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Removal of Organics from Landfill Leachate by Heterogeneous Fenton-like Oxidation over Copper-Based Catalyst

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Abstract: Landfill leachates are a mixture of high concentration organic and inorganic contaminants and need to be appropriately treated due to their toxicity and severe adverse effects on the environment. Here, we studied the treatment of landfill leachate through a heterogeneous Fenton-like oxidation process using a zirconia supported copper catalyst (Cu/ZrO_2). Reaction conditions such as pH, amount of catalyst, oxidant dose, temperature, and reaction time were investigated and their effects on pollutant abatement discussed. AOS (average oxidation state) and COS (carbon oxidation state) parameters were used for the evaluation of the degree of oxidation of the process, obtaining some insight into the formation of oxidized intermediates (partial oxidation) and the total oxidation (mineralization) of the leachate during the reaction. A two-step oxidation process enhanced the overall performance of the reaction with an abatement of organic compounds of 92% confirming the promising activity of a copper-based catalyst for the treatment of liquid waste. Higher catalytic activity was achieved when the following reaction conditions were applied: 70 °C, pH 5, 200 mg/L of catalyst, 30 mL/L of H_2O_2 dose, and 150 min. In addition, durability of the catalyst under optimized reaction conditions was verified by repeated reaction cycles.

Keywords: landfill; wastewater; AOP; catalytic treatment; Fenton-like; oxidation

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1. Introduction

Landfill is the most widely adopted method for the disposal of solid wastes [1]. Over time, the solids in the landfills undergo physicochemical and biological processes and, when rainwater runs through these sites, landfill leachate, a heavily polluted wastewater is produced [2,3]. Leachate has become a serious environmental concern because it contaminates both soil and groundwater [4]. The concentration and composition of this liquid waste typically depend on the site and the age of the landfill [5]. Leachate can be classified into three types, based on chemical oxygen demand (COD) values: young (COD > 10,000 mg/L), intermediate (COD in the range 4000–10,000 mg/L), and old (COD < 4000 mg/L) [3,6]. Conventional biological treatment processes can be applied only for young leachate [7], while, usually, they are unable to treat intermediate and old leachate due to the heavy organic loading and the presence of very stable and high molecular weight organics [8]. Therefore, treatment of leachate requires intensive physical and chemical processes to comply with the stringent environmental regulations [3,9].

Advanced oxidation processes (AOPs) are among the most effective methods applied for the treatment of leachate [2,10–13]. These processes typically rely on the generation of highly reactive hydroxyl radicals (OH), which in turn attack the organics, resulting in being extremely effective for their abatement [14]. There are various types of AOPs that can be successfully applied for the liquid waste treatment, such as Fenton, Fenton-like, ozonation, as well as electrochemical and photochemical technologies [15–23]; however, their effectiveness depends upon their ability to generate oxidizing species. The conventional Fenton process is the most widely used AOP because of its simplicity and economic feasibility, but there are several drawbacks associated with this process. For instance, it is ineffective when it is required to decompose complex organics; furthermore, high activity of the process is only achievable when strict acidic conditions are applied [24]. Moreover, it generates large volumes of residual sludge which need to be disposed of, creating an additional environmental and economic concern [25,26]. Similarly, other AOPs employing physical fields are neither economically feasible due to high energy input nor have the potential to be scaled up on industrial levels [27]. The heterogeneous Fenton method (Fenton-like) is a promising technology for the treatment of organics in wastewater because it produces less solid sludge and the catalyst can be recycled with these features making this process feasible in terms of scalability and economics [27].

However, there is a growing need for the development of new catalysts with extended recyclability, improved activity, and selectivity which can ultimately be employed in Fenton-like treatment. The organic abatement efficiency of a Fenton-like process can substantially be enhanced by replacing Fe with other transition metals as a catalytic source [28–33]. One good replacement is copper impregnated over appropriate supports. There are several advantages of employing copper such as high catalytic activity, non-toxicity, abundant availability, and lower price compared with other reactive transition metals [28,34]. Moreover, copper can also be employed in an integrated process, i.e., the photo-Fenton process [34]. Furthermore, the mechanism of $^{\bullet}OH$ generation from Cu^+ and Cu^{2+} Equations (1) and (2) is like the conventional Fenton process [28,35]:

$$Cu^{2+} + H_2O_2 \rightarrow Cu^{+} + HO_2\cdot + OH^{-} \quad (1)$$

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

Additionally, unlike iron, copper does not form stable complexes with intermediate products and consequently it is possible to boost the complete mineralization of the pollutants into water and CO_2 [36,37]. The pH is a key reaction parameter and working in almost neutral conditions allows greater sustainability of the process. Recently, different AOPs, persulfate oxidation [38], homogeneous Fenton [39], and electrocatalytic oxidation [40], have been used for the degradation of landfill leachate resulting effectively in the removal of organics, but only under strongly acidic conditions ($pH < 3$) and consequently with various drawbacks for industrial application. To overcome this issue, in the present study, a copper-based heterogeneous Fenton catalyst was investigated due to its ability in affording high catalytic activities, particularly near-neutral pH conditions [36,41]. It is worth mentioning that although supports do not directly participate in catalytic activity, the selection of the appropriate materials not only enhances the activity but also increases the stability of the catalyst, preventing leaching of the active phase that causes a reduction in catalytic performance [42]. Therefore, appropriate supports are desirable which offer strong bonding with the active phase, inhibit the loss of the metal, and prevent the transformation of a heterogeneous reaction into a homogeneous one [28]. Recently, various supports have been investigated to enhance the stability and activity of copper-based catalysts such as alumina [43], calcium phosphate [44], zeolites [45], activated carbon [46], birnessite [11], montmorillonite [47], mesoporous SBA-15 [48], graphene [49], perlite [50], etc.

In this study, we employed copper supported over zirconia as a heterogeneous catalyst for the treatment of landfill leachate because it showed promising catalytic results in Fenton-like oxidation while working with model aqueous solutions of ibuprofen [41,51]. The activity of a catalyst is investigated in terms of total dissolved organic carbon (TDOC) and chemical oxygen demand (COD) because these parameters are widely studied by industry and academia [52]. TDOC results indicate the amount of organics in the raw leachate that is mineralized during the treatment, while COD gives important information about the degradation of the compounds into more oxidized molecules. Moreover, the COD–

TOC relationship, before and after treatment, provides some insight into the formation of organic intermediates during the oxidation reaction. The efficacy of chemical oxidation of the Fenton-like process and the state of oxidation can be interpreted by means of a combination of TOC, COD, and their relationship. When organics are treated by the Fenton reaction, partial or ultimate degradation can be achieved. In partial degradation, parent compounds are degraded into more oxidized intermediates with the improvement of biodegradability and the reduction of toxicity. When ultimate degradation occurs, organics are completely oxidized into carbon dioxide, water, and other inorganics. The various degradation stages are followed using COD (degree of oxidation), while TOC provides an insight regarding the total mineralization. If mineralization is achieved during the Fenton reaction, the TOC decreases but if only partial oxidation occurs it remains constant with a decrease of the COD [52]. In addition, AOS (average oxidation state) and COS (carbon oxidation state) parameters have been evaluated for a better understanding of the degree of oxidation of a process [53–55].

AOS gives an insight into the variation of the composition of organic matter in the sample, indeed it increases during the process as more oxidized intermediates are being formed in the reaction. COS, instead, gives information about the degree of oxidation of organic matter: low COS values indicate the presence of rather the reduced organic compounds, while higher values are related to strong mineralization and the generation of highly oxidized intermediates. Summarizing, AOS is associated with partial oxidation and formation of oxidized intermediates, while COS is related to total oxidation (mineralization) of the leachate.

To optimize the efficacy of the Fenton-like process, several operating parameters such as pH, amount of catalyst, oxidant dose, temperature, and reaction time were studied and their corresponding effects on pollutant abatement are discussed. Moreover, the catalytic activity was also investigated after subsequent/multiple recycles of the catalyst. Furthermore, a two-step oxidation process was also carried out to enhance the overall process efficiency so that the finally treated leachate is conveniently integrated with the existing biological treatment facilities. The aim of the present study was the optimization of process parameters on a laboratory scale to obtain conditions of maximum activity coupled with milder reaction conditions. This study applied a simple but efficient catalyst to effectively remove refractory organics from landfill leachate. Our results demonstrate enhanced mineralization with Cu/Zr catalyst providing an efficient strategy that can enhance the removal efficiency of refractory organics in practical application. The good activity and stability of the Cu/ZrO_2 confirms its high attractiveness for the treatment of liquid waste, suggesting that this process can also be evaluated for the treatment of other heavily polluted wastewater streams.

2. Results and Discussion

All the analytical and catalytic tests were carried out after the removal of the suspended solids from landfill leachate by centrifugation. Suspended solids were removed to focus on dissolved organics that represent the more recalcitrant compounds in landfill leachate. Moreover, suspended solids could interfere with the catalyst, masking its efficiency by blocking its active sites. The characteristics of leachate selected to test oxidative Fenton-like process are presented in Table 1.

Raw landfill leachate can be classified as intermediate-age leachate with 8700 mg/Lof COD and a pH of 8.5. The pH of young leachate is less than 6.5 while it progressively increases with the aging of the leachate [9]. The concentration of heavy metal ions is quite low, which is in agreement with landfill leachate in the intermediate phase; indeed, increasing the pH reduces the solubility of many metal ions.

Copper was homogeneously dispersed over the surface of zirconia (monoclinic and tetragonal). The surface area of the material was 55 m^2/g. Characterization of the redox properties of the catalyst indicated high reducibility of the materials at low temperature (three reduction peaks at 110, 140, and 190 °C) and the presence of different types of Cu-phase over zirconia, indicating highly dispersed copper oxide and CuO interacting with the support. The high activity of ZrCu was correlated to its reduction properties. Indeed, the high reducibility at low temperature was correlated to an enhanced ibuprofen degradation under mild conditions. [41].

Table 1. Characteristics of landfill leachate.

Parameters	Value
pH	8.5
Chlorine	80 mg/L
Hardness ($CaCO_3$)	360 mg/L
COD	8700 mg/L
TOC	970 mg/L
AOX	13 mg/L
Total Nitrogen (TN)	1.94 g/L
Color	Dark brown
Al	5 mg/L
Ca	38.2 mg/L
Cr	0.7 mg/L
Fe	2.7 mg/L
Mn	0.1 mg/L
Mg	55.8 mg/L
Ni	0.4 mg/L
Zn	0.3 mg/L

The heterogeneous Fenton process was investigated on CuZr catalyst by performing reactions at 70 °C for 150 min. The catalytic activity was followed by TDOC abatement. It is of fundamental importance to evaluate the adsorption capacity of the material because the aim of the process is the degradation of the organics in landfill leachate and not only their removal by mere adsorption; moreover, the adsorption of organics over the surface could deactivate the catalyst, by poisoning it or by blocking its active sites. Preliminary blank tests were carried out. Landfill leachate mineralization was negligible (7% of TDOC abatement) over CuZr catalyst in the absence of H_2O_2 at 70 °C and therefore it is possible to exclude any important adsorption phenomena of the organics over the catalyst surface and any oxidation activity of the catalyst under these reaction conditions. A similar outcome was found with the use of H_2O_2 in the absence of catalyst at 70 °C, with negligible values of mineralization (10% of TDOC abatement).

2.1. *Effect of Reaction Variables*

Optimization of reaction variables is extremely important to improve the process efficiency, increase the mineralization, and decrease the formation of intermediate compounds, thus controlling the economics of the process. Temperature is of fundamental importance for the economics of the reaction, indeed a good compromise between low temperature and high activity is required for the sustainability of the process. Another critical parameter is the pH because it governs the activity and depends upon the catalyst and the pollutants. The optimum value is a circumneutral pH. The catalyst and oxidant doses should be the minimum amount required to sustain high activity to make the process economically feasible. In this study we analyzed in detail all these variables and their corresponding effects on pollutant abatement, TDOC, COD, and degree of mineralization/partial oxidation.

The pH of the aqueous medium is the most critical parameter which governs the efficacy of the Fenton-like process. An optimum pH is always required which facilitates the catalyst to generate maximum $^{\bullet}OH$ radicals from the oxidant. Therefore, it is essential to experimentally determine the optimum pH for the enhanced performance of the catalyst. To illustrate the activity of the catalyst at different pH values, TDOC and COD results are presented in Figure 1A. When leachate is processed at pH 3, after 150 min, the TDOC removal is only around 25%. This indicates that the employed pH is too acidic for the catalyst to produce the maximum amount of $^{\bullet}OH$ from the oxidant. Instead of forming beneficial oxidizing species, the oxidant may have formed oxonium ions and, consequently, a lower organic mitigation was afforded [5]. When the heterogeneous Fenton reactions were carried out at pH 8, the TDOC removal was markedly decreased to 17% and this is because H_2O_2 decomposes into water and oxygen at higher pH [56,57] and consequently, a lower mineralization activity of the organics in the leachate is obtained.

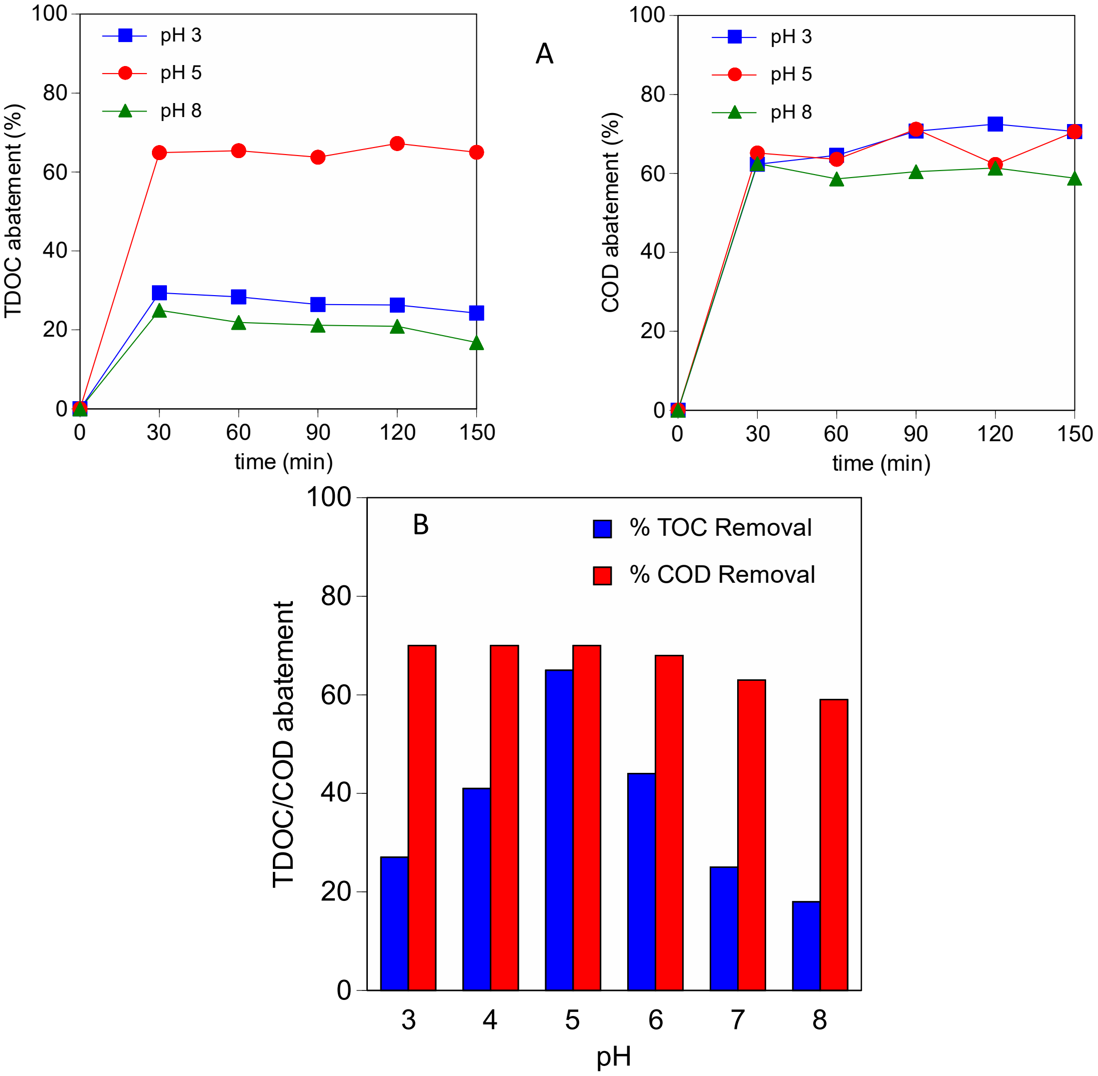


Figure 1. (**A**) Effect of pH on TDOC and COD removal efficiencies; (**B**) TDOC and COD removal efficiencies from pH 3 to 8 (reaction condition: 70 °C, 200 mg/L of catalyst, H_2O_2 30 mL/L and reaction time 150 min).

When landfill leachate is treated at pH 5 the highest TDOC reduction was achieved (66%) in the first 30 min. Choina et al. [58] suggests that the maximum activity of a catalyst in Fenton-like oxidation is achieved when the process is carried out at pH values close to its point of zero charge (PZC). The experimentally determined PZC of CuO is 6 (Guedes et al. 2009) and that of ZrO_2 is 5.5 (Zeng et al. 2008); the PZC of CuZr should therefore be in the range 5–6 and this would explain the higher activity obtained at pH 5.

The evaluation of TDOC removal efficiency of the organics, after 150 min of reaction, over a wider range of pH revealed a volcano-plot tendency, while COD abatement showed a slight decrease for pHs higher than 6 (Figure 1B) suggesting that mineralization is strictly dependent while partial oxidation (COD) is less affected by pH. The best abatement was obtained at pH 5, while moving towards greater acidity or basicity, a progressive decrease in catalytic activity was observed. While TDOC showed higher removal at pH 5, COD abatement was almost independent of the pH, achieving around 65% of abatement for all pH conditions, after 30 min of reaction.

This phenomenon suggests that complete oxidation of organics occurs at pH 5 while at pH 3 and 8 both partial and complete oxidations take place at the same time. Indeed, after 150 min of reaction at pH 5, the COD abatement was around 70% with 65% of TDOC removal, with a COD/TOC ratio (ratio between the percentage abatement of COD and TOC) near to 1 indicating that strong mineralization occurred. Consequently, pH 5 is the best condition to mineralize the organics in leachate, while lower or higher pH mainly induces degradation with the formation of more oxidized intermediates. However, in all the conditions a better biodegradability of the landfill leachate could be obtained by the Fenton-like process over CuZr. The carbon oxidation state (COS) (Figure 2A) calculated by means of Equation (10) increases from −9.5 for raw leachate to 0 after Fenton oxidation at pH 3 and 5 and to −1.5 for reaction at pH 8, indicating strong oxidation of organic matter for all pH conditions, although oxidation is more pronounced at pH 3 and 5.

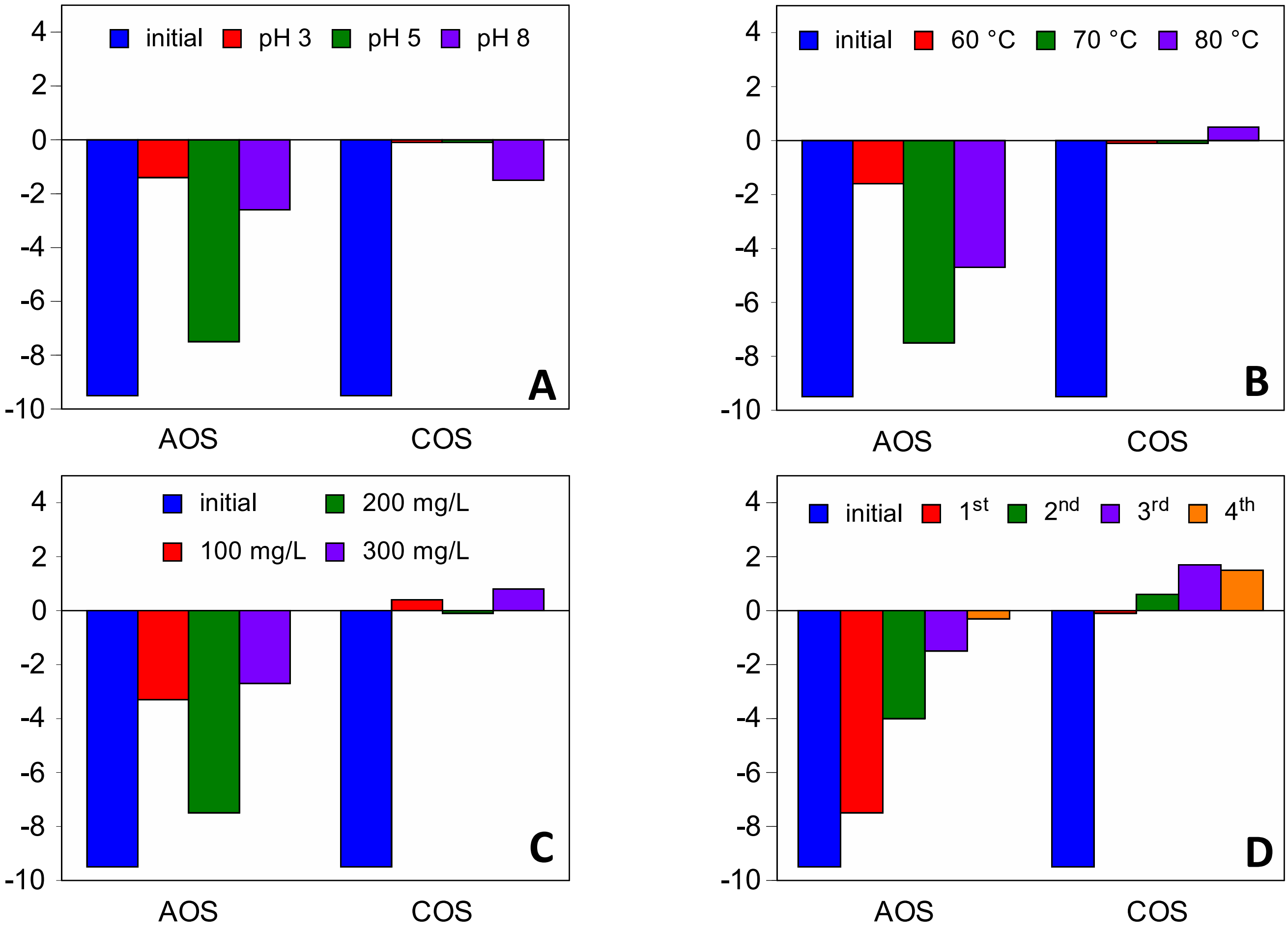


Figure 2. AOS and COS values calculate by Equations (9) and (10). (**A**) effect of pH; (**B**) effect of reaction temperature; (**C**) effect of catalyst dose; (**D**) effect of catalyst recycle.

The average oxidation state (AOS), calculated by means of Equation (9) at the beginning of the reaction was −9.5. After reaction at pH 3 and 8, increases to −1.4 and −2.6, respectively confirmed the degradation into more oxidized intermediates, while at pH 5 the value was −7.5. A high increase of COS and a low value of AOS, indicates that the sample undergoes strong oxidation, but with low formation of oxidized intermediates during the reactions, suggesting that the complete oxidation of the organics into CO_2 (mineralization) is prevalent.

A sufficient amount of thermal energy is required to cross the energy barrier for the transformation of pollutants into the desired products, i.e., H_2O and CO_2 [59]. An increase in the reaction temperature significantly enhanced the leachate abatement in terms of TDOC (Figure 3). At 60 °C only 27% of the TDOC removal efficiency was observed, clearly suggesting that the employed temperature was not sufficient to enable the reactants to cross the activation energy barrier and thus the TDOC abatement was modest [59]. When the reaction temperature was increased from 60 to 70 °C, the catalytic activity was boosted with a 65% reduction of TDOC after 30 min of reaction, while a further increase in temperature from 70 to 80 °C did not enhance the process efficacy [60–62].

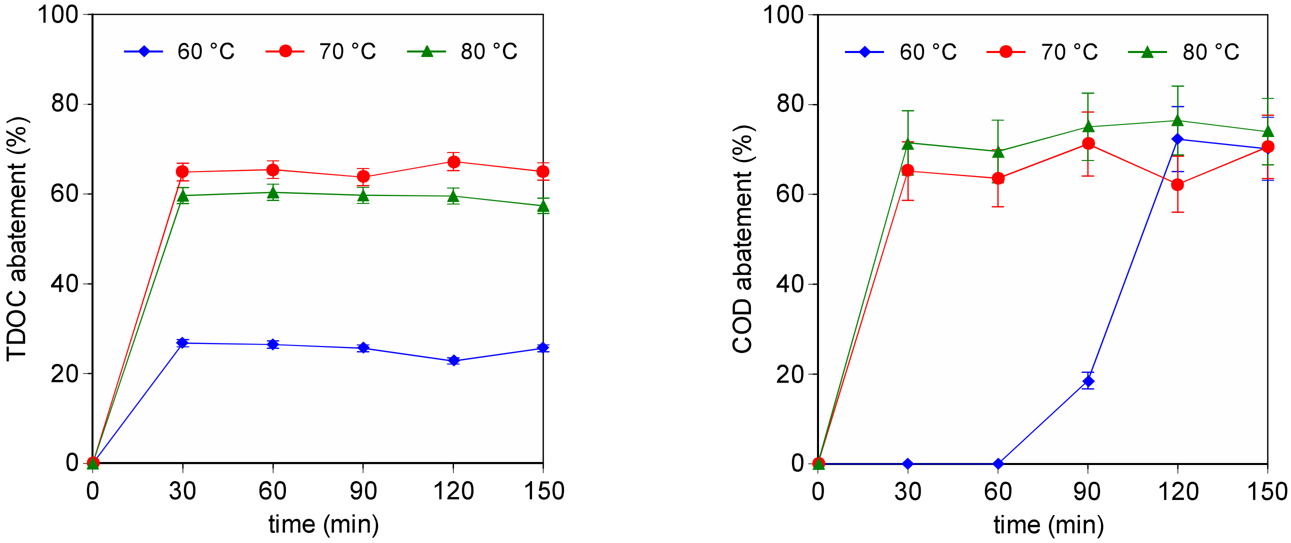


Figure 3. Effect of reaction temperature on TDOC and COD removal efficiencies (reaction condition: pH 5, 200 mg/L of catalyst, H_2O_2 30 mL/L and reaction time 150 min).

Higher temperatures yield higher rates of $^\bullet$OH radical generation but the rate of wasteful utilization of these radicals (side reactions) also increases which negatively affects the productivity of the process [63]. The COD abatements at 70 and 80 °C, after 30 min, were 65 and 71% respectively and there was only a slight increase in COD with extended reaction times. On the contrary, at 60 °C there was no observable COD abatement until 60 min suggesting that the temperature significantly affects the reaction rate and at low temperature, a longer induction time is needed to start the reaction. COS values (Figure 2B) indicate that, for all the investigated temperatures, significant oxidation of organics was obtained; COS increases from −9.5 to 0 at 60 and 70 °C and +0.5 at 80 °C. The analysis of AOS indicates that at 60 °C the formation of highly oxidized intermediates is more pronounced (higher value of AOS, −1.6), while at 70 °C the mineralization prevails (lower AOS, −7.5). At 80 °C an intermediate value of AOS was found (−4.7) indicating a balance between partial and total oxidation.

An optimized catalyst dose not only maximize the treatment efficiency but is also critically important to control the economics of the Fenton-like process [64]. The effect of variable catalyst doses on TDOC removal efficiencies evidenced that 200 mg/L is the optimum concentration (Figure 4).

These results suggest that neither a lower nor a higher catalyst dose favors the Fenton-like oxidation process for the organic mineralization [7]. A too small catalyst amount does not possess a sufficiently high number of active sites to generate enough $^\bullet$OH radicals from the oxidant and thus cannot yield reasonable treatment efficacy. On the other hand, a catalyst concentration higher than the optimal may cause a scavenging effect, i.e., the free hydroxyl radicals are consumed by the catalyst itself and thus causing a decrease in the organic abatement [5,65–67]. COD abatements after 150 min were almost independent of the amount of the catalyst used for the reaction. When 100 mg/L of catalyst was used, the reduction of COD started with a long delay compared to the other concentrations, indeed, 50% of COD abatement was reached only after 90 min of reaction, while with 200 and 300 mg/L such removals were already observed after 30 min. However, after 90 min the removal effect was similar for all the catalyst doses used, suggesting that the amount of catalyst has a key role on the reaction rate but not on the overall activity. The comparison between AOS and COS (Figure 2C) indicates that for 200 mg/L of catalyst a maximum degree of mineralization is obtained (AOS −7.5), while for 100 and 300 mg/L a certain degree of partial oxidation occurs (AOS −3.3 and −2.7, respectively).

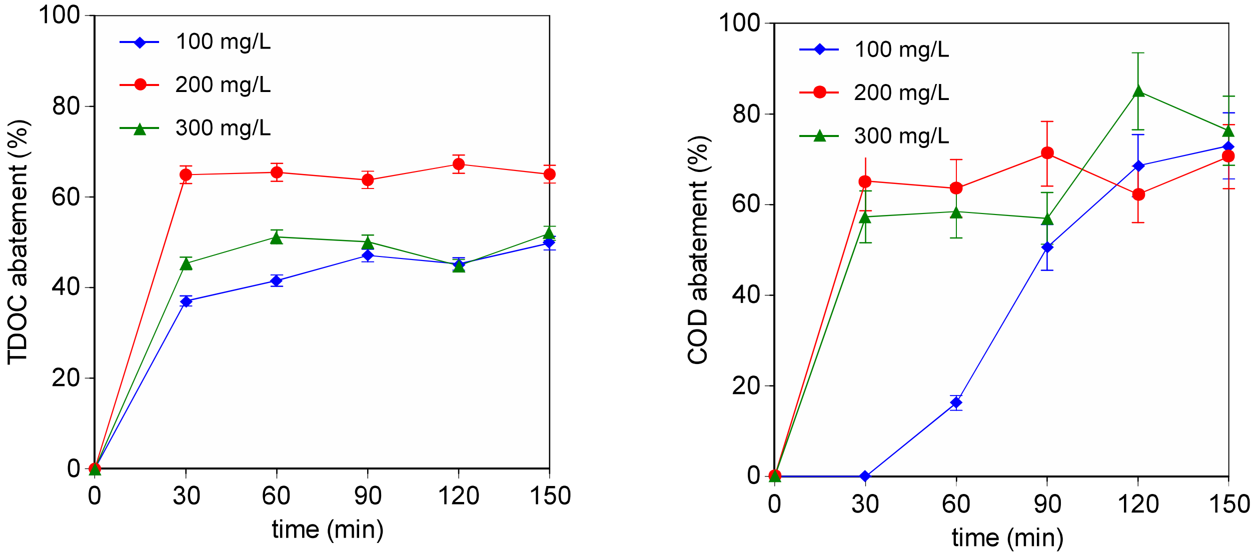


Figure 4. Effect of catalyst dose on TDOC and COD removal efficiencies (reaction condition: 70 °C, pH 5, H_2O_2 30 mL/L and reaction time 150 min).

The oxidant dose must be carefully optimized because, on the one hand, if the amount is too low, the reaction cannot proceed, on the other hand, if the quantity is too high, the process costs increase without any benefit of the treatment [66,68].

The effect of oxidant dose on the process efficiency in terms of TDOC abatement is depicted in Figure 5. When the heterogeneous Fenton process was carried out using the optimal dose of oxidant, i.e., 30 mL/L, the TDOC removal efficiency was 65% in the first 30 min and additional reaction times did not significantly increase the process efficiency. However, when the oxidant doses were increased to 40 and 50 mL/L, the observed TDOC abatements remained almost the same. These results suggest that the excess amounts of H_2O_2 scavenged part of the extra generated $^{\bullet}OH$ radicals and, consequently, no additional organic abatement could be achieved [69,70]. Due to the interference of hydrogen peroxide on the COD test, COD analysis for a high H_2O_2 dose was not performed.

Each reaction variable has an important effect on the catalytic activity of Cu/ZrO_2 catalyst. The evaluation of the optimal reaction conditions considers not only the TDOC and COD abatement but also the degree of mineralization/partial oxidation. A strong mineralization of organic compounds occurs at pH 5, while lower or higher pH values induce a greater formation of oxidized intermediates. A temperature of 70 °C is the best compromise between high mineralization and energy saving, indeed, for a lower temperature very low TDOC abatement was achieved (around 27%) with important formation of oxidized intermediates, while a higher temperature did not remarkably improve the activity in terms of TDOC and COD abatement and did not significantly affect the degree of mineralization/partial oxidation. When using 200 mg/L of catalyst, a maximum degree of mineralization was obtained while, for larger or smaller amounts, partial oxidation and formation of oxidized intermediates prevailed, a condition that is to be avoided. TDOC abatement was not significantly affected by oxidant dose and for this reason the lowest amount was chosen as the optimal reaction condition. Summarizing Cu/ZrO_2 exhibits higher activity when the following reaction conditions are applied: 70 °C, pH 5, 200 mg/L of catalyst, and 30 mL/L of H_2O_2.

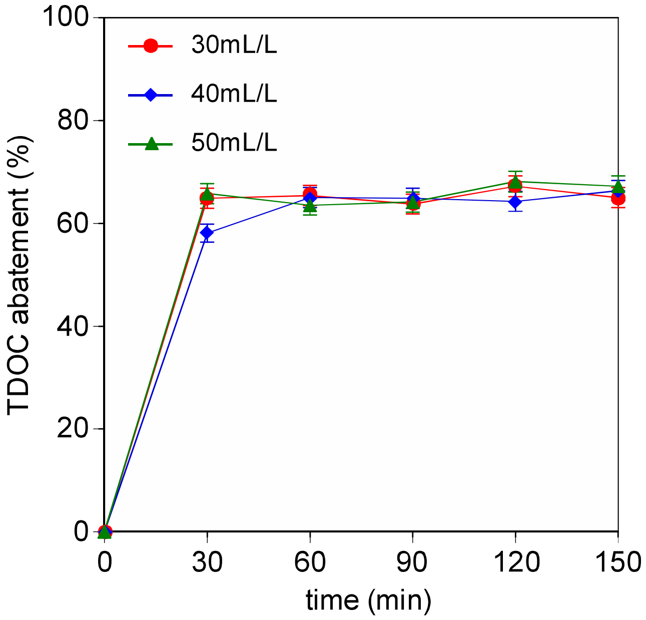


Figure 5. Dependence of process efficiency on oxidant dose (reaction condition: 70 °C, pH 5, catalyst dose 200 mg/L and reaction time 150 min).

A comparison with very recent literature results is quite difficult due to the different reaction conditions used and to the variability in landfill leachate characteristics such as the organic loading and the kind of compounds. If we compare the TOC and COD abatement for different Fenton processes, Cu/ZrO_2 catalyst proves to be a promising material, as shown in Table 2, with a TOC abatement of 65% and a COD removal of 70%, when the reaction is carried out at pH 5.

Table 2. Comparison with literature results.

Method	pH	TOC Abatement (%)	COD Abatement (%)	Ref
electro–Fenton	3	/	67	[71]
photo-Fenton	3	69	/	[72]
photo-Fenton	3	/	61	[73]
photo-electro Fenton	3	/	97	[74]
magnetic Fenton	/	75	/	[75]
homogeneous Fenton	3	74	98	[76]
homogeneous Fenton	2	/	87	[77]
homogeneous Fenton	3	/	61	[78]
heterogeneous Fenton	3	68	85	[79]
heterogeneous Fenton	5	65	70	This work
heterogeneous Fenton	3	56	/	[80]
heterogeneous Fenton	3	/	75	[81]

Heterogeneous [79–81], homogeneous [76–78] electro [71] or photo-Fenton [72–74] processes can be achieved, at pH 3, a TOC abatement in the range 56–75% and a COD removal of 61–98%. pH is a critical parameter, and it is important to assess Fenton's suitability for recalcitrant contaminants at circumneutral pH. Our catalyst shows TOC and COD abatements similar or slightly lower than other Fenton catalytic processes, but at near neutral pH, which is a significant improvement and a step forward in the development of this technology and in its application.

2.2. Two-Step Fenton-like Oxidation

Landfill leachate is a heavily polluted liquid waste, and it is possible that a single step treatment is not suitable to be integrated with the existing wastewater treatment facilities. A two-step oxidation is also necessary to monitor the extent of catalytic abatement of organics, i.e., whether the catalyst is able to further abate the organics or the maximum threshold of Fenton-like activity has been reached in the first step and the catalyst is unable to further degrade the secondary and tertiary organic metabolites. This is also very important because it gives an insight regarding the potentiality of the catalyst to completely mineralize all sort of organics in the Fenton-like process. Therefore, to increase the overall removal efficiency and enhance the mineralization/biodegradability of the liquid waste, a second oxidation step was also performed with standard operating conditions (Figure 6).

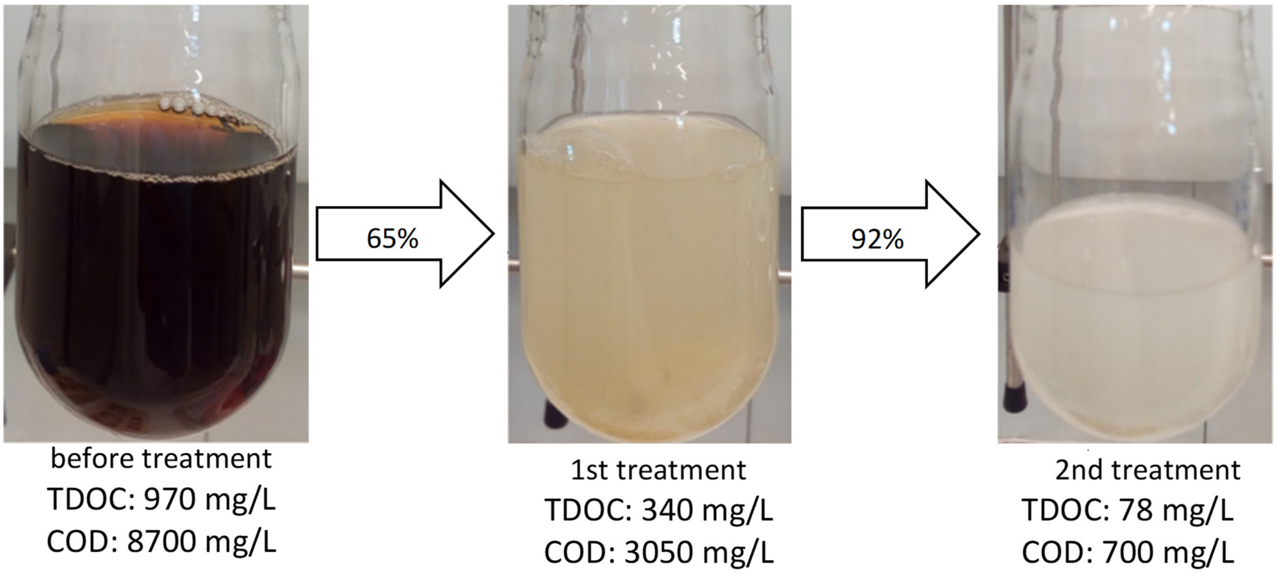


Figure 6. TDOC removal efficiency after 1st and 2nd treatments (reaction condition: 70 °C, pH 5, 200 mg/L of catalyst, H_2O_2 30 mL/L and reaction time 150 min).

When a two-step Fenton-like process was carried out, 92% of the TDOC was removed from the leachate. The result clearly suggests that the developed catalyst has the potential to reach nearly complete abatement of the organics through a series of simultaneous oxidation reactions depending upon the initial organic loading coming in the wastewater stream. Moreover, the leftover organics are likely to be small molecular weight carboxylic acids which can easily be treated through biological processes. Therefore, a two-step oxidation treatment is highly feasible in enhancing the biodegradability of the effluent followed by integration with a sewage treatment plant.

The promising activity of CuZr on landfill leachate degradation could be associated with its high reduction capacity at low temperature. As shown in previous studies [41,51], diverse CuO species are homogeneously dispersed over zirconia; these high reducible species can abate organics in landfill leachate through a radical mechanism which is often proposed in the literature for similar catalytic systems [82,83]. As copper shifts between the oxidized state (Cu^{2+}) and the reduced form Cu(0), the hydroxyl and perhydroxyl radicals can easily be produced through a Fenton-like redox process. The radical species are then responsible for the oxidation of organics in the leachate, according to the following radical mechanism reactions (S is the support and R is the organic compound):

$$\mathrm{S-Cu^{2+} + 2H_2O_2 \rightarrow S-Cu^0 + 2H^+ + 2HOO\bullet} \quad (3)$$

$$\mathrm{S-Cu^0 + 2H_2O_2 \rightarrow S-Cu^{2+} + 2OH^- + 2HO\bullet} \quad (4)$$

$$R + HOO\bullet \rightarrow R\bullet + H_2O_2 \quad (5)$$

$$R + HO\bullet \rightarrow R\bullet + H_2O \quad (6)$$

2.3. Catalytic Activity after Recycling

The recyclable nature of the catalyst in the Fenton-like process is considered as a valuable aspect for achieving the goal of environmental and economic sustainability [5]. To investigate the reusability of the catalyst, the recovered material was used without any pre-treatment, for subsequent reaction of oxidation of fresh leachate samples, keeping the rest of the process conditions the same. The effect of catalyst recycling on process effectiveness is outlined in Figure 7.

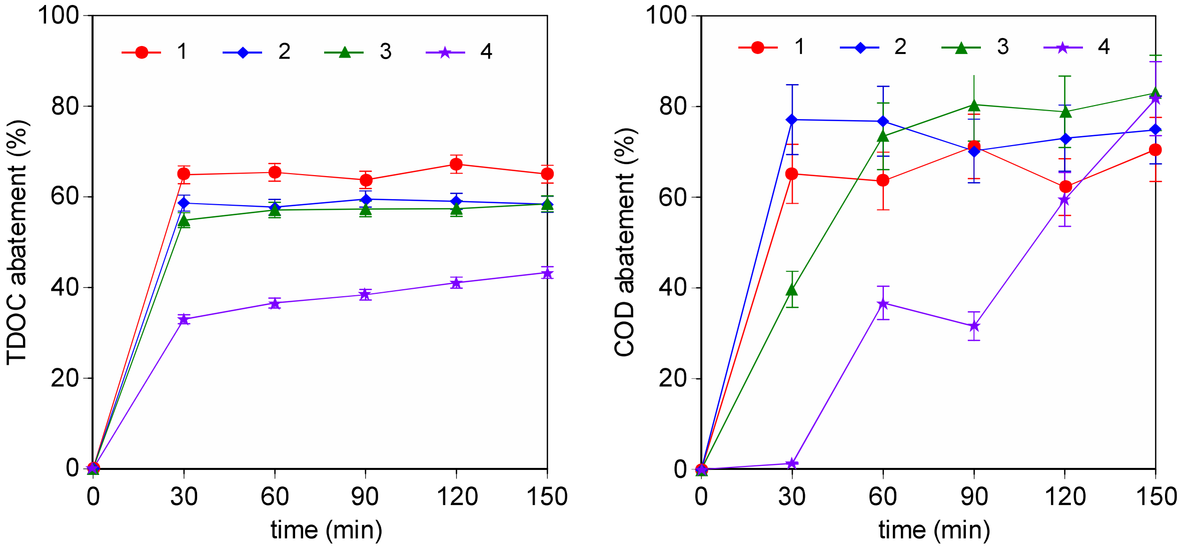


Figure 7. Effect of catalyst recycle on TDOC and COD abatements (reaction condition: 70 °C, pH 5, catalyst dose 200 mg/L, H_2O_2 dose 30 mL/L and reaction time 150 min).

The freshly employed catalyst afforded 65% of TDOC abatement in the first 30 min and later the process efficacy reached a plateau. In the 2nd and 3rd applications, the TDOC abatements slightly decreased to around 58% within 30 min., outlining no significant variation in the process efficiency. However, in the 4th cycle, the TDOC removal in the first 30 min markedly dropped to 33% and it gradually but moderately increased to 43% at the end of the Fenton reaction. This slight decline in the catalytic activity may be likely due to two phenomena [56,57]: on one side the leaching of copper from the catalyst surface (ca. 8% in every cycle), on the other the deposition of the organics over the surface which may have blocked the active sites. Overall, the catalyst experienced minimum copper loss, lower than 10% corresponding to 0.8 mg/L which is well below the guidelines of the Environmental Protection Agency (EPA) on the maximum limits of metals allowed to be released in treated water [84,85].

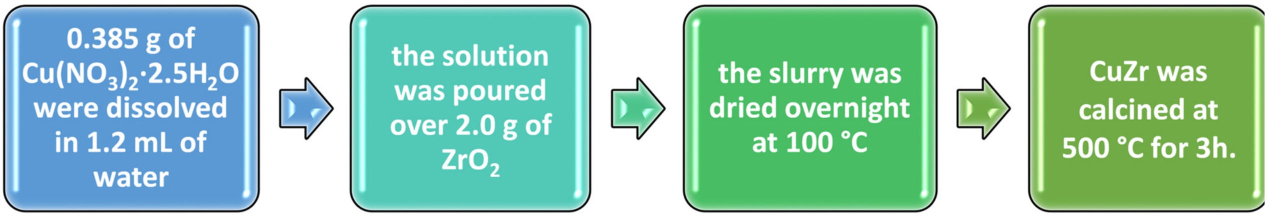
When fresh catalyst was employed in the heterogeneous Fenton process, the COD removal in 30 min was 65% and there was no significant fluctuation in the COD abatement until the end of the oxidation reaction. The second and third cycles of the catalyst yielded, respectively, 75% and 83% of COD abatement. A comparison of TOC and COD results suggests that in the second and third cycles the catalyst achieved a slightly lower degree of mineralization (ca. 58%) but was still able to induce a partial oxidation of organics in the landfill leachate, lowering the toxicity and increasing the biodegradability. In the fourth cycle the COD was negligible at 30 min, increased to 36% at 60 min and finally, at the end of the oxidation reaction, it reached 82%. These results indicate that the catalyst was still active, but it required a longer induction time to start the reaction. Summarizing, after 4 cycles the performance was definitely stable, indeed, TDOC decreased slightly from 65 to 58% at the second and third cycles and 43% at the fourth cycle, but COD abatement increased from 70 to 83%, indicating a strong ability of the material to maintain its activity for several cycles.

COS values (≥0 for all the cycles) indicate that the high oxidation degree of the landfill leachate over CuZr is maintained over several cycles, while a progressive increase of AOS suggests a modification on the ratios between total and partial oxidation of parent molecules (Figure 2D). After recycling, the catalyst activity is lower in terms of mineralization but is improved in terms of partial oxidation, indicating that CuZr is still active and is a very promising catalyst for Fenton-like oxidation of landfill leachate. These results indicate detoxification of the liquid waste after Fenton treatment, suggesting that the process can completely mineralize a part of the organic compounds and partially degrade other pollutants into less toxic molecules

3. Materials and Methods

3.1. Materials

Landfill leachate samples were collected from a landfill site located in Friuli Venezia Giulia, Italy. Samples were collected in polyethylene bottles, preserved at 4 °C and characterized by means of the Standard Methods for the Examination of Water and Wastewater [86]. Copper doped catalyst (5 wt%) was prepared by incipient wetness impregnation of ZrO_2 (MEL Chemicals) with an aqueous solution of copper (II) nitrate hemi pentahydrate (Sigma Aldrich). Briefly, for the preparation of copper-based catalyst (5 wt% Cu/ZrO_2), 0.385 g of $Cu(NO_3)_2 \cdot 2.5H_2O$ was dissolved in water (1.2 mL) and the solution was poured over 2 g of the support to reach the required amount of metal loading. After impregnation the material was dried overnight at 100 °C and calcined for 3 h at 500 °C (Scheme 1).



Scheme 1. Preparation of 5wt% Cu over ZrO_2.

3.2. Catalytic Activity Measurements

The suspended solids from landfill leachate were removed by centrifugation at 5000 rpm for an hour using an Eppendorf Centrifuge 5804 R, followed by filtration through a 0.45 µm membrane filter. The pH of the leachate samples was adjusted by the addition of H_2SO_4 (Sigma Aldrich). The leachate samples (100 mL) loaded with 200 mg/L of CuZr catalyst were heated at 70 °C under reflux and continuous stirring conditions (500 rpm), using a STEM Omni multistage reaction station (Electrothermal). Finally, 30 mL/L of H_2O_2 (3% w/w in H_2O) was added into the reaction system and the Fenton-like oxidation reaction was carried out for 150 min and the samples were collected after every 30 min of time interval to observe the periodic catalytic activity. Further, the oxidation process was optimized by evaluating the effects of catalyst dose (100, 200, and 300 mg/L), hydrogen peroxide (30, 40, and 50 mL/L), temperature (60, 70, and 80 °C), and pH (3, 5, and 8); the parameter range was selected in accordance with the results achieved in our previous study on ibuprofen abatement [41,51].

The catalyst was recovered and reused without any modification in subsequent reactions over new landfill leachate to investigate its stability. A two-step Fenton process was also performed by employing fresh catalyst in each oxidation step. The treated samples were centrifuged at 5000 rpm using an Eppendorf Centrifuge 5804 R for 10 min and the supernatant solutions were collected in vials for TDOC analysis.

Total dissolved organic carbon (TDOC) was used instead of Total organic carbon (TOC), because the suspended organic matter in the leachate may have affected the oxidation process. These disturbances mainly arose due to the deposition of suspended particles over the catalyst surface, hindering its activity as well as causing miscalculation of the oxidant dose needed to degrade pollutants from the leachate. Keeping in view these processing constraints and the need to precisely monitor the activity of the catalyst with varying parameters, TDOC was chosen as a standard process parameter. The TDOC removal efficiencies were determined using Equation (7):

$$\text{DOC removal efficiency }(\%) = \frac{\text{TDOC}_\text{i} - \text{TDOC}_\text{f}}{\text{TDOC}_\text{i}} \times 100 \tag{7}$$

The chemical oxygen demand (COD) was used to monitor the degradation of organic molecules. The COD removal efficiencies were calculated using Equation (8):

$$\text{COD removal efficiency }(\%) = \frac{\text{COD}_\text{i} - \text{COD}_\text{f}}{\text{COD}_\text{i}} \times 100 \tag{8}$$

COD and TDOC are expressed in mg O_2/L and mg C/L, respectively.

All the experiments were conducted in triplicate to verify the reproducibility of our activity measurements and the errors resulted were within 3% for TDOC and 10% for COD measurements.

To evaluate the degradation/mineralization degree of our treatment, AOS and COS were calculated using Equations (9) and (10) [54].

$$\text{AOS} = 4 - 1.5\frac{\text{COD}}{\text{TDOC}} \tag{9}$$

$$\text{COS} = 4 - 1.5\frac{\text{COD}}{\text{TDOC}_0} \tag{10}$$

TOC and COD are the values at the sampling time, while TDOC_0 is the value at the at the beginning of the experiment.

The concentration of heavy metals in landfill leachate was determined with the US EPA 3051 method using Inductivity Coupled Plasma–Atomic Emission Spectroscopy (ICP–AES vista pro.) First, a calibration curve was obtained using an ICP 23-element standard solution which was prepared in 5% HNO_3. Yttrium (Y) was used as an internal standard. The method detection limit (MDL) was calculated as 3 s/m (s = standard deviation of 10 replicate blanks and m = slope of the calibration curve for each element).

4. Conclusions

This study investigated the activity of copper-supported zirconia catalyst for the treatment of landfill leachate in a Fenton-like reaction. In addition to the investigation of process variables, the evaluation of the degradation/mineralization degree of our treatment was performed by means of AOS (average oxidation state) and COS (carbon oxidation state) parameters. These indicators are extremely important in the monitoring of the degree of oxidation and, for each investigated variable, the ratios between total and partial oxidation of parent molecules were obtained. Specifically, a high increase of COS and lower value of AOS suggests the prevalence of complete oxidation of the organics into CO_2 (mineralization), indicating a strong oxidation with low formation of oxidized intermediates. An optimized catalyst should maximize the treatment efficiency controlling the economics of the Fenton-like process. For these reasons, the investigation of the effect of several reaction variables on TDOC removal efficiencies evidenced that optimal conditions were achieved at 70 °C, pH 5 with 200 mg/L of catalyst, and 30 mL/L of H_2O_2.

CuZr is a very promising heterogeneous Fenton catalyst and can reduce 65% of the TDOC from a heavily polluted landfill leachate in a single step oxidation. A two-step Fenton process additionally reduced the organic loadings to 92%, thus making the final effluent more suitable for treatment through a sewage wastewater treatment plant. When optimal process conditions were applied, the complete oxidation of the organics into CO_2 (mineralization) prevailed on the partial oxidation into intermediates compounds. The good stability of CuZr catalyst under reaction conditions, as proved by recycling tests, confirmed the high attractiveness of copper systems supported on zirconia for the treatment of liquid waste. The findings of this study indicate that this process can also be evaluated for the treatment of other heavily polluted wastewater streams.

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References

1. Kulikowska, D.; Klimiuk, E. The effect of landfill age on municipal leachate composition. *Bioresour. Technol.* **2008**, *99*, 5981–5985. [CrossRef]
2. Li, L.; Fu, X.; Ai, J.; Zhou, H.; Zhang, W.; Wang, D.; Liu, Z. Process parameters study and organic evolution of old landfill leachate treatment using photo-Fenton-like systems: Cu^{2+} vs Fe^{2+} as catalysts. *Sep. Purif. Technol.* **2019**, *211*, 972–982. [CrossRef]
3. Li, W.; Zhou, Q.; Hua, T. Removal of Organic Matter from Landfill Leachate by Advanced Oxidation Processes: A Review. *Int. J. Chem. Eng.* **2010**, *2010*, 270532. [CrossRef]
4. Koshy, L.; Paris, E.; Ling, S.; Jones, T.; Bérubé, K. Bioreactivity of leachate from municipal solid waste landfills—Assessment of toxicity. *Sci. Total Environ.* **2007**, *384*, 171–181. [CrossRef] [PubMed]
5. Sruthi, T.; Gandhimathi, R.; Ramesh, S.; Nidheesh, P. Stabilized landfill leachate treatment using heterogeneous Fenton and electro-Fenton processes. *Chemosphere* **2018**, *210*, 38–43. [CrossRef] [PubMed]
6. Alvarez-Vazquez, H.; Jefferson, B.; Judd, S.J. Membrane bioreactors vs conventional biological treatment of landfill leachate: A brief review. *J. Chem. Technol. Biotechnol.* **2004**, *79*, 1043–1049. [CrossRef]
7. Deng, Y. Physical and oxidative removal of organics during Fenton treatment of mature municipal landfill leachate. *J. Hazard. Mater.* **2007**, *146*, 334–340. [CrossRef]
8. Primo, O.; Rueda, A.; Rivero, M.J.; Ortiz, I. An Integrated Process, Fenton Reaction−Ultrafiltration, for the Treatment of Landfill Leachate: Pilot Plant Operation and Analysis. *Ind. Eng. Chem. Res.* **2008**, *47*, 946–952. [CrossRef]
9. Abbas, A.A.; Jingsong, G.; Ping, L.Z.; Ya, P.Y.; Al-Rekabi, W.S. Review on Landfill Leachate Treatments. *Am. J. Appl. Sci.* **2009**, *6*, 672–684. [CrossRef]
10. Wu, J.J.; Wu, C.-C.; Ma, H.-W.; Chang, C.-C. Treatment of landfill leachate by ozone-based advanced oxidation processes. *Chemosphere* **2004**, *54*, 997–1003. [CrossRef]
11. Zang, C.; Hu, S.; Jin, S.; Chen, F. Catalytic Process Optimization of Birnessite-based Fenton-like Reaction with Surface Cu^{2+} Modification. *ChemCatChem* **2018**, *10*, 3576–3582. [CrossRef]
12. Wang, J.L.; Xu, L.J. Advanced Oxidation Processes for Wastewater Treatment: Formation of Hydroxyl Radical and Application. *Crit. Rev. Environ. Sci. Technol.* **2012**, *42*, 251–325. [CrossRef]
13. Aneggi, E.; Cabbai, V.; Trovarelli, A.; Goi, D. Potential of Ceria-Based Catalysts for the Oxidation of Landfill Leachate by Heterogeneous Fenton Process. *Int. J. Photoenergy* **2012**, *2012*, 1–8. [CrossRef]
14. Tarr, M.A. Fenton and Modified Fenton Methods for Pollutant Degradation. In *Chemical Degradation Methods for Wastes and Pollutants*; CRC Press: Boca Raton, FL, USA, 2003; pp. 159–190.
15. Vogelpohl, A.; Kim, S.M. Advanced oxidation processes (AOPs) in wastewater treatment. *J. Ind. Eng. Chem.* **2004**, *10*, 33–40.
16. Capodaglio, A.G. Critical Perspective on Advanced Treatment Processes for Water and Wastewater: AOPs, ARPs, and AORPs. *Appl. Sci.* **2020**, *10*, 4549. [CrossRef]
17. Ma, D.; Yi, H.; Lai, C.; Liu, X.; Huo, X.; An, Z.; Li, L.; Fu, Y.; Li, B.; Zhang, M.; et al. Critical review of advanced oxidation processes in organic wastewater treatment. *Chemosphere* **2021**, *275*, 130104. [CrossRef]
18. Torkashvand, J.; Kalantary, R.R.; Heidari, N.; Kazemi, Z.; Kazemi, Z.; Farzadkia, M.; Amoohadi, V.; Oshidari, Y. Application of ultrasound irradiation in landfill leachate treatment. *Environ. Sci. Pollut. Res.* **2021**, *28*, 47741–47751. [CrossRef]
19. Liao, Z.; Dai, S.; Long, S.; Yu, Y.; Ali, J.; Wang, H.; Chen, Z.; Chen, Z. Pd based in situ AOPs with heterogeneous catalyst of FeMgAl layered double hydrotalcite for the degradation of bisphenol A and landfill leachate through multiple pathways. *Environ. Sci. Pollut. Res.* **2018**, *25*, 35623–35636. [CrossRef]

20. Liu, Z.; Pan, L.; Hu, F.; Hu, Y. Advanced landfill leachate biochemical effluent treatment using Fe-Mn/AC activates O3/Na2S2O8 process: Process optimization, wastewater quality analysis, and activator characterization. *Environ. Sci. Pollut. Res.* **2020**, *27*, 15337–15349. [CrossRef]
21. Adityosulindro, S.; Julcour, C.; Riboul, D.; Barthe, L. Degradation of ibuprofen by photo-based advanced oxidation processes: Exploring methods of activation and related reaction routes. *Int. J. Environ. Sci. Technol.* **2021**, 1–14. [CrossRef]
22. Labrada, K.G.; Cuello, D.R.A.; Sánchez, I.S.; Batle, M.G.; Manero, M.-H.; Barthe, L.; Jáuregui-Haza, U.J. Optimization of ciprofloxacin degradation in wastewater by homogeneous sono-Fenton process at high frequency. *J. Environ. Sci. Heal. Part A* **2018**, *53*, 1139–1148. [CrossRef] [PubMed]
23. Adityosulindro, S.; Barthe, L.; González-Labrada, K.; Haza, U.J.J.; Delmas, H.; Julcour, C. Sonolysis and sono-Fenton oxidation for removal of ibuprofen in (waste)water. *Ultrason. Sonochem.* **2017**, *39*, 889–896. [CrossRef]
24. Pouran, S.R.; Raman, A.A.A.; Daud, W.M.A.W. Review on the application of modified iron oxides as heterogeneous catalysts in Fenton reactions. *J. Clean. Prod.* **2014**, *64*, 24–35. [CrossRef]
25. Garrido-Ramírez, E.; Theng, B.; Mora, M. Clays and oxide minerals as catalysts and nanocatalysts in Fenton-like reactions—A review. *Appl. Clay Sci.* **2010**, *47*, 182–192. [CrossRef]
26. Pliego, G.; Zazo, J.A.; Garcia, M.M.; Munoz, M.; Casas, J.A.; Rodriguez, J.J. Trends in the Intensification of the Fenton Process for Wastewater Treatment: An Overview. *Crit. Rev. Environ. Sci. Technol.* **2015**, *45*, 2611–2692. [CrossRef]
27. Sillanpää, M.; Ncibi, M.C.; Matilainen, A. Advanced oxidation processes for the removal of natural organic matter from drinking water sources: A comprehensive review. *J. Environ. Manag.* **2018**, *208*, 56–76. [CrossRef]
28. Bokare, A.D.; Choi, W. Review of iron-free Fenton-like systems for activating H_2O_2 in advanced oxidation processes. *J. Hazard. Mater.* **2014**, *275*, 121–135. [CrossRef] [PubMed]
29. González-Burciaga, L.A.; Núñez-Núñez, C.M.; Proal-Nájera, J.B. Challenges of TiO_2 heterogeneous photocatalysis on cytostatic compounds degradation: State of the art. *Environ. Sci. Pollut. Res.* **2021**, 1–24. [CrossRef]
30. Mirzaei, M.; Habibi, M.H.; Sabzyan, H. Synthesis, characterization, and dye degradation photocatalytic activity of the nano-size copper iron binary oxide. *Environ. Sci. Pollut. Res.* **2021**, *29*, 9173–9192. [CrossRef]
31. Aneggi, E.; Trovarelli, A.; Goi, D. Degradation of phenol in wastewaters via heterogeneous Fenton-like Ag/CeO 2 catalyst. *J. Environ. Chem. Eng.* **2017**, *5*, 1159–1165. [CrossRef]
32. Cardoso, I.M.F.; Cardoso, R.M.F.; da Silva, J.C.G.E. Advanced Oxidation Processes Coupled with Nanomaterials for Water Treatment. *Nanomaterials* **2021**, *11*, 2045. [CrossRef] [PubMed]
33. Hussain, S.; Aneggi, E.; Goi, D. Catalytic activity of metals in heterogeneous Fenton-like oxidation of wastewater contaminants: A review. *Environ. Chem. Lett.* **2021**, *19*, 2405–2424. [CrossRef]
34. Kezzim, A.; Boudjemaa, A.; Belhadi, A.; Trari, M. Photo-catalytic degradation of ibuprofen over the new semiconducting catalyst α-(Cu, Fe)$_2$O$_3$ prepared by hydrothermal route. *Res. Chem. Intermed.* **2017**, *43*, 3727–3743. [CrossRef]
35. Huang, Z.; Chen, Z.; Chen, Y.; Hu, Y. Synergistic effects in iron-copper bimetal doped mesoporous γ-Al_2O_3 for Fenton-like oxidation of 4-chlorophenol: Structure, composition, electrochemical behaviors and catalytic performance. *Chemosphere* **2018**, *203*, 442–449. [CrossRef] [PubMed]
36. Nieto-Juarez, J.I.; Pierzchła, K.; Sienkiewicz, A.; Kohn, T. Inactivation of MS2 coliphage in Fenton and Fenton-like systems: Role of transition metals, hydrogen peroxide and sunlight. *Environ. Sci. Technol.* **2010**, *44*, 3351–3356. [CrossRef]
37. Salazar, R.; Brillas, E.; Sirés, I. Finding the best Fe^{2+}/Cu^{2+} combination for the solar photoelectro-Fenton treatment of simulated wastewater containing the industrial textile dye Disperse Blue 3. *Appl. Catal. B Environ.* **2012**, *115*, 107–116. [CrossRef]
38. Chen, G.; Wu, G.; Li, N.; Lu, X.; Zhao, J.; He, M.; Yan, B.; Zhang, H.; Duan, X.; Wang, S. Landfill leachate treatment by persulphate related advanced oxidation technologies. *J. Hazard. Mater.* **2021**, *418*, 126355. [CrossRef]
39. Teng, C.; Zhou, K.; Zhang, Z.; Peng, C.; Chen, W. Elucidating the structural variation of membrane concentrated landfill leachate during Fenton oxidation process using spectroscopic analyses. *Environ. Pollut.* **2020**, *256*, 113467. [CrossRef]
40. Zhang, Z.; Teng, C.; Zhou, K.; Peng, C.; Chen, W. Degradation characteristics of dissolved organic matter in nanofiltration concentrated landfill leachate during electrocatalytic oxidation. *Chemosphere* **2020**, *255*, 127055. [CrossRef]
41. Hussain, S.; Aneggi, E.; Briguglio, S.; Mattiussi, M.; Gelao, V.; Cabras, I.; Zorzenon, L.; Trovarelli, A.; Goi, D. Enhanced ibuprofen removal by heterogeneous-Fenton process over Cu/ZrO_2 and Fe/ZrO_2 catalysts. *J. Environ. Chem. Eng.* **2020**, *8*. [CrossRef]
42. Subbulekshmi, N.; Subramanian, E. Nano CuO immobilized fly ash zeolite Fenton-like catalyst for oxidative degradation of p -nitrophenol and p -nitroaniline. *J. Environ. Chem. Eng.* **2017**, *5*, 1360–1371. [CrossRef]
43. Bradu, C.; Frunza, L.; Mihalche, N.; Avramescu, S.-M.; Neaţă, M.; Udrea, I. Removal of Reactive Black 5 azo dye from aqueous solutions by catalytic oxidation using CuO/Al_2O_3 and NiO/Al_2O. *Appl. Catal. B Environ.* **2010**, *96*, 548–556. [CrossRef]
44. Induja, S.; Raghavan, P. Catalytic efficiency of copper oxide in degradation of phenol using sintered calcium phosphate (SCaP) as catalyst support. *Catal. Commun.* **2013**, *33*, 7–10. [CrossRef]
45. Dong, J.; Tian, T.; Ren, L.; Zhang, Y.; Xu, J.; Cheng, X. CuO nanoparticles incorporated in hierarchical MFI zeolite as highly active electrocatalyst for non-enzymatic glucose sensing. *Colloids Surfaces B Biointerfaces* **2015**, *125*, 206–212. [CrossRef] [PubMed]
46. Liou, R.-M.; Chen, S.-H. CuO impregnated activated carbon for catalytic wet peroxide oxidation of phenol. *J. Hazard. Mater.* **2009**, *172*, 498–506. [CrossRef] [PubMed]

47. Sohrabnezhad, S.; Moghaddam, M.M.; Salavatiyan, T. Synthesis and characterization of CuO–montmorillonite nanocom-posite by thermal decomposition method and antibacterial activity of nanocomposite. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2014**, *125*, 73–78. [CrossRef] [PubMed]
48. Huo, C.; Ouyang, J.; Yang, H. CuO nanoparticles encapsulated inside Al-MCM-41 mesoporous materials via direct synthetic route. *Sci. Rep.* **2014**, *4*, 3682. [CrossRef]
49. Lu, Y.; Liu, X.; Qiu, K.; Cheng, J.; Wang, W.; Yan, H.; Tang, C.; Kim, J.-K.; Luo, Y. Facile Synthesis of Graphene-Like Copper Oxide Nanofilms with Enhanced Electrochemical and Photocatalytic Properties in Energy and Environmental Applications. *ACS Appl. Mater. Interfaces* **2015**, *7*, 9682–9690. [CrossRef]
50. Nasrollahzadeh, M.; Sajadi, S.M.; Rostami-Vartooni, A.; Bagherzadeh, M.; Safari, R. Immobilization of copper nanoparticles on perlite: Green synthesis, characterization and catalytic activity on aqueous reduction of 4-nitrophenol. *J. Mol. Catal. A Chem.* **2015**, *400*, 22–30. [CrossRef]
51. Hussain, S.; Aneggi, E.; Trovarelli, A.; Goi, D. Heterogeneous Fenton-like oxidation of ibuprofen over zirconia-supported iron and copper catalysts: Effect of process variables. *J. Water Process Eng.* **2021**, *44*, 102343. [CrossRef]
52. Zhang, H.; Choi, H.J.; Huang, C.-P. Optimization of Fenton process for the treatment of landfill leachate. *J. Hazard. Mater.* **2005**, *125*, 166–174. [CrossRef]
53. Mirzaee, S.A.; Jaafarzadeh, N.; Jorfi, S.; Gomes, H.T.; Ahmadi, M. Enhanced degradation of Bisphenol A from high saline polycarbonate plant wastewater using wet air oxidation. *Process Saf. Environ. Prot.* **2018**, *120*, 321–330. [CrossRef]
54. Arques, A.; Amat, A.M.; García-Ripoll, A.; Vicente, R. Detoxification and/or increase of the biodegradability of aqueous solutions of dimethoate by means of solar photocatalysis. *J. Hazard. Mater.* **2007**, *146*, 447–452. [CrossRef]
55. Rouidi, L.M.; Maurício, R.; Boukhrissa, A.; Ait-Amar, H.; Balamane, O. Characterization and treatment of landfill leachates by electro-Fenton process: A case study in Algeria. *Water Environ. Res.* **2020**, *92*, 123–137. [CrossRef]
56. Laiju, A.R.; Sivasankar, T.; Nidheesh, P.V. Iron-loaded mangosteen as a heterogeneous Fenton catalyst for the treatment of landfill leachate. *Environ. Sci. Pollut. Res.* **2014**, *21*, 10900–10907. [CrossRef] [PubMed]
57. Xavier, S.; Gandhimathi, R.; Nidheesh, P.V.; Ramesh, S.T. Comparison of homogeneous and heterogeneous Fenton processes for the removal of reactive dye Magenta MB from aqueous solution. *Desalination Water Treat.* **2015**, *53*, 109–118. [CrossRef]
58. Choina, J.; Kosslick, H.; Fischer, C.; Flechsig, G.-U.; Frunza, L.; Schulz, A. Photocatalytic decomposition of pharmaceutical ibuprofen pollutions in water over titania catalyst. *Appl. Catal. B Environ.* **2013**, *129*, 589–598. [CrossRef]
59. Xu, H.-Y.; Liu, W.-C.; Qi, S.-Y.; Li, Y.; Zhao, Y.; Li, J.-W. Kinetics and optimization of the decoloration of dyeing wastewater by a schorl-catalyzed Fenton-like reaction. *J. Serb. Chem. Soc.* **2014**, *79*, 361–377. [CrossRef]
60. Hashemian, S. Fenton-Like Oxidation of Malachite Green Solutions: Kinetic and Thermodynamic Study. *J. Chem.* **2013**, *2013*, 809318. [CrossRef]
61. Ifelebuegu, A.O.; Ezenwa, C.P. Removal of Endocrine Disrupting Chemicals in Wastewater Treatment by Fenton-Like Oxidation. *Water Air Soil Pollut.* **2011**, *217*, 213–220. [CrossRef]
62. Xu, H.-Y.; Prasad, M.; Liu, Y. Schorl: A novel catalyst in mineral-catalyzed Fenton-like system for dyeing wastewater discol-oration. *J. Hazard. Mater.* **2009**, *165*, 1186–1192. [CrossRef] [PubMed]
63. Munoz, M.; Pliego, G.; De Pedro, Z.M.; Casas, J.A.; Rodriguez, J.J. Application of intensified Fenton oxidation to the treatment of sawmill wastewater. *Chemosphere* **2014**, *109*, 34–41. [CrossRef] [PubMed]
64. Wang, J.; Zhuan, R. Degradation of antibiotics by advanced oxidation processes: An overview. *Sci. Total Environ.* **2020**, *701*, 135023. [CrossRef] [PubMed]
65. Nidheesh, P.V.; Gandhimathi, R.; Ramesh, S.T. Degradation of dyes from aqueous solution by Fenton processes: A review. *Environ. Sci. Pollut. Res.* **2013**, *20*, 2099–2132. [CrossRef]
66. Wang, N.; Zheng, T.; Zhang, G.; Wang, P. A review on Fenton-like processes for organic wastewater treatment. *J. Environ. Chem. Eng.* **2016**, *4*, 762–787. [CrossRef]
67. Qi, Y.; Mei, Y.; Li, J.; Yao, T.; Yang, Y.; Jia, W.; Tong, X.; Wu, J.; Xin, B. Highly efficient microwave-assisted Fenton degradation of metacycline using pine-needle-like $CuCo_2O_4$ nanocatalyst. *Chem. Eng. J.* **2019**, *373*, 1158–1167. [CrossRef]
68. Gan, P.P.; Li, S.F.Y. Efficient removal of Rhodamine B using a rice hull-based silica supported iron catalyst by Fenton-like process. *Chem. Eng. J.* **2013**, *229*, 351–363. [CrossRef]
69. Panda, N.; Sahoo, H.; Mohapatra, S. Decolourization of Methyl Orange using Fenton-like mesoporous Fe_2O_3–SiO_2 composite. *J. Hazard. Mater.* **2011**, *185*, 359–365. [CrossRef]
70. Jiang, C.; Pang, S.; Ouyang, F.; Ma, J.; Jiang, J. A new insight into Fenton and Fenton-like processes for water treatment. *J. Hazard. Mater.* **2010**, *174*, 813–817. [CrossRef]
71. He, Z.; Liu, Y.; Wang, J.; Lv, Y.; Xu, Y.; Jia, S. Enhanced degradation of old landfill leachate in heterogeneous electro–Fenton catalyzed using Fe_3O_4 nano–particles encapsulated by metal organic frameworks. *J. Clean. Prod.* **2021**, *321*, 128947. [CrossRef]
72. Makhatova, A.; Mazhit, B.; Sarbassov, Y.; Meiramkulova, K.; Inglezakis, V.J.; Poulopoulos, S.G. Effective photochemical treatment of a municipal solid waste landfill leachate. *PLoS ONE* **2020**, *15*, e0239433. [CrossRef]
73. Poblete, R.; Perez, N. Use of sawdust as pretreatment of photo-Fenton process in the depuration of landfill leachate. *J. Environ. Manag.* **2019**, *253*, 109697. [CrossRef] [PubMed]

74. Asaithambi, P.; Govindarajan, R.; Yesuf, M.B.; Alemayehu, E. Removal of color, COD and determination of power consumption from landfill leachate wastewater using an electrochemical advanced oxidation processes. *Sep. Purif. Technol.* **2020**, *233*, 115935. [CrossRef]
75. Gallo-Cordova, A.; Castro, J.J.; Winkler, E.L.; Lima, E.; Zysler, R.D.; Morales, M.D.P.; Ovejero, J.G.; Streitwieser, D.A. Improving degradation of real wastewaters with self-heating magnetic nanocatalysts. *J. Clean. Prod.* **2021**, *308*, 127385. [CrossRef]
76. Durai, N.J.; Gopalakrishna, G.V.T.; Padmanaban, V.C.; Selvaraju, N. Oxidative removal of stabilized landfill leachate by Fenton's process: Process modeling, optimization & analysis of degraded products. *RSC Adv.* **2020**, *10*, 3916–3925. [CrossRef]
77. Dantas, E.R.B.; Silva, E.J.; Lopes, W.S.; Nascimento, M.R.D.; Leite, V.D.; de Sousa, J.T. Fenton treatment of sanitary landfill leachate: Optimization of operational parameters, characterization of sludge and toxicology. *Environ. Technol.* **2019**, *41*, 2637–2647. [CrossRef]
78. Mahtab, M.S.; Islam, D.T.; Farooqi, I.H. Optimization of the process variables for landfill leachate treatment using Fenton based advanced oxidation technique. *Eng. Sci. Technol. Int. J.* **2021**, *24*, 428–435. [CrossRef]
79. Niveditha, S.; Gandhimathi, R. Flyash augmented Fe_3O_4 as a heterogeneous catalyst for degradation of stabilized landfill leachate in Fenton process. *Chemosphere* **2020**, *242*, 125189. [CrossRef]
80. Wang, F.; Gu, Z.; Hu, Y.; Li, Q. Split dosing of H_2O_2 for enhancing recalcitrant organics removal from landfill leachate in the Fe0/H_2O_2 process: Degradation efficiency and mechanism. *Sep. Purif. Technol.* **2021**, *278*, 119564. [CrossRef]
81. Taşcı, S.; Özgüven, A.; Yıldız, B. Multi-Response/Multi-Step Optimization of Heterogeneous Fenton Process with Fe_3O_4 Catalyst for the Treatment of Landfill Leachate. *Water Air Soil Pollut.* **2021**, *232*, 1–19. [CrossRef]
82. Sun, Y.; Tian, P.; Ding, D.; Yang, Z.; Wang, W.; Xin, H.; Xu, J.; Han, Y.-F. Revealing the active species of Cu-based catalysts for heterogeneous Fenton reaction. *Appl. Catal. B Environ.* **2019**, *258*, 117985. [CrossRef]
83. Sun, B.; Li, H.; Li, X.; Liu, X.; Zhang, C.; Xu, H.; Zhao, X.S. Degradation of Organic Dyes over Fenton-Like Cu2O–Cu/C Catalysts. *Ind. Eng. Chem. Res.* **2018**, *57*, 14011–14021. [CrossRef]
84. EPA United States Environmental Protection Agency. Clean Water Act. Available online: https://www.epa.gov/laws-regulations/summary-clean-water-act (accessed on 6 June 2021).
85. European Council. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 Establishing a Frame-Work for Community Action in the Field of Water Policy. Available online: https://eur-lex.europa.eu/eli/dir/2000/60/oj (accessed on 6 June 2021).
86. APHA; AWWA; WEF. *Standard Methods for the Examination of Water and Wastewater*, 20th ed.; American Public Health Association, American Water Works Association, Water Environment Federation: Washington, DC, USA, 1999.