such as pyrite and chalcopyrite [11-15]; synthetic iron-loaded structures, such as carbon nanotubes [16]; resins [17], zeolites or biosorbents [18], zero-valent iron (ZVI) [3]; and, metal-organic frameworks [19]. However, in most of cases, these materials do not couple high removal of TOC and recyclability. Quite promising results were obtained by combining natural heterogeneous catalysts and relatively high pressures [15], but it would be useful to find other heterogeneous catalysts characterized by faster removal of TOC in a large range of pH. In this frame, the utilization of layered double hydroxide (LDH) as heterogeneous catalysts for electro-Fenton-like process was here proposed for the first time. LDH is a cheap hydrotalcite-like compound, characterized by a 2D flat

## Introduction

In recent years, it has been shown that electro-Fenton (EF) is a very promising method for the removal of organics from wastewater for many reasons: *i*) relatively low operative and capital costs with respect to other electrochemical processes; *ii*) effective removal of several organics by hydroxyl radicals (reactions (1) and (2)) generated by Fenton's reaction (3); *iii*) unlike Fenton process, generation on site, by cathodic O<sub>2</sub> reduction, of H<sub>2</sub>O<sub>2</sub> (reaction (4)); *iv*) regeneration of Fe<sup>2+</sup> from cathodic reduction of Fe<sup>3+</sup> (reaction (5)); and, *v*) low amounts of sludge production [1-4].



network structure with a formula  $[M_{1-x}M_x^{3+}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n}m\text{H}_2\text{O}$  in which  $M^{2+}$  and  $M^{3+}$  refers to metal cations, such as  $\text{Mg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Co}^{3+}$ , respectively, and  $\text{A}^{n-}$  represents organic or inorganic inter layer anions [20,21]. In the last years, LDHs based catalysts were proposed for many environmental applications, including catalytic wet peroxide oxidation and catalytic ozonisation [22], Fenton and Fenton-like processes [23–29] as well as photo-Fenton [30]. It has been reported that LDHs exhibited good performances for Fenton-like reactions due to strong metal synergic interactions and low metal leaching compared to other solid catalysts [23,24,29]. In particular, a Ni-Cu-Al- $\text{CO}_3$ -LDH was selected for this research, based on the good results obtained by Dubey and co-authors for the oxidation of phenol by hydrogen peroxide using hydrotalcites containing Cu, Ni and Al as catalysts [31]. Hence, in this work, LDH was synthesized and characterized before being used as a catalyst. The performances of the process, named in the following electro-Fenton-like-LDH (EFL-LDH) were assessed studying the oxidation and mineralization of solutions of 8-hydroxyquinoline-5-sulfonic acid (8-HQS). 8-HQS was selected as representative of nitrogen-heterocyclic compounds (NHCs), which are widely used in chemical industry for a variety of applications, including pharmaceuticals, cosmetics, pesticides, disinfectants, agrochemicals, dyestuffs, antifreeze, corrosion inhibitor, coal-tar wastes and creosote wood preservation [30–33] and that can possess toxic, carcinogenic, mutagen and recalcitrant properties even when present in low concentrations [34–36]. The degradation of 8-HQS by EFL-LDH was investigated at different air pressures, to enhance the solubility of oxygen in water using a carbon-felt cathode. Moreover, the effect of numerous operative parameters was investigated.

## Results and Discussion

### Analysis of the LDH sample

The XRD pattern (fig. 1a) of Ni-Cu-Al- $\text{CO}_3$ -LDH sample shows diffraction peaks series, at  $2\theta = 11^\circ$ ,  $23^\circ$ ,  $35^\circ$  and  $60^\circ$ , respectively, which was consistent with the reflection of (003), (006), (009) and (110) crystal planes in LDH phase. The identification was performed by comparison with the data reported in [38,39]. The diffraction peaks are rather broad, suggesting that the grain size is very small. To confirm this assumption, we evaluated the grain size using Scherrer's equation [40], and we found an average size of  $3.25 \pm 0.15$  nm. Besides, the strong (003) diffraction peak is characteristic of the successive stacking of layers along c-axis, with basal spacing  $d_{003}$  (0.76 nm) similar to the value previously reported in literature [40]. This confirmed the formation of Ni-Cu-Al- $\text{CO}_3$  LDH powder.

Fig. 2 depicts the scanning electron microscopy (SEM) image and energy dispersive x-ray (EDS) spectrum of the prepared powder. Higher magnification of the SEM image (fig. 2a) proves that the surface of the catalyst was not uniform and a large number of pores could be clearly observed on the surface, which ultimately improves the surface area of the material. It shows the formation of nano size particles of Ni-Cu-Al-LDH in the order of 84–148 nm. EDS analysis (fig. 2b) confirms the presence of raw elements Ni, Cu and Al with a percentage of each one  $34.59\% \pm 1.1$ ,  $22.18\% \pm 0.7$  and  $43.24\% \pm 1.8$ , respectively. In particular, the reported values are a mean of values obtained performing the EDS in

different points of the sample, analyzing always an equal area. It demonstrates that the catalyst was a polymer containing Cu–Al hydrotalcite.

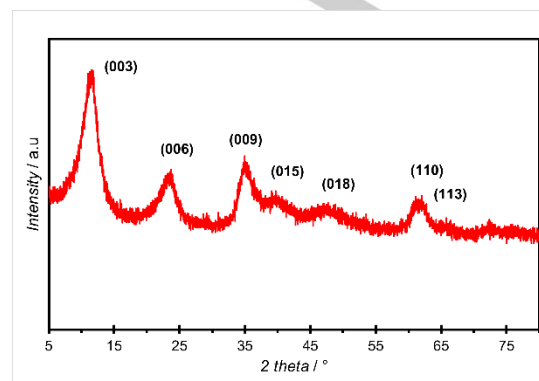
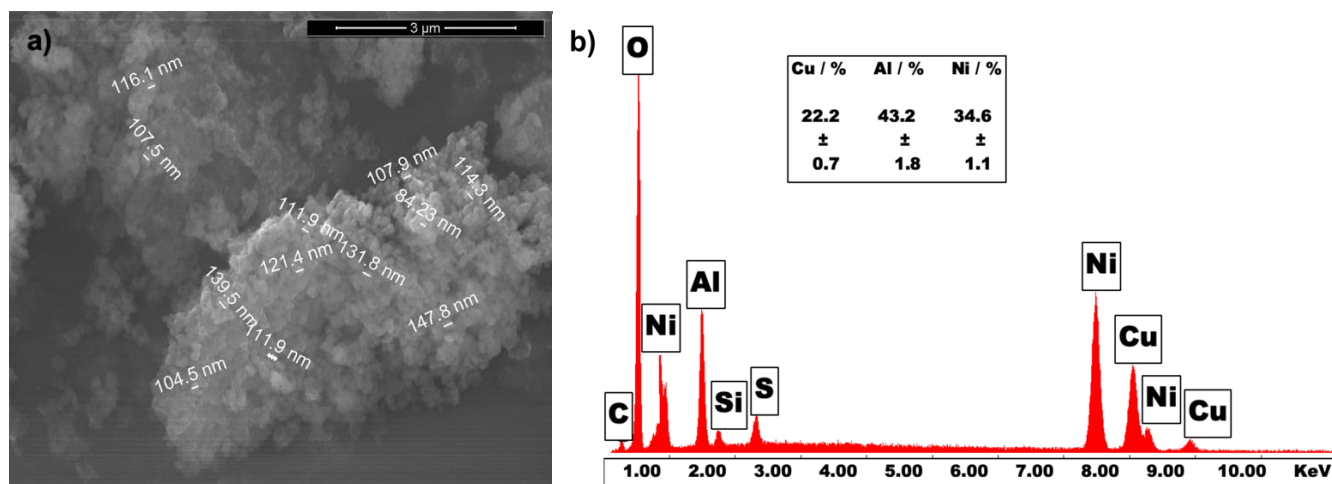


Figure 1. XRD pattern of NiCuAl- $\text{CO}_3$  LDH powder

### Treatment of 8-HQS solutions by EFL-LDH

#### Preliminary electrolyses with LDH catalyst at various air pressures

First electrolyses were performed for 6 h under amperostatic mode ( $70 \text{ A m}^{-2}$ ) with an aqueous solution of 0.4 mM 8-HQS as model organic compound, 0.05 M  $\text{Na}_2\text{SO}_4$  as supporting electrolyte and an initial pH of 3. Ni-Cu-Al-LDH (in the following named LDH) was used as heterogeneous catalyst, carbon felt as cathode and Ti/IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> as anode, at various air pressures (1, 7 and 10 bar). Fig. 3a and 3b report the trend with the time of  $[\text{8-HQS}]/[\text{8-HQS}]^0$  and  $\text{TOC}/\text{TOC}^0$  (where  $[\text{8-HQS}]$ ,  $[\text{8-HQS}]^0$  and  $\text{TOC}$ ,  $\text{TOC}^0$  are the experimental and initial values of the concentration of 8-HQS and of TOC, respectively). At 1 bar and after 6 h, a reduction of both concentration of 8-HQS and TOC was achieved (fig. 3a and fig. 3b), showing that the proposed process is able to remove part of 8-HQS and to achieve a partial mineralization. However, the process was rather slow and only a limited reduction of 8-HQS (43%) and TOC (32%) after 6 hours, were achieved. It was previously shown that the adoption of an air pressure higher than the atmospheric one can accelerate significantly the generation of hydrogen peroxide at carbonaceous cathodes and consequently the electro-Fenton process, due to the higher solubility of oxygen [8–10,15]. Hence, since the proposed process is based on the generation of  $\text{H}_2\text{O}_2$ , electrolyses were repeated at 7 and 10 bars. First, some experiments were performed for 2 hours at  $70 \text{ A m}^{-2}$  at 1 and 10 bars in the absence of the catalyst and the pollutant in order to evaluate the conversion of oxygen to hydrogen peroxide at various pressures. According to the literature [8], the increase of the pressure from 1 to 10 bars resulted in a strong increase of the concentration of  $\text{H}_2\text{O}_2$  from less than 1 mM to about 5 mM. As shown in fig. 3a, the utilization of higher pressures allowed accelerating drastically the removal of 8-HQS. Indeed, after 6 hours,  $[\text{8-HQS}]/[\text{8-HQS}]^0$  was 57, 27 and 12% at 1, 7 and 10 bars, respectively. Notably, also the mineralization was drastically enhanced (fig. 3b). As an example, the ratio  $\text{TOC}/\text{TOC}^0$  was 68 and 21% after 6 hours at 1 and 10 bars, respectively. It has been previously pointed out that the utilization of pressured air lower than 18 bars affects in a very small way both operative and capital



**Figure 2.** SEM image (fig. 2a) and EDS spectrum (fig. 2b) of Ni-Cu-Al-CO<sub>3</sub>-LDH powder. In the table inserted in fig. 2b, the first line reports the estimated chemical composition averages (%) computed from three data points and the second line is the standard deviation (%).

costs for EF [28] or other electrochemical processes, such as CO<sub>2</sub> cathodic reduction [41]. Hence, the adoption of pressurized air seems a very effective way to enhance the performances of the proposed process. In order to explore better the role of air pressure, electrolyses were repeated at 12 bars. However, as shown in fig. 3c, the final values of [8-HQS]/[8-HQS]<sup>0</sup> and TOC/TOC<sup>0</sup> decreased with the pressure up to 10 bar and slightly increased for a further enhancement of the pressure to 12 bars. According to the literature, this result could be due to the fact that too high concentrations of H<sub>2</sub>O<sub>2</sub>, achieved at the highest adopted pressures, could be detrimental to the process for a self-scavenging effect; indeed, hydroxyl radicals may be scavenged by excess H<sub>2</sub>O<sub>2</sub> according to the reaction (7) and the formed HO<sub>2</sub>• has a lower oxidation potential than hydroxyl radicals HO• [18,42-44].

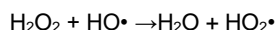
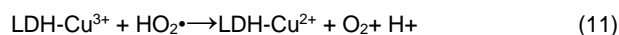
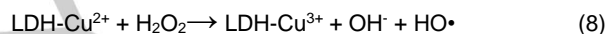


Fig. 3c reports also the final mineralization current efficiency (MCE) as a function of the imposed air pressure. It can be seen that the adoption of pressurized air allows enhancing drastically the MCE, because a larger part of the charge passed is devoted to hydrogen peroxide thanks to the higher solubility of oxygen under pressurized conditions. Indeed, the increase of the pressure from 1 to 10 bars gave an enhancement of the final MCE from 7 to 25%. Therefore, in the following sections, the effect of different operating parameters, including current density, pH, the amount of catalyst, was investigated by performing the treatment of 8-HQS contaminated solutions by a pressurized electro-Fenton-like-LDH (PrEFL-LDH) process at 10 bars.

To better evaluate the role of the catalyst, some electrolyses were repeated at 10 bars in the absence of LDH catalyst. As shown in fig. 3a and 3b, the removal of both 8-HQS and TOC was quite low with respect to that achieved with the catalyst. The oxidation in the absence of LDH was probably achieved by means of adsorbed hydroxyl radicals generated at the anode and H<sub>2</sub>O<sub>2</sub> produced at the cathode. The removal of TOC after 6 h was of about 16 and 79% in the absence and in the presence of LDH, respectively (fig. 3b). Hence, it can be confirmed that the removal of 8-HQS and its mineralization achieved in the presence of LDH are obtained mainly by an oxidation process mediated by the catalyst. According to the literature [31], the reaction mechanism (reactions (8) – (14)) is likely to involve the oxidation of Cu<sup>2+</sup> ions

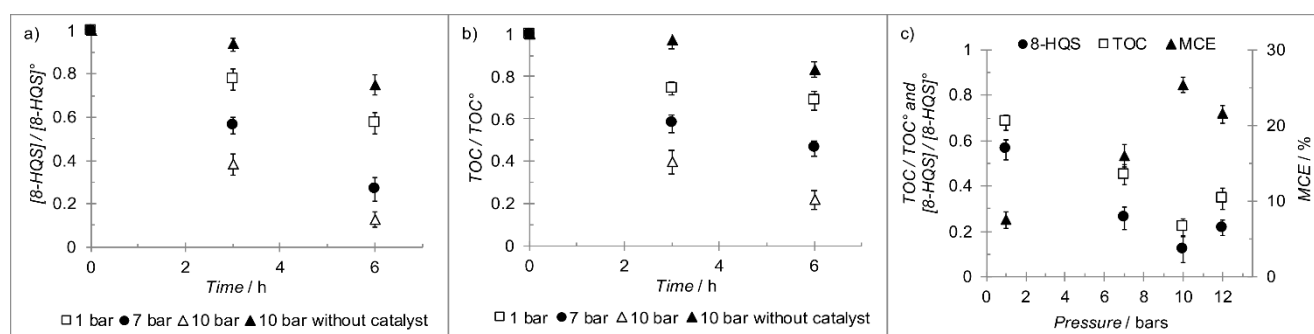
in the catalyst structure by hydrogen peroxide with the formation of hydroxyl radicals (reaction (8)), which can attack the organic leading to its mineralization, while Cu<sup>3+</sup> is further reduced to Cu<sup>2+</sup> by another molecule of H<sub>2</sub>O<sub>2</sub> [30]. In particular, according to the literature, the formation of HO• could be enhanced, for layered hydroxides, by defect sites generated from the surface oxygen vacancies that can adsorb hydrogen peroxide facilitating its reaction with Cu<sup>2+</sup> [30].



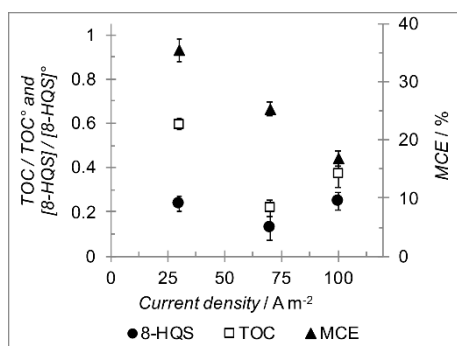
#### Effect of current density

The current density, *j*, determines the production of oxidizing agents in the process. An increase of *j* is expected to accelerate the electrode reactions, thus generating more anode M(•OH) as well as more hydrogen peroxide at the cathode that, in turn, may produce larger amounts of •OH from reaction (8). However, for excessively high current density, according to the literature, the cathodic generation of H<sub>2</sub>O<sub>2</sub> can decrease as well as the abatement of organics by EF [5]. A similar behaviour is observed in Fig. 4, which reports the final values of the concentration of 8-HQS, TOC and MCE for a set of PrEFL-LDH electrolyses performed at 10 bars and various current densities (30, 70 and 100 A m<sup>-2</sup>) for 6 h. Indeed, the increase of current density from 30 to 70 A m<sup>-2</sup> resulted in a decrease of both the final concentration of 8-HQS ([8-HQS]/[8-HQS]<sup>0</sup> from 24 to 12%) and TOC ([TOC]/[TOC]<sup>0</sup> from 60 to 20%). However, MCE decreased from 35 to 25% due to a higher impact of cathodic parasitic processes such as hydrogen evolution (reaction (12)). For a further increase of *j* to 100 A m<sup>-2</sup> higher final values of the concentrations of 8-HQS and TOC were observed (fig. 4) coupled with a decrease of MCE to 17%. Indeed, at high current densities, the formation rate of H<sub>2</sub>O<sub>2</sub> is limited by mass transfer phenomena and part of the excess of charge passed is likely to be involved in the cathodic reduction of H<sub>2</sub>O<sub>2</sub> to water (reaction 13) and generation of hydrogen bubbles via reaction (12), that could limit the mass transfer of oxygen to the cathode surface [5,9].





**Figure 3.** Effect of time on the concentration of 8-HQS (fig. 3a) and TOC (fig. 3b) during amperostatic electrolyses ( $70 \text{ A m}^{-2}$ ) of an aqueous solution of  $0.4 \text{ mM}$  8-HQS and  $0.05 \text{ M Na}_2\text{SO}_4$  in the absence or in the presence of  $1 \text{ g L}^{-1}$  LDH with carbon felt cathode and  $\text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$  anode, at various air pressures (1, 7 and 10 bars). Initial  $\text{pH} = 3$ ; stirring rate =  $500 \text{ rpm}$ . Fig. 3c reports the effect of the air pressure on the final concentrations of 8-HQS and TOC achieved after 6 h as well as the final MCE.



**Figure 4.** Effect of current density on the concentration of 8-HQS (●), on the TOC (□) and on the MCE (▲) achieved after 6 h by amperostatic electrolysis ( $30, 70$  and  $100 \text{ A m}^{-2}$ ) of an aqueous solution of  $0.4 \text{ mM}$  8-HQS and  $0.05 \text{ M Na}_2\text{SO}_4$  in the presence of  $1 \text{ g L}^{-1}$  LDH with carbon felt cathode and  $\text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$  anode.  $P_{\text{Air}} = 10 \text{ bar}$ . Initial  $\text{pH} = 3$ . Stirring rate =  $500 \text{ rpm}$ .

Furthermore, at the anode higher current densities can accelerate the anodic oxidation of  $\text{H}_2\text{O}_2$  to oxygen (reaction (14)).



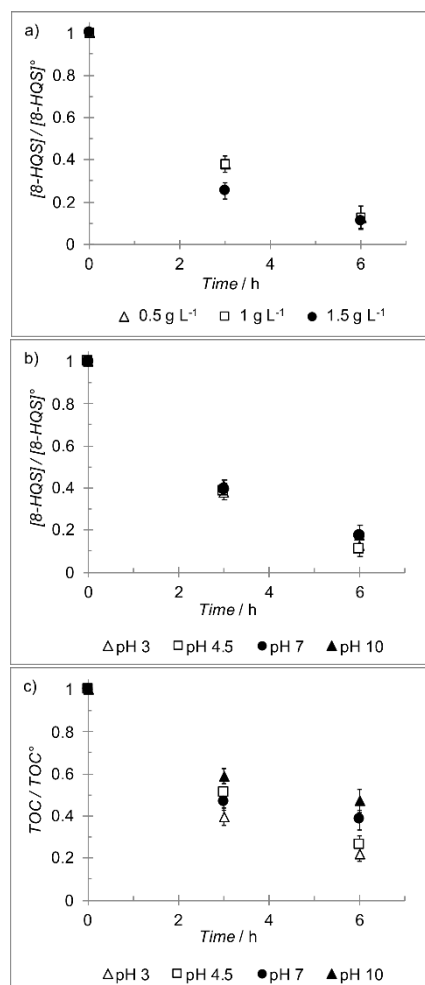
#### Effect of catalyst dosage

For some iron based LDH catalysts employed for Fenton reaction, a significant effect of the catalyst dosage was observed, which was attributed to the increased amount of iron in solution that enhanced the removal kinetics [24]. In order to evaluate the effect of catalyst dosage in the case of  $\text{Ni-Cu-Al-CO}_3\text{-LHD}$ , some electrolyses were performed at  $\text{pH} = 3$  with an amount of catalyst of  $0.5, 1$  and  $1.5 \text{ g L}^{-1}$ . As shown in fig. 5a, no significant effect of the catalyst dosage on the removal of 8-HQS was observed. Similarly, catalyst dosage had a very small effect on the removal of TOC (removal of TOC after 6 hours between 83 and 88% for the three dosages used), thus also showing that a relatively small amount of catalyst can be used for the removal of 8-HQS. The capability to work with various  $\text{pH}$  is a key factor to evaluate a catalyst for the degradation of organics since wastewater can

present a large range of  $\text{pH}$  and the correction of  $\text{pH}$  by addition of acids or bases is rather expensive. As an example, the removal of nitrobenzene by Fenton-like process with Co-Fe layered double hydroxides was strongly reduced by a small increase of  $\text{pH}$  from 2 to 4 [24], while for the treatment of an aqueous solution of anthraquinones by Fenton-like process with a Co-Cu LDH, the highest removals were achieved at a  $\text{pH}$  of 6.8 [29]. Hence, some electrolyses were performed at different values of  $\text{pH}$  (3, 4.5, 7 and 10) at 10 bars. As shown in fig. 5b a very high removal of 8-HQS was achieved at all investigated  $\text{pH}$ . As an example, after 6 h, the removal of 8-HQS was about 82% at  $\text{pH} 4.5$  and 87% at  $\text{pH} 10$ . Fig. 5c reports the trend of  $\text{TOC}/\text{TOC}^\circ$  with the time at the different  $\text{pH}$ . In all cases a high removal of TOC is achieved, even if the process is faster at lower  $\text{pH}$ , thus showing that the adopted catalyst can be effectively used for the treatment of organics in water both in acidic, neutral and basic conditions.

#### Effect of the nature of the catalyst

According to above mentioned results, the adopted catalyst seems particularly promising for the treatment of water contaminated by organic matter. Hence, its performances, in terms of removal of both the concentration of 8-HQS and TOC, were compared with that of other widely investigated catalysts: homogeneous  $\text{FeSO}_4$  and two natural heterogeneous catalysts, i.e. pyrite ( $\text{FeS}_2$ ), which contains only iron, and chalcopyrite ( $\text{CuFeS}_2$ ), that contains both iron and copper. Experiments were performed at 10 bars and  $\text{pH} 7$ . As shown in fig. 6a, all adopted catalysts allowed to reduce significantly the concentration of 8-HQS. In particular, the lowest concentrations were achieved with pyrite (45 and 31% of the initial value after 3 and 6 h) and LDH (39 and 17% of the initial value after 3 and 6 h). The reduction of TOC was lower. In particular, for  $\text{FeSO}_4$ , pyrite and chalcopyrite a similar trend of TOC vs. time was observed with a  $\text{TOC}/\text{TOC}^\circ$  ratio of 60-66% after 3 h and of 52-54% after 6 h (fig. 6b). A more relevant reduction of TOC was achieved for  $\text{PrEFL-LDH}$  ( $\text{TOC}/\text{TOC}^\circ = 47$  and 38% after 3 and 6 h, respectively), confirming the good performances of the process. The comparison between  $\text{PrEFL-LDH}$  and EF with homogeneous  $\text{FeSO}_4$  was performed also under other operative conditions and, in particular, at  $\text{pH} 3$  where homogenous EF gives the best results. Fig. 6c reports the final values of the ratio  $\text{TOC}/\text{TOC}^\circ$  after 6 h of electrolyses changing both pressure and  $\text{pH}$ . At  $P_{\text{Air}} = 1 \text{ bar}$  and

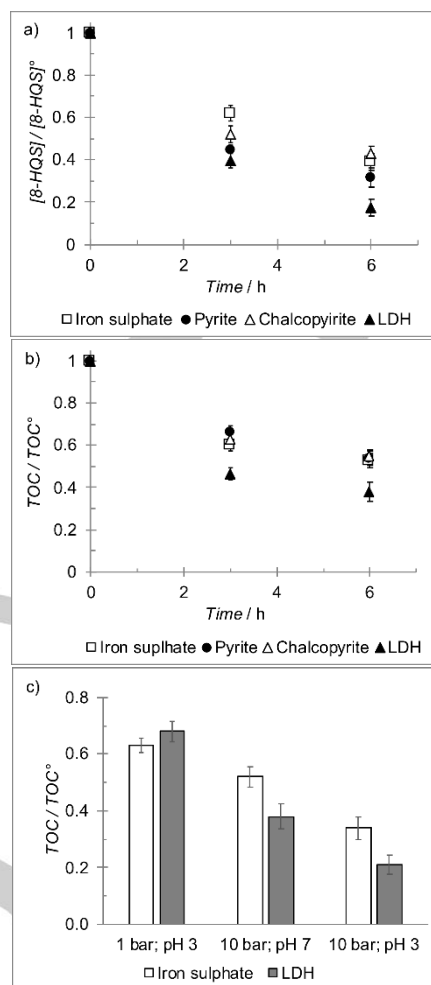


**Figure 5.** Effect of catalyst dosage (fig. 5a) on the concentration of 8-HQS and of initial pH on the concentration of 8-HQS (fig. 5b) and TOC (fig. 5c) during amperostatic electrolyses (70 A m<sup>-2</sup>) of an aqueous solution of 0.4 mM 8-HQS and 0.05 M Na<sub>2</sub>SO<sub>4</sub> with carbon felt cathode and Ti/IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> anode.  $P_{\text{Air}} = 10$  bar. For the effect of the catalyst dosage, initial pH = 3. For the effect of pH, catalyst dosage 1 g L<sup>-1</sup>. Stirring rate = 500 rpm.

pH 3, the elective operating conditions for FeSO<sub>4</sub>, rather high values of  $\text{TOC} / \text{TOC}^0$  were still present at the end of the electrolyses with both catalysts, thus showing that these conditions are not very effective for TOC removal.

Slightly better results were achieved for the homogeneous catalyst ( $\text{TOC} / \text{TOC}^0 = 60\%$  and  $67\%$  for FeSO<sub>4</sub> and LDH, respectively); this is probably due to the fact that the heterogeneous catalyst performances are more limited from the low concentrations of hydrogen peroxide present at 1 bar, since its contact with H<sub>2</sub>O<sub>2</sub> is limited to the catalyst's surface.

Indeed, at  $P_{\text{Air}} = 10$  bars, where a high concentration of hydrogen peroxide is expected, the best performances were achieved at both pH 3 and pH 7 with PrEFL-LDH.



**Figure 6.** Effect of the nature of the catalyst on the concentration of 8-HQS (fig. 6a) and TOC (fig. 6b) during amperostatic electrolyses (70 A m<sup>-2</sup>) of an aqueous solution of 0.4 mM 8-HQS and 0.05 M Na<sub>2</sub>SO<sub>4</sub> with carbon felt cathode and Ti/IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> anode.  $P_{\text{Air}} = 10$  bars. Initial pH = 7; catalyst dosage 1 g L<sup>-1</sup> for heterogeneous catalysts and 0.5 mM for FeSO<sub>4</sub>. Stirring rate = 500 rpm. Fig. 6c reports a comparison between the final TOC achieved for LDH and FeSO<sub>4</sub> after 6 hours at the same operative conditions reported above but changing air pressure (1 and 10 bars) and pH (3 and 7).

### Effect of the nature of the anode and reusage

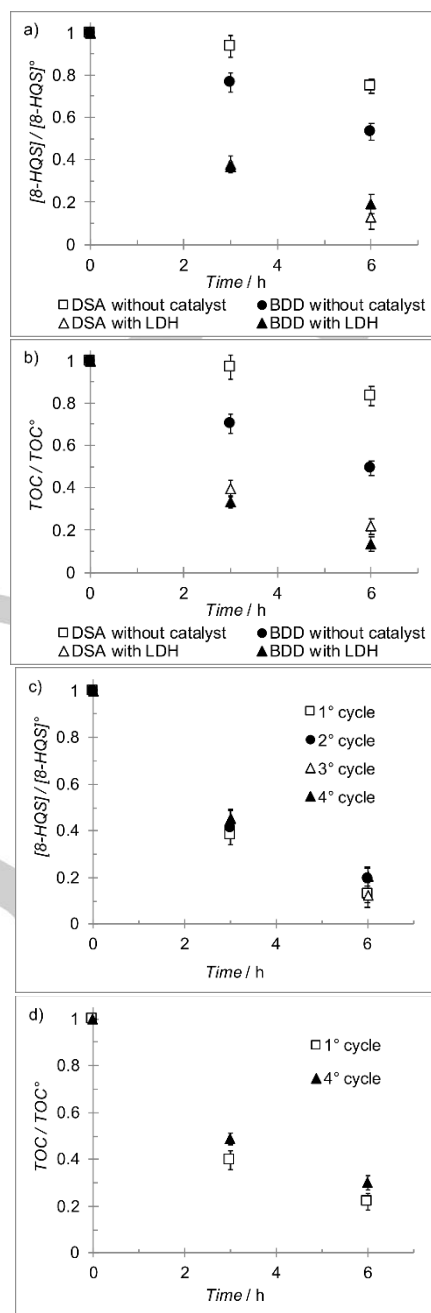
In undivided cells, the oxidation of organics can be performed by both hydroxyl radicals generated by Fenton-like reactions and hydroxyl radicals generated at the anode. Hence, the effect of anode nature was evaluated by using Ti/IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>, which is a not expensive material and it is characterized by low removal of organics and a Boron Doped Diamond (BDD) anode, which, conversely, is rather expensive but very effective for the mineralization of a large number of organics [1,4,45]. As shown in fig. 7a and 7b, in the absence of the heterogeneous catalyst, the replacement of the Ir-based anode with BDD resulted in a stronger decrease in the organic concentration; indeed, after 6 h, the ratio  $[8\text{-HQS}] / [8\text{-HQS}]^0$  decreased from 0.75 to 0.53 changing the Ir-based anode with BDD. Similarly, the utilization of BDD allowed to enhance the removal of TOC ( $\text{TOC} / \text{TOC}^0$  about 0.83 and 0.5 with Ir and BDD anodes, respectively), thus confirming the more effectivity of BDD with respect to Ir-based anodes for the mineralization of organics. It is interesting to compare the performances of the processes performed with i) BDD anode

without heterogeneous catalyst, named BDD anodic oxidation (AO-BDD), where the removal of 8-HQS is mainly achieved by hydroxyl radicals generated at the anode, and *ii*) Ir-based anode and LDH catalyst, (PrEFL-LDH), where the removal of organic is mainly achieved by hydroxyl radicals generated in the bulk by reaction between hydrogen peroxide and LDH. It is worth to mention that higher removals of both 8-HQS and TOC were achieved with LDH and Ir-based anode, thus showing that PrEFL-LDH is more effective than one of the most potent routes for oxidation of organics such as AO-BDD. After 6 h, the ratio  $[8\text{-HQS}]/[8\text{-HQS}]^0$ , for AO-BDD and PrEFL-LDH, were 0.53 and 0.19, respectively. Similarly, the ratio  $\text{TOC}/\text{TOC}^0$  for AO-BDD and PrEFL-LDH were 0.5 and 0.22, respectively. Eventually, some electrolyses were carried out by using both a BDD anode and LDH, thus allowing to achieve the highest removal of TOC (after 6 h  $\text{TOC}/\text{TOC}^0 = 0.13$ ). A slightly higher removal of 8-HQS was obtained after 6 h with DSA with respect to BDD; this could be due to the fact that BDD is more effective than DSA for the removal of the intermediates (as shown by the higher removal of TOC), and then it uses the same amount of charge passed for both the partial oxidation of 8-HQS and of the intermediates.

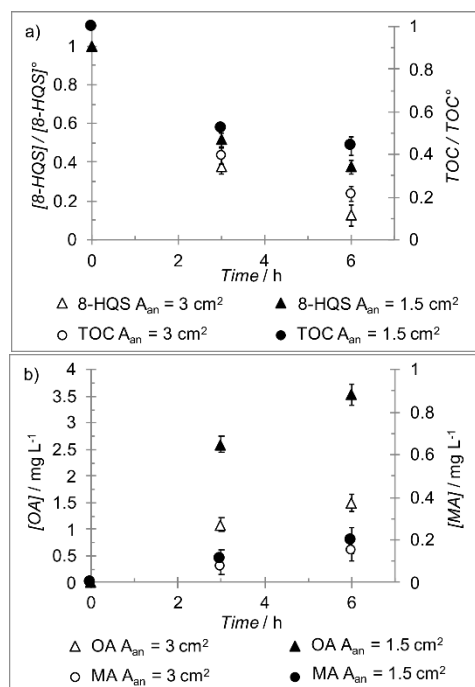
The reuse issue is another important aspect in order to evaluate heterogeneous catalysts for EF-like processes. Here the reproducibility was tested by reusing various times a given sample of LDH catalyst with an initial dosage of  $1\text{ g L}^{-1}$  to consecutively degrade 50 mL of 0.4 mM 8-HQS with 0.05 M  $\text{Na}_2\text{SO}_4$  at pH 3 and 10 bars by PrEFL-LDH at  $70\text{ A m}^{-2}$  for 6 h (fig. 7c and 7d). After each experimental test, about 73 % of the catalysts was recovered by filtration. The first 3 tests were carried out reusing only the collected catalyst while the last experiment was carried out restoring the initial amount of the catalyst. The percentage of the concentration of 8-HQS removed was very similar for all adopted 4 cycles. The removal of TOC achieved at the end of the 4<sup>th</sup> cycle was 70%, only slightly lower than 78% TOC decay obtained in the 1<sup>st</sup> cycle. This means that LDH was quite stable, being successfully reused for consecutive heterogeneous treatments of the 8-HQS solution, even if a significant percentage of the catalyst was lost between each test.

#### Analysis of carboxylic acids production and effect of the surface of the anode

The mineralization of aromatic and polyaromatic compounds usually leads to the generation of short-chain linear carboxylic acids as final products [1,4,7,11]. This was corroborated from HPLC analysis of the 0.4 mM 8-HQS solution treated by PrEFL-LDH with  $1\text{ g L}^{-1}$  catalyst at  $j = 70\text{ A m}^{-2}$ , Ir-based anode and pH 3. Indeed, oxalic and maleic acids were detected, even if with low concentrations which increased with the time (fig. 8). In the literature, it has been shown several times that electro-Fenton treatment of cyclic and aromatic compounds gives rise to the formation of various carboxylic acids that are rather resistant to EF and accumulates in the solution, thus reducing the final removal of TOC [2,5].



**Figure 7.** Effect of anode nature and reuse of the catalyst on the concentration of 8-HQS (fig. 7a and 7c) and TOC (fig. 7b and 7d) during amperostatic electrolyses ( $70\text{ A m}^{-2}$ ) of an aqueous solution of 0.4 mM 8-HQS and 0.05 M  $\text{Na}_2\text{SO}_4$  with carbon felt cathode and  $\text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$  (DSA) or BDD anode.  $P_{\text{Air}} = 10\text{ bar}$ . Initial pH = 3; catalyst dosage  $1\text{ g L}^{-1}$ . Stirring rate = 500 rpm. Experiments for reuse were carried out using DSA anode.



**Figure 8.** Effect of anode surface on the concentration of 8-HQS (triangle symbols) and TOC (circle symbols) (fig. 8a) and on the concentrations of oxalic acid (triangle symbols) and maleic acid (circle symbols) (fig. 8b) during amperostatic electrolyses ( $70 \text{ A m}^{-2}$ ) of an aqueous solution of  $0.4 \text{ mM}$  8-HQS and  $0.05 \text{ M}$   $\text{Na}_2\text{SO}_4$  with carbon felt cathode and  $\text{Ti/IrO}_2\text{-Ta}_2\text{O}_5$  anode at 10 bars. Initial pH = 3. Catalyst dosage  $1 \text{ g L}^{-1}$ . Stirring rate =  $500 \text{ rpm}$ .

However, it has been previously shown that the utilization of pressurized air enhances the removal of carboxylic acids and of TOC [8-10]. In our case, where both pressurized air and the innovative LDH catalysts were used a quite low concentrations of carboxylic acids were recorded, thus allowing good final removals of TOC.

It has been previously discussed that in PrEFL-LDH with Ir-based anode, the degradation of 8-HQS is achieved mainly by  $\text{HO}\cdot$  produced by means of LDH catalyst. The utilization of Ir-based anode in an undivided cell is expected to have two opposite effects: from one hand, it oxidizes  $\text{H}_2\text{O}_2$  (reaction reported in reaction (14)) and, from the other hand, it contributes to the mineralization of 8-HQS and its oxidation products by hydroxyl radicals generated by anodic oxidation of water (reaction (6)). To evaluate which of these two effects predominates, some electrolyses were performed by reducing the  $\text{Ti/IrO}_2\text{-Ta}_2\text{O}_5$  anode surface from  $3$  to  $1.5 \text{ cm}^2$ . Indeed, according to the literature, the reduction of the anode surface leads to an enhancement of the concentration of  $\text{H}_2\text{O}_2$  in the bulk [43], but also to a lower production of  $\text{M}(\cdot\text{OH})$  at the anode. As shown in figure 8, the experiments performed with the reduced surface gave lower abatement of both 8-HQS and TOC and a higher accumulation of both oxalic and maleic acids, thus showing that also using relatively cheap  $\text{Ti/IrO}_2\text{-Ta}_2\text{O}_5$  materials, the anode on overall has a positive effect on the removal of 8-HQS and other organics generated during its oxidation.

## Conclusion

The pressurized electro-Fenton-like process with Ni-Cu-Al- $\text{CO}_3$ -LDH catalyst (PrEFL-LDH) was investigated in the frame of the removal and mineralization of 8-hydroxyquinoline-5-sulfonic acid in water. Very high removals of both 8-HQS and TOC (87 and 79%, respectively) were obtained using PrEFL-LDH at  $P_{\text{Air}} = 10$  bar, pH = 3 using a  $\text{Ti/IrO}_2\text{-Ta}_2\text{O}_5$  anode. Moreover, it was found that:

- PrEFL-LDH presented good performances in a large range of pH (3-10);
- PrEFL-LDH gave better removals of 8-HQS and TOC with respect to that achieved by both i) EF catalysed by homogeneous ( $\text{FeSO}_4$ ) or natural heterogeneous catalysts (pyrite and chalcocopyrite) and ii) anodic oxidation at Boron Doped Diamond anode;
- Ni-Cu-Al-LDH retained the catalytic activity after four cycles;
- the removal of 8-HQS and TOC are optimized for a pressure of 10 bars and a current density of  $70 \text{ A m}^{-2}$ , while a not significant effect was obtained changing the catalyst dosage from  $0.5$  to  $1.5 \text{ g L}^{-1}$ ;
- the decrease of the anode surface resulted in lower abatements of 8-HQS and TOC and in a larger accumulation of oxalic and maleic acids.

In conclusion, this work has shown that PrEFL-LDH process can be effectively used for the removal of organics. The performances of PrEFL-LDH should be in future evaluated using a large series of model organic pollutants and real wastewater to fully evaluate its potentialities.

## Experimental Section

### Preparation of Ni-Cu-Al layered double hydroxide

The catalyst preparation was performed using a well-established procedure [46]. A mixture of a solution obtained by dissolving NaOH ( $0.1 \text{ M}$ ) and  $\text{Na}_2\text{CO}_3$  ( $0.1 \text{ M}$ ) in distilled water was added dropwise (at room temperature and pH =  $10 \pm 0.2$ ) to  $50 \text{ mL}$  of a solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$  ( $0.02 \text{ M}$ ),  $\text{CuSO}_4$  ( $0.02 \text{ M}$ ) and  $\text{AlCl}_3 \cdot 6 \text{ H}_2\text{O}$  ( $0.02 \text{ M}$ ) and stirred vigorously for 3 h. To facilitate the crystallization of the formed precipitate, the contents were kept in an airtight bottle at  $60^\circ\text{C}$  for 18 h. Subsequently, the precipitate was washed several times with distilled water using a centrifuge GYROZEN 416 at a speed of  $2600 \text{ rpm}$  for 3 min in order to remove the chloride and sodium ions present. Once the product has been purified, it was dried in an isothermal oven PROLABO at  $60^\circ\text{C}$  for 20 h, and then ground into homogeneous powder. The resulting powder was stored in a covered glass container at room temperature.

### Chemicals and analytical methods

8-hydroxyquinoline-5-sulfonic acid ( $\text{C}_9\text{H}_7\text{NO}_4\text{S}$ ) was supplied by Sigma-Aldrich ( $> 99\%$  purity). All of the reactants, in this study, were of analytical grade and used without further purification. Two types of catalysts were used: synthetic and natural. As a synthetic catalyst  $0.5 \text{ mM}$  of ferrous sulphate heptahydrate ( $\text{FeSO}_4 \cdot 7 \text{ H}_2\text{O}$ , in analytical grade from Fluka) and different amount of prepared LDH catalyst were used. As natural catalysts, chalcocopyrite ( $\text{CuFeS}_2$ ) and pyrite ( $\text{FeS}_2$ ), extracted from Jendouba (Tunisia), were also used in this work. Analytical grade anhydrous sodium sulfate,  $\text{Na}_2\text{SO}_4$ , ( $0.05 \text{ M}$ ), used as supporting electrolyte, was purchased from Sigma-Aldrich. Sulfuric acid and sodium hydroxide purchased from Sigma-Aldrich were added in solution to adjust the pH to the target value, measured with a HANA pH-meter.



The concentration of 8-HQS was determined from the decay of the absorbance at  $\lambda = 356$  nm using Agilent Cary 60 UV spectrophotometer. The mineralization of the pollutant during the electrochemical treatment was followed from the abatement of the total organic carbon (TOC), analyzed by a TOC analyser Shimadzu-L-ESN.

The percentage of mineralization current efficiency (MCE) in each treatment at a given current  $I$  (in A) was estimated from eq. (15):

$$\text{MCE} = 100 \, n F V \Delta \text{TOC} / (a m I t) \quad (15)$$

Where  $V$  is the solution volume (in L),  $\Delta \text{TOC}$  is the TOC removed (in mg L<sup>-1</sup>) at time  $t$  (in h),  $a$  is a unit homogenization factor =  $4.32 \cdot 10^7$  as a ( $3600 \text{ s h}^{-1} \times 12000 \text{ mg C mol}^{-1}$ ) and  $m = 9$  is the number of carbon atoms of 8-HQS. The number of consumed electrons was 46, considering the total mineralization of 8-HQS according to the following equation:



The carboxylic acids generated during the treatment of the aqueous solutions of 8-HQS were identified and analyzed by Agilent HP 1100 HPLC equipped by Rezex ROA-Organic Acid H<sup>+</sup> (8%) column at 55°C and coupled to a UV detector fixed at a wavelength  $\lambda = 210$  nm and a mobile phase of 0.005 N H<sub>2</sub>SO<sub>4</sub> eluted at 0.6 mL min<sup>-1</sup>. A pure standard of oxalic acid (Sigma-Aldrich) and maleic acid (Sigma-Aldrich) were adopted to calibrate the instrument for its quantitative determination.

The crystal structure was analyzed by X-ray analysis using a RIGAKU diffractometer (model: D-MAX 25600 HK). Diffraction spectra were acquired in the  $2\theta$  range from 10 to 60°. The morphology was examined by a QUANTA 200 FEI field emission gun (FEG) Environmental Scanning Electron Microscope (ESEM), supplied with X-ray energy-dispersive spectrometer (EDS) to characterize the chemical composition.

### Electrolytic system

All the electrolytic trials were performed in a high pressure AISI 316 stainless steel cell with a cylindrical geometry (in detail described in [9]) containing 50 mL of the 8-HQS solution maintained at room temperature with an initial concentration of the selected organic pollutant of 0.4 mM, under vigorous stirring. The stirring of the solution was made with a magnetic stirrer (nominal stirring speed at 500 rpm). The cathode was a carbon-felt piece (2 cm<sup>2</sup>) whereas the anode was Ti/IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> (3 cm<sup>2</sup>, commercial DSA®, supplied by De Nora SpA) or Boron Doped Diamond (3 cm<sup>2</sup>, BDD, supplied by Condias) thin-film electrode in a parallel position to the cathode. Before each experiment, electrodes were cleaned with an ultrasound bath for 10 min in bi-distillate water and then rinsed with it. The electrodes gap was 1 cm. Air (purity 99.999%, supplied by Rivoira) was used to pressurize the reactor, which ensures H<sub>2</sub>O<sub>2</sub> generation at the cathode according to reaction 4. In order to regulate the operating pressure, the system was constituted with a pressure gauge and a pressure relief valve. Electrolyses were performed in presence of several amounts of LDH catalyst ranging from 0.5 to 1.5 g L<sup>-1</sup> in 0.05 M Na<sub>2</sub>SO<sub>4</sub>. The initial pH of the solution was assessed as 4.5 when not stated. A constant current intensity was applied to the electrolytic system under amperostatic mode supplied by Amel 2053 potentiostat/ galvanostat. Each electrolysis was repeated at least twice, with differences in terms of the 8-HQS concentration and values of TOC lower than 5% in most of the cases.

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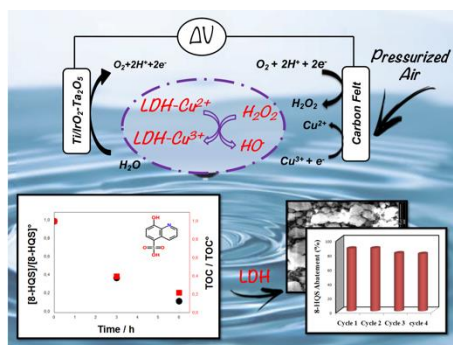
**Keywords:** EAOP • Heterogeneous catalysis • Ni-Cu-Al layered double hydroxide • Nitrogen heterocycles • Pressurized-electro-Fenton-like-LDH

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## Entry for the Table of Contents



The pressurized electro-Fenton-like process with Ni-Cu-Al- $\text{CO}_3$ -LDH heterogeneous catalyst assured high mineralization of 8-hydroxyquinoline-5-sulfonic acid (8-HQS) contaminated aqueous solution allowing to reach a quite high removal of both 8-HQS concentration and total organic carbon up to about 87 and 79%, respectively, after 6 hours. Moreover, the utilization of this catalyst retained its catalytic activity after four cycles.