



Valorisation of the residual aqueous phase from hydrothermally liquefied black liquor by persulphate-based advanced oxidation

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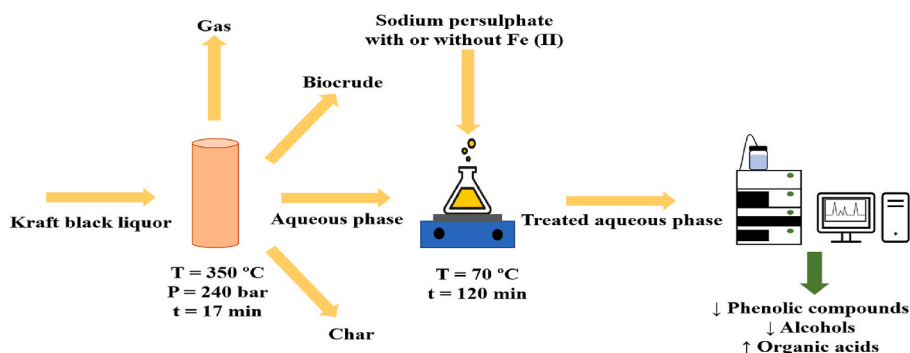
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HIGHLIGHTS

- Persulphate-based advanced oxidation reduced the toxicity of the stream.
- ≤ 50 mM $S_2O_8^{2-}$: oxidation of phenolics and alcohols to intermediates.
- > 50 mM $S_2O_8^{2-}$: oxidation of intermediates to acetic acid.
- ≤ 9 mM Fe^{2+} : enhancement of the degradation of phenolics and alcohols.
- > 9 mM Fe^{2+} : reduction of oxidation yield due to sulphate radicals sequestration.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrothermal liquefaction of Kraft black liquor is a promising method for the production of valuable organic chemicals. However, the separation of the biochar and biocrude leaves a residual aqueous phase in large volumes, which needs to be properly managed to make the process profitable. In this work, the persulphate-based advanced oxidation was assessed, for the first time ever, as a pretreatment of this aqueous phase to reduce its content of phenolic compounds and alcohols, which hinder further valorisation strategies. Results revealed that the phenolic compounds and the alcohols were oxidised in presence of low persulphate anion concentrations (< 50 mM), mainly to quinone-like compounds and organic acids. At higher oxidant concentrations, these intermediates were subsequently oxidised to valuable acetic acid. When Fe (II) was added as the catalyst, low concentrations (< 9 mM) enhanced the degradation of both phenolic compounds and alcohols due to the increase of the sulphate radicals, consequently reducing persulphate requirements for their removal. Nevertheless, higher Fe (II) doses produced the sequestration of sulphate radicals, thus decreasing the oxidation performance and generating undesired parallel reactions.

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1. Introduction

Owing to the continuous population growth and industrialisation, the need to seek new renewable sources of energy and/or chemicals is becoming evident. In this regard, the different waste biomasses produced as byproducts during many industrial processes show a huge potential as feedstock for a wide range of chemical and energy products (Arpit et al., 2022).

Nowadays, the management of these waste biomasses is usually focused on direct energy production by incineration, pyrolysis or anaerobic digestion, among other methods, even when their water content is high. However, this approach goes against the circular economy principles and the waste hierarchy as it is first recommended to reuse these streams or obtain chemicals from them and, as a last resort, to produce energy and disposal (Burguete et al., 2016; Egüez, 2021; Rekos et al., 2022; Yana et al., 2022).

One of these waste biomasses is Kraft black liquor. This aqueous stream comes from the Kraft pulp-making process and is generated during the cooking stage, where a solution of NaOH and Na₂S is mixed at high temperature and pressure with the wood chips to extract the cellulose. The resulting alkaline stream, or black liquor, carries away the rest of the compounds of the wood, mainly lignin and hemicelluloses, as well as the inorganic salts added during the cooking. Due to its high polluting capacity because of the presence of toxic compounds, alkaline pH and high organic content, black liquor must be properly managed before its discharge. So, in order to make the Kraft process more cost-effective, this stream is usually concentrated by evaporation and subsequently burned within the same pulp mill to obtain energy and recover the spent chemicals simultaneously (Morya et al., 2022; Pola et al., 2022). However, owing to its heterogeneous composition, black liquor contains several compounds with a high added value but low calorific values that are thus undervalued during their combustion (Kumar and Alén, 2015). This fact, together with some operational problems related to the conventional recovery process, are leading to the development of more profitable and greener alternatives, mainly focused on obtaining chemical products of industrial interest (Bajpai, 2017; Pola et al., 2022).

Among the available techniques for valorising wet biomasses, as is the case of the Kraft black liquor, different hydrothermal treatments are gaining interest because they require neither pre-drying nor the addition of reagents and are more environmentally friendly than incineration (Burguete et al., 2016; López et al., 2015; Vallejos, 2017). In this regard, hydrothermal liquefaction is a very promising hydrothermal process because it allows the production of a biocrude (liquid fuel) that serves as a substitute feedstock for crude oil. This treatment consists of carrying out reactions at temperatures above 250 °C, but below the critical point of water (374 °C), and in the presence of an inert atmosphere at high pressures to maintain the reaction medium in a liquid state (Elliott et al., 2015). This technique has been successfully conducted using different biomass feedstocks, such as algae, food waste, sludge, manure and lignocellulosic residues (Elliott et al., 2015; Watson et al., 2020). Nevertheless, when it comes to Kraft black liquor, hydrothermal liquefaction has been studied to a much lesser extent and only at a laboratory scale in a batch way (Lappalainen et al., 2020).

During the processing of either Kraft black liquor or other wet waste biomasses by hydrothermal liquefaction, not only an organic liquid fraction (biocrude) is produced, but also a residual aqueous phase in a much higher proportion (Fan et al., 2018; Leng et al., 2021). The proper management of this latter stream, with a high organic load and, frequently, containing toxic compounds, largely determines the profitability of the whole process. Taking into account that this aqueous phase also contains valuable compounds that can be recovered, different valorisation strategies are being proposed to use it as a source of nutrients, energy, fuels or other chemicals, and even, as a fermentation medium for the bioproduction of different metabolites (Leng et al., 2021; Watson et al., 2020). Nevertheless, the presence of phenolic compounds in this stream, especially when it comes from black liquor or other

lignocellulosic feedstocks, severely limits many of these options (Pipitone et al., 2020; Watson et al., 2020; Zoppi et al., 2021).

In this sense, persulphate-based advanced oxidation processes have demonstrated an interesting capacity to selectively oxidise several organic pollutants, including phenolic compounds (Lee et al., 2020). Although persulphate anions react slower than other oxidants, when they are chemically or thermally activated, sulphate radicals are formed, which are stronger oxidants and very effective even with recalcitrant compounds (Romero et al., 2010). For example, applied to aromatic compounds, with temperatures above 30 °C and the presence of Fe (II) as the catalyst, it has been possible to degrade compounds such as diuron or phenol in aqueous streams (Ma et al., 2017; Romero et al., 2010). Thus, it is interesting to point out that, even though persulphate-based advanced oxidation has not yet been used to treat the aqueous phase resulting from the hydrothermal liquefaction of Kraft black liquor, it does seem to be a potentially attractive method as pretreatment to improve the subsequent management of this stream.

Therefore, the aim of this work is to assess, for the first time ever, the potential of persulphate-based advanced oxidation, promoted or not by iron salts, to produce a selective oxidation of the phenolic compounds present in the aqueous phase resulting from the hydrothermal liquefaction of Kraft black liquor in order to facilitate its further processing.

2. Materials and methods

2.1. Materials

The aqueous phase obtained after the hydrothermal liquefaction of Kraft black liquor from The Navigator Company (Portugal) was used in this work. The hydrothermal treatment was carried out in a continuous tubular reactor (see the setup in Fig. 1) at 350 °C, 240 bar and 17 min of residence time under an inert atmosphere. These operational conditions were selected in terms of enhancing biofuel yield and chemical composition after carrying out several continuous hydrothermal liquefaction experiments at 240 bar and different temperatures (325–375 °C) and residence times (11–20 min).

After withdrawing the liquid phase from the reactor, the aqueous fraction was separated from the biocrude by liquid-liquid extraction (Forchheim et al., 2012). To do this, the liquid fraction was firstly acidified to pH = 4 with HCl. Subsequently, the biocrude was recovered using ethyl acetate as the solvent (0.4 mL per 1 mL of acidified sample), whereas the resulting aqueous phase was stored at 4 °C until its use. The main chemical properties of this latter stream are shown in Table 1.

In addition to these substances, two other phenolic compounds have been detected in relevant concentrations; however, they did not correspond with any of the compounds that had been calibrated or tested. Therefore, depending on the order of elution, they have been named “Phenolic 1” and “Phenolic 2”, with the retention time of the former being similar to catechol and the latter, to phenol. Apart from organic compounds, the concentration of inorganic carbon was negligible (<5 mg/L).

2.2. Persulphate-based advanced oxidation process

Persulphate-based advanced oxidation relies on the formation of sulphate radicals (SO₄⁻), which can be produced through two different reaction mechanisms (Ec. 1 and 2):



Chemical activation of persulphate is commonly carried out using transition metal ions, particularly iron salts due to their low cost, easy availability and high catalytic efficiency. This leads to the formation of sulphate radicals and produces faster reactions, increasing the solubility

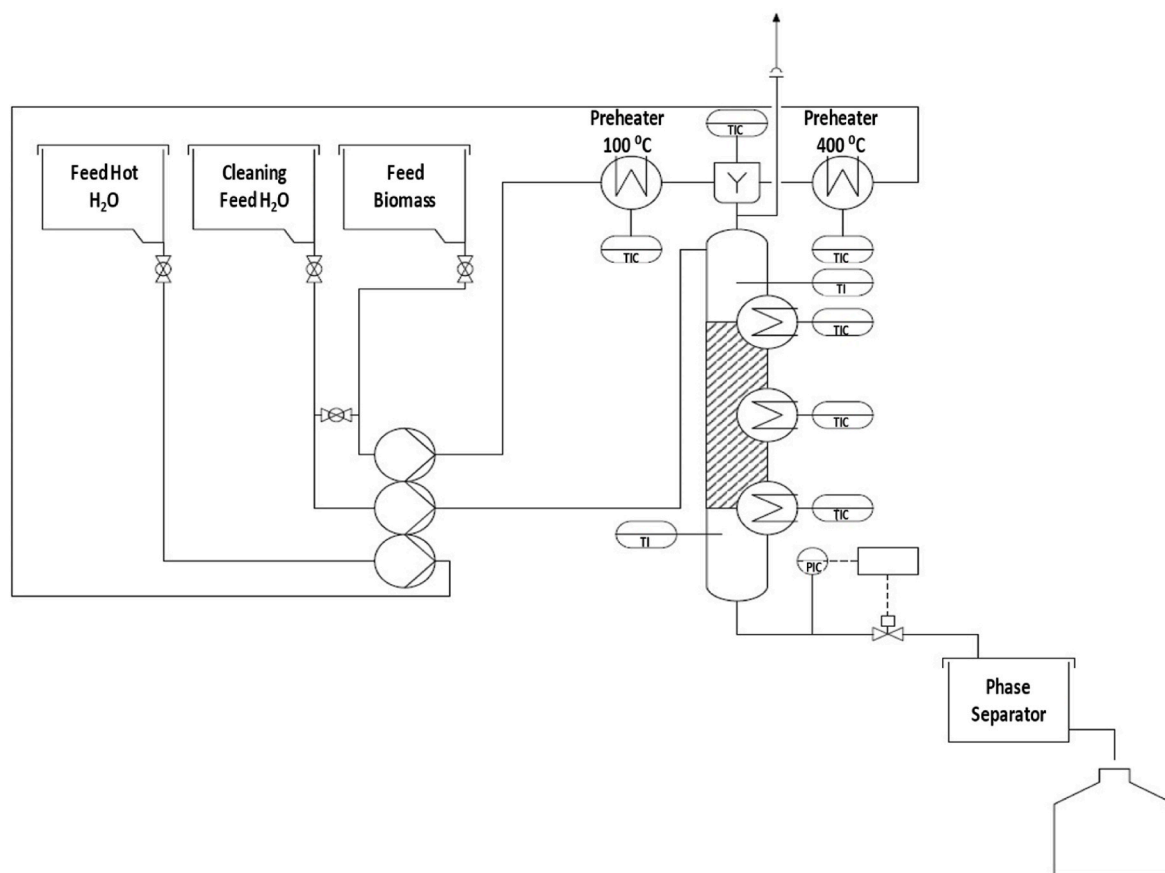


Fig. 1. Scheme of the experimental setup used for the continuous hydrothermal liquefaction of black liquor.

Table 1
Chemical composition of the aqueous phase.

Parameters	Mean values
Total Organic Carbon (g/L)	29.7 ± 0.2
Catechol (mg/L)	63 ± 5
Formic acid (g/L)	3.8 ± 0.5
Acetic acid (g/L)	5.0 ± 0.5
Glycolic acid (g/L)	1.3 ± 0.5
Lactic acid (g/L)	2.2 ± 0.5
Methanol (g/L)	2.6 ± 0.2
Ethanol (g/L)	1.0 ± 0.2
Fructose (mg/L)	72 ± 5
Cl ⁻ (g/L)	24.53 ± 0.03
SO ₄ ²⁻ (g/L)	1.78 ± 0.01
Na ⁺ (g/L)	15.9 ± 0.1
K ⁺ (mg/L)	965 ± 2

of persulphate in water, reducing the mass transfer resistance between phases and allowing rapid injection into the contaminated water for in-situ remediation. However, when Fe²⁺ is used, the dose of catalyst must be optimised because excess Fe²⁺ reacts with sulphate anions faster than they are generated (Ec. 3 and 4), whereas too little Fe²⁺ cannot properly activate the persulphate. In this sense, an appropriate Fe²⁺/S₂O₈²⁻ molar ratio is usually 1:1 or 1:2 (Karim et al., 2021).



Therefore, in view of the above, sodium persulphate (>98% of purity, CAS 7775-27-1, Acros organics) and iron (II) sulphate heptahydrate (≥99.5%, CAS 7782-63-0, Merck) were used as the oxidising agent and the catalyst, respectively (Lee et al., 2020; Liang et al., 2004; Romero

et al., 2010).

Moreover, it should be noted that sulphate radicals (SO₄^{·-}) can react with the chlorine ions (Cl⁻) present in the residual aqueous phase, which can produce other radicals (Cl·, Cl₂· and OH·) that affect the oxidation performance. Although this impact can be negligible, positive or negative depending on the concentration of chlorine ions and persulfate anions and the generation of their derivative radicals (SO₄^{·-}, Cl·, Cl₂· and OH·), many studies have reported that high concentrations of chlorine ions (>10 mM) can enhance the degradation of organic compounds, such as phenolics, due to the rapid production of more active chloride species (Oyekunle et al., 2021).

Regarding the operational conditions, a constant temperature of 70 °C was maintained during the treatments. This temperature has been reported to greatly accelerate the degradation of phenol by thermal activation of the persulphate (Ma et al., 2017).

Oxidation experiments were carried out as follows: after heating 10 mL of the aqueous phase up to 70 °C in a closed beaker using a hot plate magnetic stirrer, different volumes of concentrated persulphate (500 g/L) and catalyst (350 g/L) solutions were added in order to obtain the desired final concentrations in the reaction medium; in particular, 5, 50, 120, 223 and 395 mM persulphate anion and 9, 18 and 48 mM ferrous ion (see table S1 in the Supplementary Material).

The reaction took place for 120 min under agitation, withdrawing samples after 30, 60 and 120 min. The samples were cooled down to 4 °C with cold water to stop the reaction and stored at this temperature until their analysis (Romero et al., 2010).

2.3. Analytical methods

Total and inorganic carbon fraction were measured using a DIMA-TOC 2100 analyser (Dimatec Analysentechnik GmbH), while organic

carbon fraction was calculated by difference.

The pH has been measured with pH-indicator strips from 2.5 to 4.5.

Phenolic compounds were measured using a High-Performance Liquid Chromatography (HPLC) equipped with a Kinetex® C18 PFP OOD-4462-EO (Phenomenex) column at a temperature of 30 °C and a diode-array detector (DAD) set at 210 nm. The mobile phase, which was an aqueous solution of H₃PO₄ and NaH₂PO₄ and methanol in 80:20 ratio, was set up at a flow rate of 0.75 mL/min.

Concentrations of carboxylic acids, alcohols and reducing sugars were also measured by HPLC using an Aminex HPX 87H (Biorad) column, a refractive index detector (RID) and a diode-array detector (DAD) set at 210 nm. The mobile phase was an H₂SO₄ 4 mM solution set up at 0.65 mL/min. Glycolic and lactic acids were detected at 75 °C, while the rest of the compounds, at 25 °C.

Concentrations of inorganic ions in the raw residual aqueous phase have been determined by ion chromatography using a METROHM 883 Basic IC plus ion chromatograph.

3. Results and discussion

In order to achieve a deeper understanding of the roles of either persulphate or iron salts during the advanced oxidation of the different compounds present in the aqueous phase from the hydrothermal treatment of Kraft black liquor, two series of experiments, without or with

iron salts, were carried out separately.

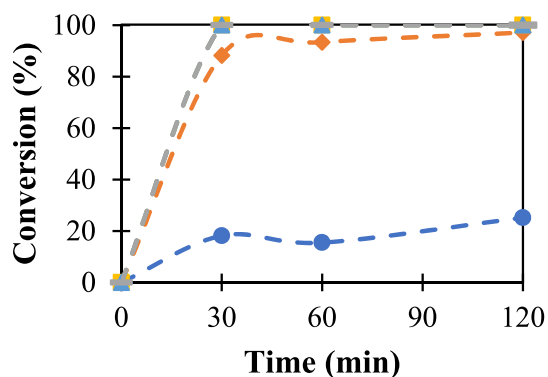
3.1. Persulphate-based advanced oxidation without catalyst

Firstly, the oxidation of the aqueous phase from the hydrothermal liquefaction of Kraft black liquor was carried out using different initial persulphate anion concentrations (from 5 to 395 mM), but without iron salts. In this way, persulphate molecules were only thermally activated. The effects of these different persulphate concentrations on the evolutions of the main phenolic compounds detected are shown in Fig. 2.

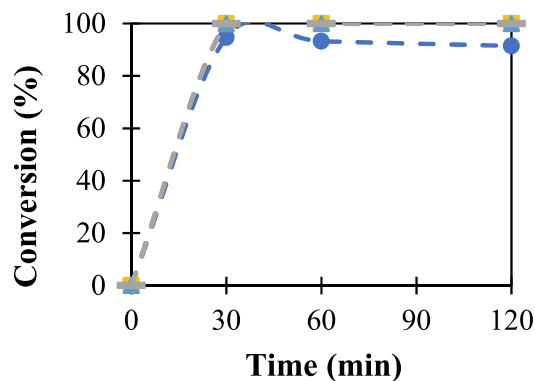
As can be seen in Fig. 2, phenolic compounds were greatly affected by the presence of persulphate in the medium, even at the lowest concentration tested. Thus, just adding 5 mM of persulphate anion, the phenolic compounds experienced removals ranging from 18% to 95% in 30 min, suggesting a strong affinity of the oxidant for these compounds. The oxidation of these phenolic compounds has been reported to be caused by the attack or destruction of the benzene rings by the sulphate radicals (Xia et al., 2020).

Predictably, increasing the initial persulphate anion concentration not only improved the removal of the phenolics, but also their oxidation rates. In this sense, this higher reactivity was accompanied by a higher acidification of the medium, related to the production of acidic compounds, and changes in colour, associated with toxic intermediates formed by the partial degradation of these aromatic compounds (Xia

a) Catechol



b) Phenolic 1



c) Phenolic 2

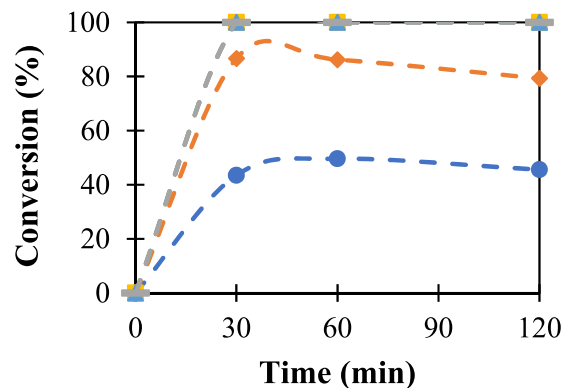


Fig. 2. Evolution of the phenolic compounds found in the aqueous phase during the non-catalysed oxidation. Persulphate anion concentration: 5 (●), 50 (◆), 120 (■), 223 (▲) and 395 (■) mM.

et al., 2020; Zhao et al., 2016). These coloured compounds include dihydroxylated rings, such as resorcinol and hydroquinone, which in turn generate higher coloured compounds, such as ortho- and para-benzoquinone. In addition, these compounds can react with their own quinones to generate charge-transfer complexes (quinhydrone), compounds which take on a dark colour at low concentrations. All these intermediates have been reported to be highly bio-toxic, even at very low concentrations, so the appearance of colour is usually used as a good indicator of toxicity during the oxidation of phenolic wastewaters (Collado et al., 2010; Mijangos et al., 2006).

In this regard, during the advanced oxidation of the aqueous phase from the hydrothermal liquefaction of Kraft black liquor, it was observed that the rapid removal of the main phenolic compounds, which took less than 30 min, was not accompanied by an effective reduction in the colour, that is to say, in toxicity. In order to better understand this behaviour, table S2 in the Supplementary Material shows how the pH and colour changed for different initial persulphate concentrations after

30, 60 and 120 min. Regarding the results obtained, Phenolic 1 was easily removed, requiring just an initial persulphate concentration of 5 mM for its almost complete elimination. Phenolic 2 and catechol were more persistent to oxidation, although it was also possible their complete removal by increasing the persulphate anion concentration up to 120 mM. Nevertheless, this persulphate concentration was not high enough to produce a significant decrease in the colour and, therefore, in the final toxicity. In fact, results suggested that higher oxidant concentrations would be required to remove not only the main phenolic compounds detected, but also the toxic coloured intermediates generated during the degradation of the formers.

Once the oxidation of the phenolic compounds by persulphate was proved to be fast and effective, the effect of the initial oxidant doses on the concentrations of other non-phenolic compounds present in the aqueous phase from the hydrothermal liquefaction of black liquor was also studied in order to discuss the reaction selectivity. To this end, Fig. 3 shows how the concentration of these compounds changed in presence

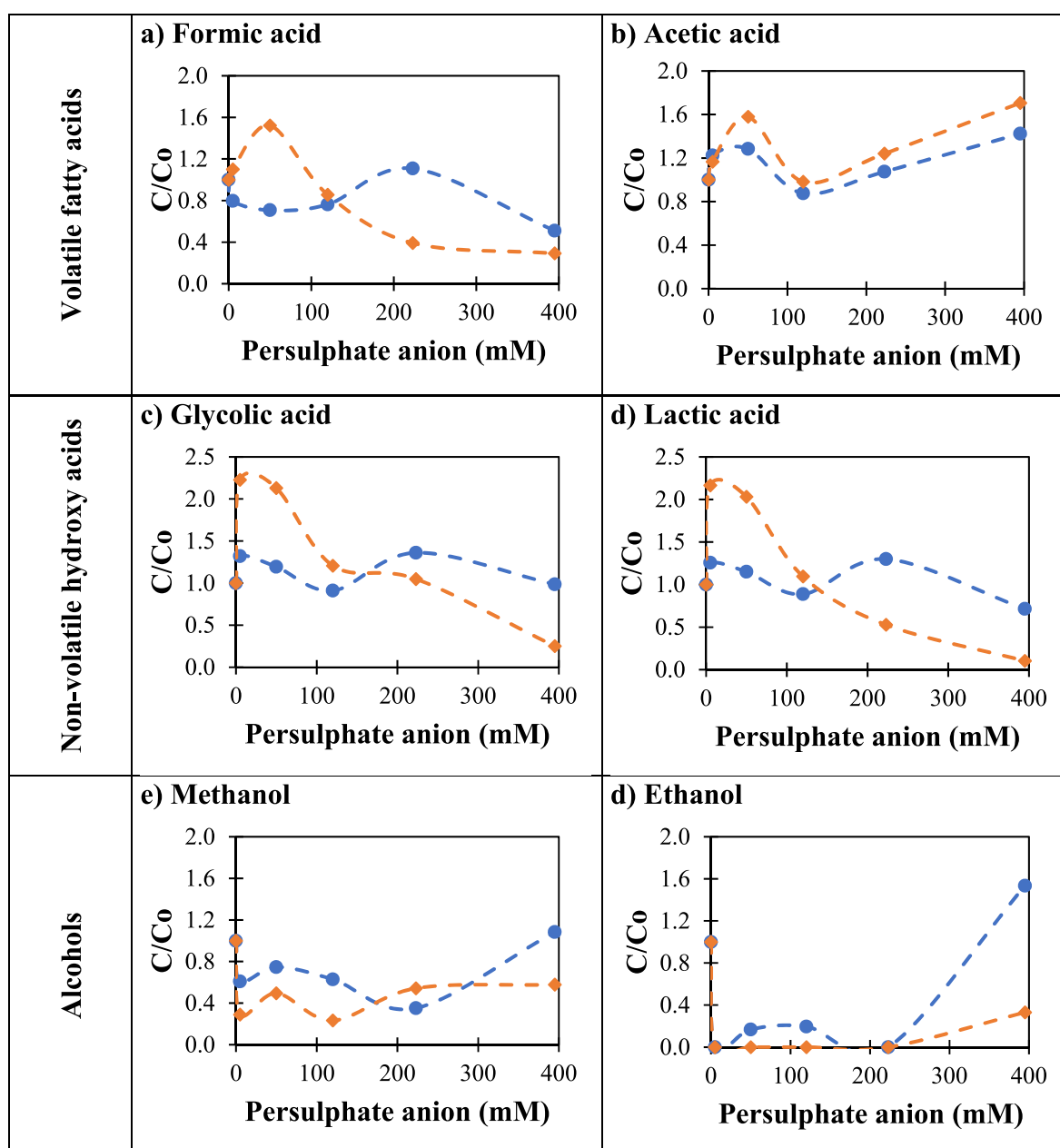


Fig. 3. Concentration changes of the main carboxylic acids and alcohols detected in the aqueous phase after 30 (●) and 120 min (◆) of non-catalysed oxidation.

of different initial persulphate concentrations after 30 min (thereafter, the concentration of phenolic compounds remained constant) or after 120 min (the last time tested).

Focusing firstly on the organic acids, results revealed that after 30 min of reaction, their concentrations changed moderately, with maxima for 223 mM of persulphate, except for acetic acid. Nevertheless, at the end of the reaction (120 min), these maxima were higher and were reached with a lower persulphate concentration (≤ 50 mM). This is a typical behaviour of oxidation intermediates, which are partially oxidised organic matter which can be further oxidised to other shorter compounds, such as organic acids, if the concentration of oxidising agent (persulphate) is high enough. This trend was particularly marked for glycolic and lactic acids (non-volatile hydroxy acids), whose initial concentrations (1.3 and 2.2 g/L, respectively) were doubled after 120 min of treatment with the lowest initial persulphate anion concentration (5 mM). Regarding acetic and formic acids (volatile fatty acids), their formation was also significant, but slower than for the previous ones as their maximum concentrations were achieved using 50 mM of initial persulphate anion concentration. Moreover, it is interesting to note that, in contrast to the rest of the acids, the acetic acid formation was even slightly promoted by high persulphate sodium doses, being the predominant final compound in the oxidised aqueous phase at initial persulphate anion concentrations higher than 223 mM. In fact, with 395 mM of initial persulphate anion, the final concentration of acetic acid was 8.6 g/L, 71% higher than the initial one, while the concentration of the second most abundant compound (formic acid) was 1.1 g/L. The behaviour of these compounds corroborates the physical changes and the reaction mechanism explained. At low doses of sodium persulphate, all of them were produced as a result of the degradation of the organic matter, with their subsequent oxidation being not achieved. In contrast, at high doses of oxidant, they were increasingly oxidised, except for acetic acid, which is very persistent to oxidation and is produced as a final intermediate before the conversion to carbon dioxide and water (Garg et al., 2007; Mussatto et al., 2007). This trend is in agreement with that obtained in other studies, although with different operating conditions and raw material. For example, Chou et al. (2013) studied the formation and degradation of oxalic, malic, lactic and acetic acids in landfill leachate under microwave oxidation process with different persulphate doses (0, 0.2, 0.5 and 1 M). When 0.2 or 0.5 M of persulphate was used, lactic acid was firstly degraded but, after 25 min of treatment, its concentration started to increase due to its formation from the degradation of other organic compounds. However, when 1 M of persulphate was used, hardly any formation of this compound could be observed due to its oxidation.

Finally, both ethanol and methanol followed a very similar trend, although the final concentrations achieved differed. The former, with an initial concentration of 1 g/L, was almost completely degraded in less than 30 min, even in the presence of only 5 mM of persulphate anion concentration. Ethanol concentration was significant when the highest persulphate concentration was employed and after 30 min. The high degradation after 120 min and its behaviour with the different persulphate concentrations suggest that this alcohol is easily oxidised once it has been formed. In the case of methanol, its concentration also decreased rapidly but it was not completely removed, remaining around 30% of the initial methanol concentration in the aqueous phase regardless of the persulphate sodium added. This corroborates a higher affinity of sulphate radicals for ethanol than for methanol (Clifton and Huie, 1989). Anyway, these reductions were attributed to hydrogen abstraction by sulphate radicals, primary alcohols being selectively oxidised into the corresponding carboxylic acids (formic or acetic acids) (Xia et al., 2020).

3.2. Persulphate-based advanced oxidation with catalyst

Once the non-catalytic persulphate-based advanced oxidation of the aqueous phase from the hydrothermal liquefaction of black liquor was

studied, the effect of adding from 9 to 48 mM of ferrous ion as the homogeneous catalyst, but maintaining an initial concentration of 50 mM of oxidant, was analysed. Moreover, an experiment using 18 mM of ferrous ion in absence of persulphate anion was performed in order to discuss the effect of the catalyst alone (see Fig. 4 below and table S3 in the Supplementary Material).

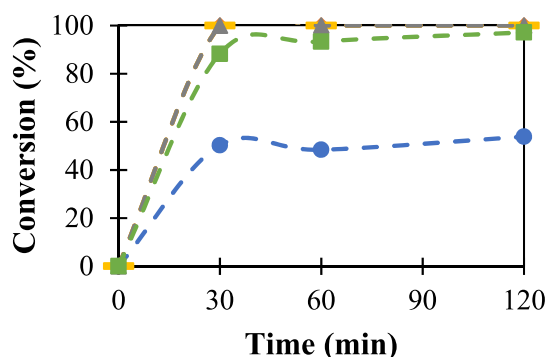
Results revealed that ferrous ions had a significant positive impact on the removal of phenolic compounds. In fact, even in absence of the oxidising agent, their concentrations decreased drastically, achieving reductions of 50%, 57% and 98% for catechol, Phenolic 2 and Phenolic 1, respectively, after 30 min using 18 mM of initial ferrous ion concentration. When persulphate anions were also present in the medium, even at the lowest concentration of catalyst tested (9 mM), both catechol and Phenolic 2 were completely degraded in 30 min as well, in comparison to around 87% conversions observed using only 50 mM of persulphate anion. In this regard, it is known that iron species (both dissolved and precipitated) and quinones are key participants in a wide range of environmental redox reactions. Thus, studies done with catechol and Fe (II) have reported that both compounds form a complex that subsequently produces Fe (III) in acidic conditions, generating semi-quinone radicals as well, that can oxidise Fe (II) back to Fe (III) (Jiang et al., 2015; Santana-Casiano et al., 2010). Nevertheless, until today, chemical interactions between phenolics and iron, combining redox processes and complex formation, have not been fully elucidated (Bijlsma et al., 2020). When ferrous ions were added in presence of persulphate anions, both iron-driven mechanisms, that is to say, the Fe-complexation and the persulphate activation by Fe, took place simultaneously, speeding up the removal of the phenolic compounds. Thus, complete oxidation of the three phenolic compounds was obtained with 9 mM of ferrous ion in presence of 50 mM of persulphate anion, which was not the case for the same oxidant concentration but in the absence of catalyst. This was expected as many authors have reported that iron-based materials, such as ferrous and ferric compounds, iron oxides or sulphides, are effective activators of persulphate to generate sulphate radicals at a higher rate, increasing the conversions (Karim et al., 2021).

Ferrous ions not only accelerated the removal of these phenolic compounds, but also produced noticeable changes in the physical properties of the aqueous phase. As can be seen in table S3 in the Supplementary Material, the addition of the catalyst (ferrous ion) in form of iron (II) sulphate in absence of persulphate anions, together with the action of heat (70 °C), slightly reduced the pH but turned the colour of the aqueous phase into dark blue. In presence of 50 mM of persulphate anions, the ferrous ions accelerated the oxidation reaction due to the formation of more sulphate radicals (Romero et al., 2010), drastically reducing the pH and turning the solution into a very dark bluish-brown colour. These colour changes were attributed to the partial oxidation of the organic compounds and the formation of coloured complexes between phenolic compounds and iron (Bijlsma et al., 2020).

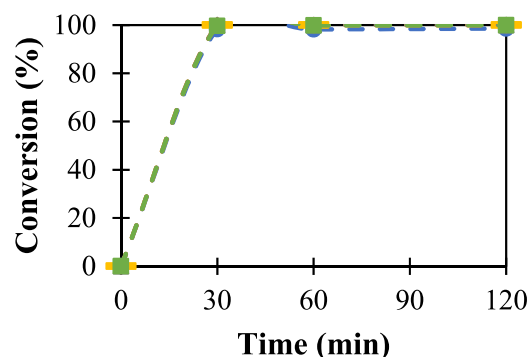
Once this was discussed, the effect of iron (II) sulphate on the evolution of the main non-phenolic compounds is shown in Fig. 5, again for when the main phenolic compounds have been completely removed (30 min) and for the longest reaction time tested (120 min).

Regarding the organic acids, results revealed that Fe (II), in absence of persulphate, had not a significant impact on either their formation or degradation. When 50 mM of persulphate was also added, organic acid concentrations remained constant for short reaction times, in contrast to the phenolic compounds, which were completely removed. However, for long reaction times, low Fe (II) concentrations favoured the formation of glycolic, lactic and formic acids to a greater extent than the non-catalysed oxidation, which is consistent with a higher generation of persulphate radicals in presence of iron salts. Thus, the oxidation of the aqueous phase in presence of 50 mM of persulphate anion and 9 mM of ferrous ion involved significant enhancements in their concentration after 120 min, almost tripling the initial values for glycolic (from 1.3 to 3.6 g/L) and lactic (from 2.2 to 5.7 g/L) acids and doubling that of

a) Catechol



b) Phenolic 1



c) Phenolic 2

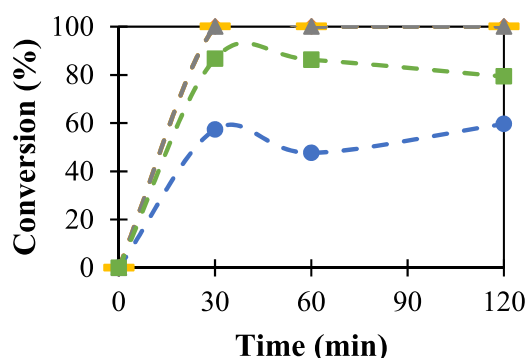


Fig. 4. Evolution of the phenolic compounds found in the aqueous phase during the catalysed oxidation. Ferrous ion concentration: 0 (■), 9 (◆), 18 (●) and 48 (▲) mM with 50 mM of persulphate anions and 18 (●) mM without oxidant.

formic acid (from 3.8 to 7.4 g/L). For the same conditions but without catalyst, the concentration of these acids were 3.1, 4.9 and 5.9 g/L, respectively. In the case of acetic acid, its concentration decreased with low concentrations of iron probably due to its partial oxidation to formic acid, this outweighing its formation from the decomposition of the organic compounds. Nevertheless, once the ferrous ion concentration was higher than 9 mM, the final concentrations of glycolic, lactic and formic acids decreased again, reaching similar values to those found in the initial aqueous phase for an initial concentration of catalyst equal to or higher than 18 mM. Parallely, no changes in initial acetic acid concentrations were detected in the same range.

Moving on to alcohols, this trend was also observed for methanol, iron showing a catalytic effect for concentrations lower than 18 mM. In the case of ethanol, its removal was almost complete for all the ferrous ion concentrations tested, as had already happened for the non-catalysed oxidation. Nevertheless, its degradation seemed to be slowed down at high iron concentrations and short reaction times (30 min). At this point, it is interesting to note that, in absence of persulphate, iron (II) sulphate was able to reduce the concentration of both ethanol and methanol. Thus, in presence of 18 mM of ferrous ion alone, the concentrations of ethanol and methanol decreased by 92% and 45%, respectively, after 120 min of catalysed oxidation. This fact may be related to the attack of the radicals formed during the decomposition of the phenolic compounds-iron complexes previously reported.

Therefore, it can be concluded that ferrous ion concentrations higher

than 18 mM inhibit the oxidation, avoiding the degradation of the intermediate compounds produced. This is caused because a high concentration of ferrous ions produces secondary reactions, reducing the available sulphate radicals and limiting the oxidative capacity (Liang et al., 2004; Romero et al., 2010).

3.3. Comparison

Finally, a comprehensive discussion on the differences between catalysed and non-catalysed persulphate-based advanced oxidation of the residual aqueous phase from hydrothermally liquefied black liquor is necessary to determine the effective management and valorisation of this stream.

In view of the results, the best experiments were 50 mM of persulphate anion without catalyst and with 9 mM of ferrous ion. In this sense, the compositions of the residual aqueous phase before and after (120 min) both treatments are shown in Table 2.

As can be seen and as already explained, even in the absence of the catalyst, the concentration of phenolic compounds and alcohols in the residual aqueous phase was drastically reduced, while the concentration of organic acids increased significantly. Obviously, the selection of one of these alternatives will depend on the further use of the treated residual aqueous phase, but it seems reasonable to choose the iron-catalysed oxidation as the most advisable option. The presence of iron led to a higher degradation of alcohols and phenolic compounds, which

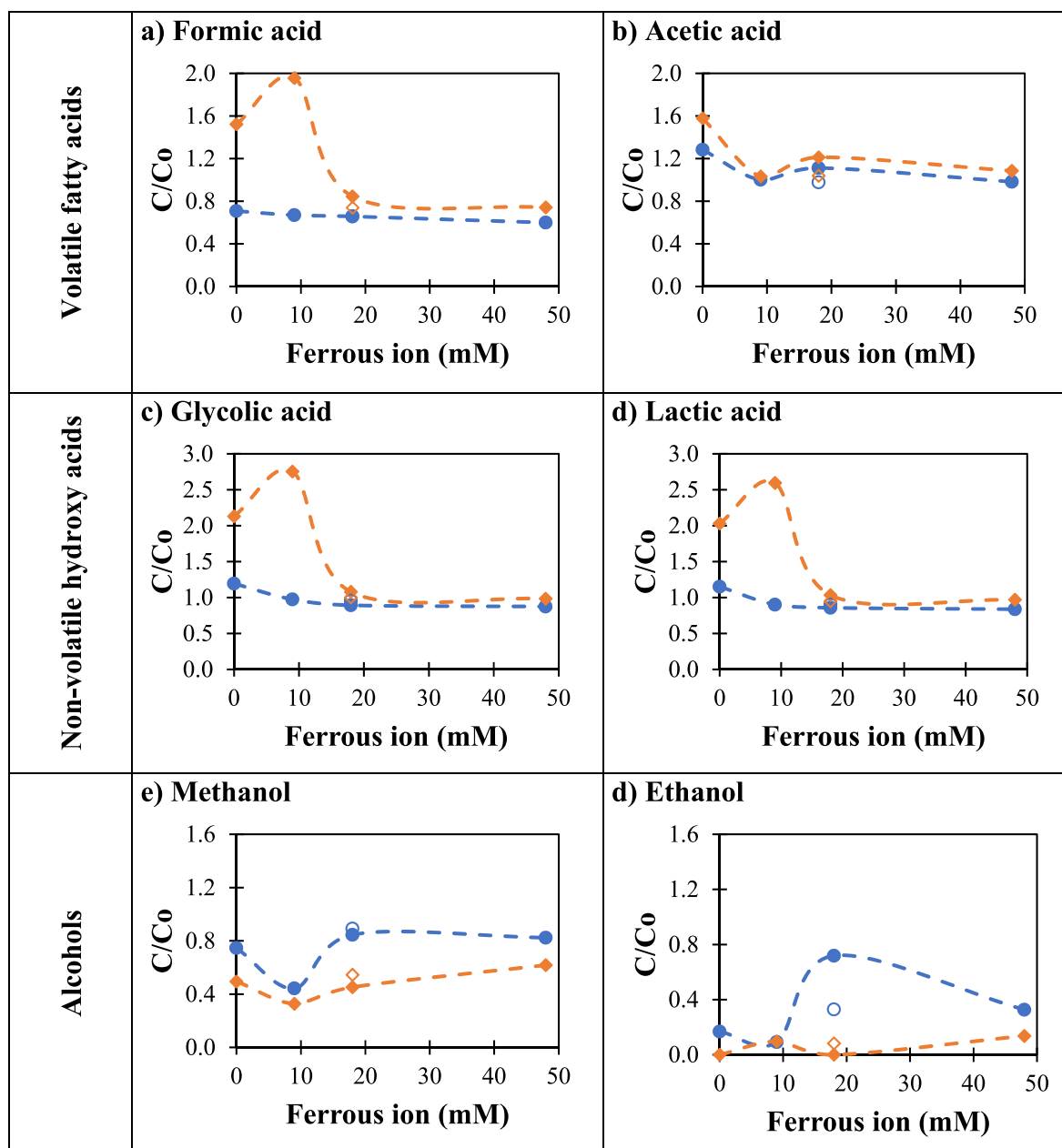


Fig. 5. Concentration changes of the main carboxylic acids and alcohols detected in the aqueous phase after 30 (●) and 120 min (♦) of advanced oxidation with 50 mM persulphate anions and 0, 9, 18 and 48 mM of ferrous ion. Unfilled data points represent the experiment of 18 mM of Fe (II) without oxidant.

are known to act as inhibitors in biological processes or as poisons in heterogeneous catalytic processes. Thus, the iron-promoted persulphate oxidation of the raw aqueous phase generates an effluent that would be suitable for use in fermentation processes, anaerobic digestion, catalytic treatments such as aqueous phase reforming or for the extraction of organic acids. In any case, based on the previous results, a similar detoxified effluent can be expected from the non-catalysed persulphate-based advanced oxidation, but with a longer reaction time. So, in addition to the effluent requirements, the balance between reaction time and iron dosage should be another decision criterion in order to minimise costs associated with heating and reagents. At this point, it is also interesting to note the great versatility of persulphate-based oxidation for obtaining customised pools of acids by modifying the time, temperature and iron concentration conditions. In this way, this pretreatment can be tuned to optimise the yield of further treatments such as biopolymer production, hydrogen generation by biological or thermal processes, or its use as a carbon source for denitrification treatments.

4. Conclusions

Persulphate-based advanced oxidation was found to be a treatment capable of oxidising the phenolic compounds and alcohols present in the residual aqueous phase from the hydrothermal liquefaction of Kraft black liquor, thus reducing its toxicity. Simultaneously, persulphate also caused the removal of the alcohols, particularly for ethanol. In addition, low persulphate anion concentration (<50 mM) favoured the formation of formic, glycolic and lactic acids, whereas acetic acid was the predominant one for higher persulphate concentrations.

When the ferrous ion was tested as the catalyst, its presence at low concentrations (<9 mM) enhanced the oxidation of phenolic compounds and alcohols, requiring lower persulphate concentration to achieve similar degradation results. Nevertheless, higher catalyst concentrations resulted in a worsening in the oxidation performance due to the sequestration of sulphate radicals and the occurrence of undesired parallel reactions.

Table 2

Chemical composition of the residual aqueous phase before and after 120 min of advanced oxidation with 50 mM of persulphate anion in absence and presence of 9 mM of ferrous ion.

Compounds	Raw residual aqueous phase	Non-catalysed oxidation	Catalysed oxidation
Catechol (mg/L)	63	2.0	0
“Phenolic 1”	C _{o1}	0	0
“Phenolic 2”	C _{o2}	0.2C _{o2}	0
Formic acid (g/L)	3.8	5.9	7.5
Acetic acid (g/L)	5.0	8.6	5.6
Glycolic acid (g/L)	1.3	3.1	4.0
Lactic acid (g/L)	2.2	4.9	6.2
Methanol (g/L)	2.6	1.4	0.9
Ethanol (g/L)	1.0	0	0.1

Comparing the two best scenarios (50 mM of persulphate anion in absence and presence of 9 mM of ferrous ion), the best results were achieved with catalysed oxidation. In this respect, lower concentrations of phenolic compounds and alcohols and higher concentrations of organic acids were obtained. However, less acetic acid was produced and another reagent (the catalyst) was necessary. Therefore, the choice of the most appropriate treatment has to be made according to the subsequent valorisation strategy of this stream.

CRedit authorship contribution statement

Lucía Pola: Conceptualization, Investigation, Formal analysis, Data curation, Writing – original draft. **Sergio Collado:** Conceptualization, Methodology, Writing – review & editing. **Maximilian Wörner:** Methodology, Investigation. **Ursel Hornung:** Funding acquisition, Supervision, Resources. **Mario Díaz:** Funding acquisition, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.chemosphere.2023.139737>.

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