

Steel Scale Waste as a Heterogeneous Fenton-like Catalyst for the Treatment of Landfill Leachate

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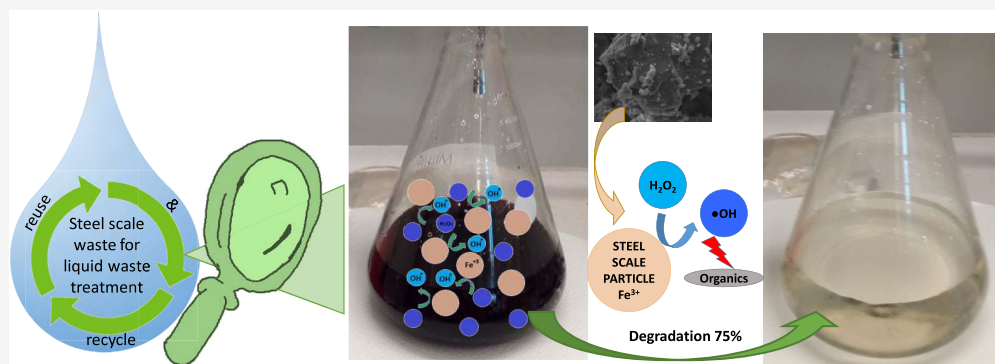
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ABSTRACT: Sustainable industrial processes are essential for better economic growths and for the conservation of the environment. Steel scale waste (SSW) is a byproduct of steel production containing oxides in a large quantity; presently, it is mainly disposed off to landfill. However, being a rich iron source, it appears attractive for processes based on Fenton technology that is catalyzed by iron species. This study originates from the idea of exploiting waste (steel waste) to be used in the treatment of liquid waste, in the perspective of more sustainable processes within a circular economy. Herein, we have employed steel scale waste as a heterogeneous Fenton-like catalyst for the treatment of landfill leachate, changing its profile from a waste to a reagent. To the best of our knowledge, this study is the first attempt to utilize steel scale for the treatment of landfill leachate. At mild conditions, SSW successfully removed about 75% of the recalcitrant organic loading from landfill leachate. This study highlighted that SSW is a promising material for the treatment of heavily polluted wastewater streams. These findings appear extremely important in a circular economy perspective because steel scale waste is produced in huge quantities and could be effectively used as a catalyst in a highly polluted liquid waste treatment process.

1. INTRODUCTION

A large amount of nonbiodegradable and nonrecyclable solid waste ends up in landfills worldwide every year.¹ However, landfills produce large volumes of leachate when rainwater runs through these sites. The characteristics of leachate may vary depending upon the leachate age, landfill site, solid waste, and climate.^{2,3} Landfill leachate is a very complex liquid waste mainly consisting of refractory organics, heavy metals, ammoniacal nitrogen, and chlorides.^{4–6} Discharge of untreated landfill leachate may cause serious environmental pollution of soil and water bodies.^{7,8} Currently, stringent legislation prohibits the direct discharge of leachate either to the sewage treatment plant or to the environment and a rigorous treatment is mandatory to meet the environmental guidelines.^{2,5,9} Biological treatment of landfill leachate would be an ideal process, considering its simplicity and economic feasibility. However, biological processes are not effective in the treatment of landfill leachate due to its high loading of refractory organics.^{10–12} On the other hand, physical processes merely offer separation of the pollutants, and afterward, a

highly concentrated polluted stream must be dealt with, giving rise to another environmental hazard.^{13,14} Some authors have proposed adsorption as an efficient treatment of colored wastewater^{15,16} but the main drawback of this technique is that organics are not degraded. In this work, we aim to obtain not only the contaminant removal from a liquid waste, but to achieve the degradation/mineralization of the organics to reduce the environmental issue related to highly refractory compounds. In this light, advanced oxidation processes (AOPs) are environmentally friendly and efficient in the abatement of pollutants from liquid streams.^{17,18} In last few decades, advanced oxidation processes have gained enormous

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acceptability among the research community for the treatment of liquid waste due to their efficiency to mineralize organic compounds, enhancing their biodegradability.¹⁹ All AOPs are essentially based on a core mechanism of organic abatement through generation and utilization of hydroxyl radicals. In recent decades, the Fenton reaction using Fe(II) species in the presence of an oxidant, has gained special attention due to the high process efficiency, simplicity, and nontoxic reagents.^{5,19–23} However, there are some drawbacks such as severe acidic conditions of the process and the generation of large volumes of iron sludge, which eventually require separation from the liquid and disposal, creating an additional environmental problem.^{24,25} To mitigate the processing constraints of the homogeneous Fenton reaction, the heterogeneous Fenton-like process harnessing Fe(III) or other transition metals as catalysts has successfully been used for the liquid waste treatment.^{26–40} The Fenton-like process better performs with respect to the traditional Fenton reaction but preparation of heterogeneous catalysts requires additional resources and effort.^{41,42} Moreover, the overall cost for the liquid waste treatment increases, making the process less convenient. Also, during the Fenton-like process, the catalysts may be deactivated, poisoned, and may lose activity due to the metal leaching. From a sustainability standpoint, it is critical that such materials are readily available, cost effective, and reduce the overall environmental stress.⁴³

Steel scale wastes (SSWs), one of the byproducts of steel production, is formed on the surface of steel monoliths during their high-temperature thermal treatments, which are made after casting to improve steel microstructures and properties. SSW contains iron oxides and minor fractions of other metal oxides as a function of steel composition; it is generally called “calamine” by the metallurgists and is presently mainly disposed off to landfill. Disposal of large volumes of metallic solid waste may disturb the environmental balance of soil and groundwater; however, it was recently proposed by several authors^{44–48} as a component for the production of counterweight mortars or concretes, due to its high specific gravity.

In addition, SSW is rich in iron content and therefore could be used as a heterogeneous catalyst for the treatment of liquid waste. This concept of using solid waste for liquid waste treatment is very important to achieve the goals of sustainable growth and waste minimization. In a similar approach, in recent years, SSW showed good performances for the removal of heavy metals,⁴⁹ phosphates,⁵⁰ dyes,⁵¹ and model pollutants from wastewaters.⁵² In this research, we investigated the catalytic ability of steel scale waste as a possible heterogeneous Fenton-like catalyst for the treatment of a complex liquid waste such as leachate under variable conditions of SSW dose, pH, temperature, and oxidant dose. In addition, its catalytic activity in a second phase use was also investigated.

The novelty of this work consists in the conversion of a waste (SSW) into a valuable product, i.e., an extremely efficient catalyst for the treatment of liquid waste by Fenton-like technology. This research highlights the oxidation capacity of SSW for the low-cost treatment of heavily polluted liquid waste, opening a new perspective in circular economy. To the best of authors' knowledge, this study is the first attempt to utilize SSW for the treatment of landfill leachate.

2. EXPERIMENTAL SECTION

2.1. Materials. Steel scale waste used in this study as a Fenton-like catalyst is produced by a foundry process in a

steelmaking industry placed in the Friuli-Venezia Giulia region (North-East of Italy); SSW derives from the production of Hadfield steel (high manganese steel). The leachate used in this research was drawn from an aged landfill near the city of Udine (North-East of Italy). All of the chemicals used in the present study, H₂O₂ (35%), NaOH (99.0%), and H₂SO₄ (98%), are from Sigma-Aldrich.

2.2. Methods. **2.2.1. Textural and Morphological Characterization of SSW.** Textural characteristics of SSW were measured according to the BET method by nitrogen adsorption at -196 °C, using a Tristar 3000 gas adsorption analyzer (Micromeritics).

Structural features were characterized by X-ray diffraction (XRD). XRD profiles were recorded on a Philips X'Pert diffractometer (equipped with a real-time multiple strip detector) operated at 40 kV and 40 mA using Ni-filtered Cu K α radiation. Spectra were collected using a step size of 0.02° and a counting time of 20 s per angular abscissa in the range 20–80°. The Philips X'Pert HighScore software was used for phase identification.

The powder morphology has been observed by field-emission scanning electron microscopy (SEM, JEOL model JSM-7610FPlus). The specimens have been coated by a thin gold layer by sputtering prior to the observations. The observations have been performed in secondary electron mode using an acceleration voltage of 5 keV. The chemical composition was determined by the energy-dispersive X-ray spectroscopy (EDXS) (Oxford Instruments X-Max 20) analysis using a Quant Standardization of 5 keV.

2.2.2. Adsorption Tests. First, SSWs are ground and sieved into four different particle sizes, namely, raw, 350, 200, and 100 μ m. Second, SSWs were added into the landfill leachate, stirred for 2 h at 25 °C as well as at 70 °C to observe the adsorption behaviors. Moreover, the steel scale was washed with distilled water and acidic distilled water to monitor the change in total organic carbon (TOC).

2.2.3. Microwave-Irradiated Acid Solubilization of SSW. First, 0.3 g of SSW in triplicates was directly transferred into Teflon tubes followed by the addition of 8 mL of HNO₃ (69%, Carlo Erba chemicals) and 2 mL of HCl (37%, Sigma-Aldrich). The samples were heated at 185 °C using microwave irradiation for 1 h (Milestone Ethos Easy). The samples were left to cool and later transferred to a glass flask and volume was brought to 20 mL by ultrapure water. The samples were left to stabilize for 24 h. The stabilized samples were filtered through 0.20 μ m poly(tetrafluoroethylene) (PTFE) filters and diluted 1:10 using ultrapure water (U.S. EPA 3051).

2.2.4. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) Analysis. The metallic composition of SSW and concentration of heavy metals in landfill leachate were determined according to the U.S. EPA 3051 method using inductively coupled plasma-atomic emission spectroscopy (ICP-AES Agilent 5800). First, a calibration curve was obtained using an ICP 23-element standard solution (Merk IV), which was prepared in 5% HNO₃. Yttrium (Y), 1 mg/L, was used as an internal standard. The method detection limit (MDL) was calculated as $3s/m$, where s is the standard deviation of 10 replicate blanks and m is the slope of the calibration curve for each element.

2.2.5. Fenton-like Oxidation. 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 μ m membrane filter. The pH of the

leachate samples was adjusted by the addition of NaOH or H₂SO₄ (Sigma-Aldrich), and an optimum pH for maximum catalytic activity was experimentally determined before conducting the standard experiments. The leachate samples (100 mL) loaded with 1 g/L of SSW with variable particle sizes were heated at 70 °C under reflux and continuous stirring conditions at 500 rpm, using an Omni Multistage Reaction Station. Finally, 30 mL/L of hydrogen peroxide (H₂O₂) was added into the reaction system and the Fenton-like oxidation reaction was carried out for 150 min collecting samples every 30 min to determine the catalytic activity dependence over time. Additionally, the oxidation process was optimized evaluating the effect of catalyst dose (0.1–2 g/L), hydrogen peroxide (10–60 mL/L), temperature (20–70 °C), SSW particle size (50–350 μm), and pH (2–9). Catalytic activity of recycled steel scale was also investigated, and the percentage of residual hydrogen peroxide was determined in each cycle. The treated samples were centrifuged at 5000 rpm using Eppendorf Centrifuge 5804 R for 10 min and the supernatant solutions were collected for TOC analysis.

2.2.6. TOC Analysis. The organic content of the raw leachate and treated samples was analyzed using a TOC-VCPN, Shimadzu Analyzer (V-series) with an auto sampler. First, the standard solutions with known concentrations of 2.5, 5.0, 10.0, and 20.0 mg C/L were prepared using potassium hydrogen phthalate stock solution. A calibration curve was obtained by analyzing the standard samples, and after each analysis, the injection syringe was auto sparged with 2 M HCl. The samples were analyzed without dilution and using the same calibration curve to determine TOC present in each sample. Several experiments were also carried out to verify the reproducibility of our activity measurements and the errors resulted to be within 3%.

3. RESULTS AND DISCUSSION

3.1. Characterization of Steel Scale. Surface area measurements on the different SSW fractions (100, 200, 350 μm, and raw sample) evidenced that SSW particles are nonporous materials; for all fractions, an almost zero surface area was found, in agreement with the SEM investigation. The structural features of the SSW (Figure 1) were analyzed using powder X-ray diffraction (XRD). Although the XRD patterns show a high background noise as a consequence of the great

amount of iron, which causes fluorescence phenomena, it is observed that all of the SSW fractions simultaneously contain wustite (FeO, main reflection at 41.7°), hematite (Fe₂O₃, main reflection at 33.2°), and magnetite (Fe₃O₄, main reflection at 35.2°). Reflections are more intense for the fraction with a lower particle size, reasonably due to a higher number of particles per weight unit.

The SEM analysis of raw steel scale depicted a rather homogeneous morphology with the presence of little and scattered clusters laying over a compact solid surface (Figure 2).

As shown in Figure S1, the global material consists of a series of aggregates. The morphology of SSW is modified by the Fenton treatment. After application in Fenton-like oxidation, SSW revealed a more heterogeneous morphology and particles containing cavities on their surface, indicating that part of the solid composite has been lost during the oxidation reaction (Figure 2). The appearance of cavities after Fenton-like oxidation could be probably due to the loss of some components of the original starting material such as aluminum, magnesium, silicon and calcium-based components,⁵² which derive from the steel and are present in the SSW as trace oxides.

The elemental composition of SSW, determined using the energy-dispersive spectrometry (EDS) analysis (Table 1) revealed a very high content of Fe (55–68%) and Mn (8–14%), with traces of other elements, Si, Al, Ca, and Mg. After application in Fenton-like oxidation, a slight decrease of Fe (39–57%) and Mn (7–10%) is observed, due to their release during the oxidation reaction. In perfect agreement with SEM images, the elemental analysis obtained by EDS shows a significant decrease of Al, Ca, Mg, and Si after the Fenton reaction, confirming their removal during the process with the formation of cavities in the structure. The metallic composition of SSW has also been obtained through acid solubilization followed by microwave irradiation and finally ICP analysis of the extract; Fe and Mn are confirmed to be the main components of the steel scale, as expected (Table S1).

3.2. Effect of Adsorption. Preliminary blank tests were carried out. Landfill leachate conversion was negligible (14% of total dissolved organic carbon (TDOC) abatement) in the absence of the catalyst when H₂O₂ was used at 70 °C. In the absence of the catalyst, the Fenton reaction cannot take place and the TOC abatement is definitely low. This is in agreement with the metallic composition of landfill leachate (obtained by ICP analysis) that evidenced a very low amount of iron (Table S2). This amount is not sufficiently high to catalyze the homogeneous reaction and, to degrade the organic loading, a heterogeneous catalyst is required. The aim of the process is the degradation of organics in the landfill leachate and not only their removal by mere adsorption; for this reason, the evaluation of the adsorption capacity on the material is fundamental. The adsorption capacity of SSW for TOC removal from landfill leachate was investigated at 25 and 70 °C, over four different particle sizes, namely, raw, 100, 200, and 350 μm and the results are presented in Figure 3. It is evident that regardless of the temperature, 25 or 70 °C, the influence of the particle size on the adsorption behavior of SSW is negligible, as the TOC removal is almost the same, i.e., in the narrow range of 5–15%. These results indicate that SSW has a very little capacity to remove organics through adsorption so that TOC is mainly removed through heterogeneous Fenton-

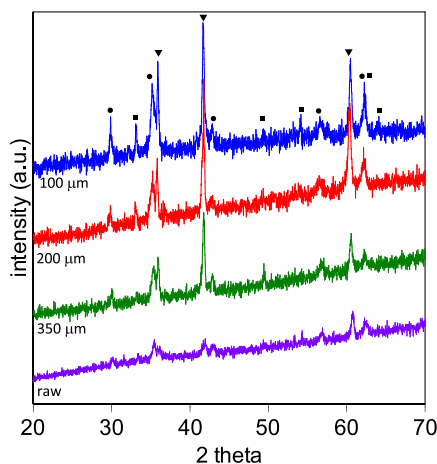


Figure 1. XRD profiles of the SSW fractions (▼, FeO; ■, Fe₂O₃; ●, Fe₃O₄).

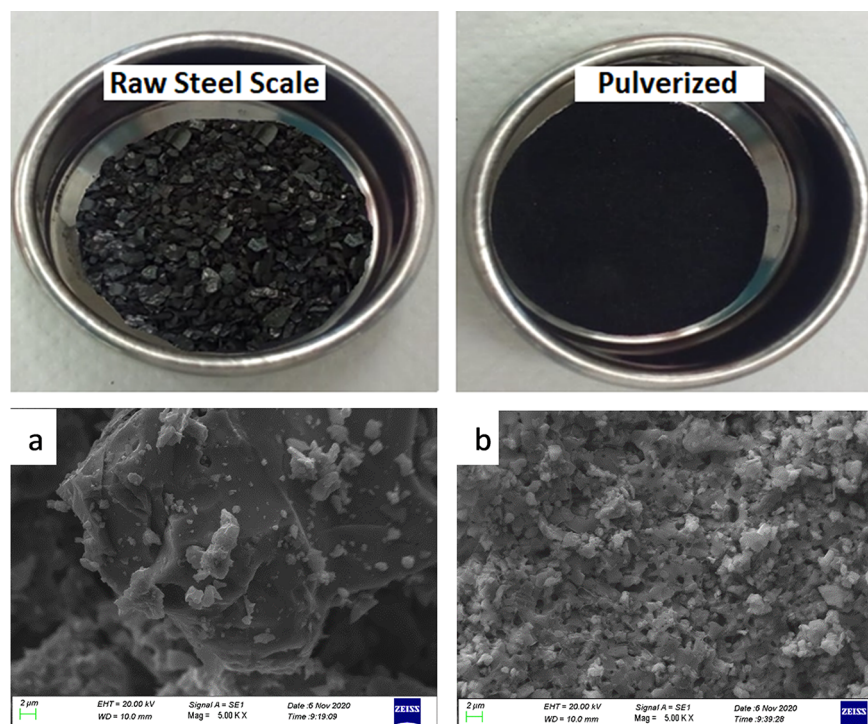


Figure 2. Raw, pulverized, and SEM micrographs (5k \times magnification) of SSW before (a) and after (b) application in Fenton-like oxidation.

Table 1. Elemental Composition of SSW Measured through EDS

element	Fe (%)	Mn (%)	C (%)	Si (%)	Al (%)	Ca (%)	Mg (%)
before	55–68	8–14	0	0–3.5	0–1.7	0–0.8	0.8–1.0
after	39–57	7–10	15	0.5	0	0	0

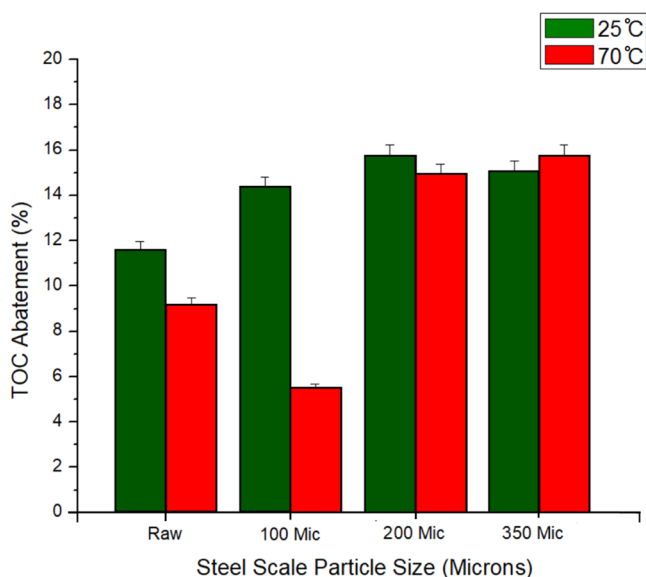


Figure 3. Effect of SSW particle size and temperature over adsorptive removal of TOC.

like oxidation. This behavior is directly related to the very low surface area of the samples.

3.3. Effect of Steel Scale Particle Size. The size of the steel scale particles can significantly affect the efficacy of the Fenton-like oxidation. Therefore, the effect of particle sizes of steel scale over the overall oxidation efficiency has been investigated (Table 2). Initially, when SSW with very fine

Table 2. Effect of SSW Particle Size and Catalyst Dose on TOC Abatement Efficiencies^a

particle size (μm)	landfill leachate TOC abatement (%)	catalyst dose (mg/L) ^b	landfill leachate TOC abatement (%)	IBP TOC abatement (%)
50	50	0.1	32	80
100	75	0.2	41	81
150	67	0.5	63	88
200	63	0.75	59	88
250	63	1	75	86
300	56	1.5	70	86
350	53	1.75	70	85
raw	51	2	68	84

^aReaction conditions: pH 3, catalyst dose—1 g/L, H₂O₂ dose—40 mL/L (3%), temperature—70 °C, and reaction time—150 min.

^bExperiments have been carried out over steel scale with a particle size of 100 μm .

particle size, i.e., 50 μm , is used, only 50% of the TOC has been abated. On the contrary, when the particle size is doubled, i.e., 100 μm , the efficacy of the Fenton-like oxidation is increased to 75%. When larger particle sizes, from 150 μm to raw SSW, are used, the organic abatement progressively declined from 67 to 51%, respectively.

These results indicate that although in the 50 μm fraction, the number of particles per unit of weight is much higher, there is a tendency to form clusters with a consequent lower process efficiency (Figure S2).⁵³

This agglomeration behavior of the fine particles may also become prominent when the liquid phase imparts wettability

to the particles. However, an optimal size distribution of particles, i.e., 100 μm , minimizes the probability of agglomeration, exposing maximum of its active sites (higher number of particles per unit of weight) and thus yielding better catalytic activity. On the other hand, further enlargement of particles may have better suppressed the agglomeration phenomenon, but the number of particles per unit of weight progressively decreases, resulting in a continuous decline of the TOC abatements.⁵⁴

3.4. Effect of Steel Scale Dose. Although SSW is an industrial waste, catalyst dose optimization remains a critical factor not only to afford maximum process efficiency but also to minimize the overall cost of Fenton-like oxidation. To investigate the optimal catalyst loading, variable SSW doses have been tested for the treatment of landfill leachate and the results are illustrated in Table 2. It is evident that by working with smaller catalyst doses, i.e., 0.1 and 0.2 g/L, only 32 and 41% of TOC abatements are obtained, respectively. These results indicate that the SSW loadings are too little to decompose all of the oxidants into OH^\bullet because the overall number of available active sites is low for a sufficient OH^\bullet generation.⁵⁵ In addition, when steel scale loadings are further increased up to 1 g/L, Fenton-like oxidation produced 75% of TOC reduction. This result highlights that higher leachate degradation occurs when the optimal H_2O_2 /catalyst ratio is used due to a maximum conversion of oxidant into hydroxyl radicals, achieving the highest TOC abatement. Another reason for the increased catalytic activity with rising catalyst dose is the dual-phase reaction because part of the Fe is leached out into the aqueous phase, contributing toward the homogeneous Fenton reaction.⁵² A further increase in the catalyst does not produce an increase in the catalytic activity; indeed, for doses above 1 g/L, a slight decrease in activity is observed due to a scavenging effect of the OH^\bullet radicals (Figure S3).^{56,57}

Catalytic tests were also carried out on a model solution with ibuprofen (IBP, 10 mg/L) to verify the performance on different liquid wastes and the wide application possibilities of steel scale waste as catalysts for the Fenton process. Ibuprofen (IBP) has been chosen because it is a nonsteroidal, anti-inflammatory drug, which is widely used, and along with its metabolites it is very persistent with severe impacts on humans and the aquatic environment. SSW is also very active in the abatement of ibuprofen, reaching a decrease in TOC of IBP solution of about 85%. As reported in Table 2, in the case of ibuprofen, the influence of the catalyst dose is less significant than in landfill leachate, mainly due to the different initial organic load (the initial TOC is around 7 and 900 mg/L for IBP and leachate, respectively) of the two substrates. Furthermore, landfill leachate is also a complex liquid matrix that contains several refractory organic compounds. Despite the extreme complexity of leachate compared to the model solution, however, it can be observed that SSW is a remarkably active and promising material for the Fenton-like treatment. In the case of complex matrices, however, as shown in Table 2, it is necessary to optimize the quantity of the catalyst to effectively reduce the initial organic load.

3.5. Effect of pH. An optimal pH is not only necessary to achieve high catalytic activity in the heterogeneous Fenton reaction but also equally important to transform the maximum amount of oxidant into hydroxyl radicals.⁵ Moreover, heterogeneous catalysts afford better activities when oxidation reactions are performed at a pH, which conforms to the point

of zero charge (PZC) of the catalyst.⁵⁸ Furthermore, the loss of the active sites from the catalyst surface is also minimal when the Fenton-like reaction is carried out at optimum pH conditions. The investigation of the effect of pH on TOC abatement from leachate is reported in Figure 4A.

When the Fenton-like reaction is performed under very strong acidic conditions of pH 2, only 54% of the TOC has been abated. Further, when the pH of the leachate is adjusted to 3, the TOC removal efficiency is markedly increased to 75%, which is in accordance with previous findings.⁵⁹ These results clearly suggest that the rate of OH^\bullet generation and the oxidation potential (E) of OH^\bullet are optimal at pH 3 and consequently the extent of organic abatement is maximum. On the other hand, very strong acidic conditions may adversely impact the Fenton-like oxidation due to a number of reasons such as the suppression of the heterogeneous reaction between Fe and H_2O_2 , lower rate of OH^\bullet generation, generation of oxonium ions instead of OH^\bullet and scavenging of generated OH^\bullet by H^+ ions⁶⁰ as shown in Figure S4. As the operating pH is shifted toward milder acidic conditions (i.e., 4 and 5), the oxidation strength of the Fenton process starts to decline and TOC abatements are reduced to 61 and 53%. Again, this can be attributed to the slower rate of OH^\bullet generation and reduction in the oxidation potential of OH^\bullet because oxidation potential varies from $E_0 = 2.8$ V to $E_{14} = 1.95$ V depending upon the solution pH.⁶¹ However, when near neutral to alkaline conditions (i.e., pH 6–8) are used in the Fenton-like reaction, the TOC removal dropped sharply to 12–14%, showing that Fenton-like oxidation is inhibited under neutral and alkaline conditions because carbonates and bicarbonates in the leachate start to scavenge the OH^\bullet and ultimately the oxidation of organics is hindered.⁶² Moreover, the transformation of the oxidant into useful radicals is also diminished because it decomposes into water and oxygen (Figure S4).

The Fenton reaction requires a specific set of conditions to achieve maximal abatement of organic substrates, and pH is a fundamental factor in the homogeneous process due to the precipitation of iron as hydroxide and the formation of sludge.⁶³ The formation of iron sludge is one of the major drawbacks in the homogeneous Fenton reaction. One way to minimize sludge production is to use heterogeneous catalysts, as performed in this study. We have carefully checked the formation of sludge during the reaction at the variation of several factors and no sludge formation was ever observed during the landfill leachate reaction on SSW, as can be seen in Figure S5, where landfill leachate was shown before and after the reaction.

3.6. Effect of Oxidant Dose. The oxidant is the source of OH^\bullet and an optimum dose is not only critical for the maximum organic abatement but also equally important to minimize the cost of the Fenton-like process. To measure the influence of H_2O_2 dose on the organic mineralization, variable oxidant doses have been used keeping rest of the conditions identical and the results are presented in Figure 4B.

Working with a minimal oxidant dose, i.e., 10 mL/L, a mineralization of 46% of the organics from the leachate has been obtained. In addition, increasing the oxidant dose from 20 to 40 mL/L enhanced the TOC abatement from 50 to 75%, respectively, but when the oxidant dose is increased beyond 40 mL/L, the organic degradation is reduced. These results indicate that an increase in the oxidant dose increases the generation of OH^\bullet ,⁶⁴ but an excess amount may also enhance the scavenging effect caused by the oxidant itself.⁶⁵ The self-

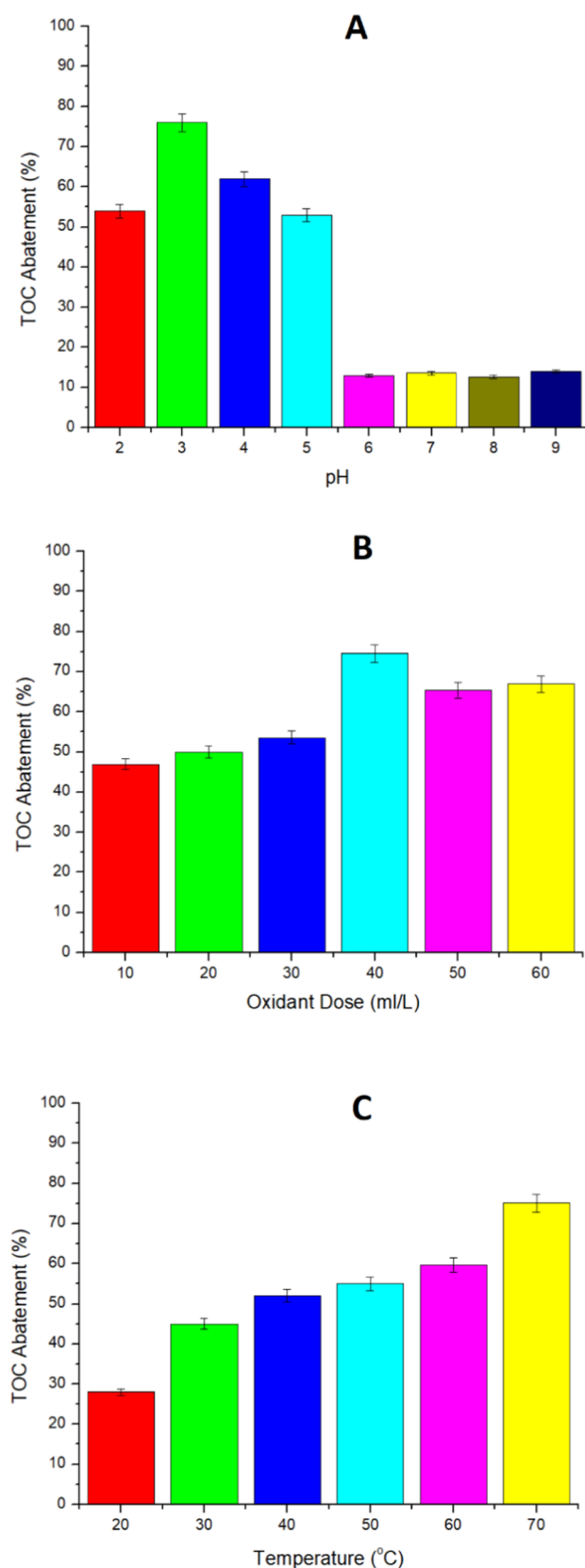
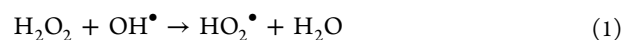


Figure 4. Effect of pH (A), oxidant dose (B), and temperature (C) on TOC abatement efficiencies (reaction conditions: SSW particle size—100 μm and reaction time—150 min).

scavenging effect, i.e., the reaction between the oxidant and the OH^\bullet , produces HO_2^\bullet radicals (eq 1), which have low oxidation

potential and ultimately the efficacy of the Fenton-like process does not increase as intended by increasing the oxidant dose⁶⁶



When best reaction conditions are used, the reduction of the organic loading in the landfill leachate is very high, as can also be observed by the difference in color before and after the reaction (Figure S5).

3.7. Effect of Temperature. Generally, a minimum amount of activation energy is always required in Fenton-like oxidation reactions to produce the oxidizing species, i.e., OH^\bullet , which in turn attack the organics in the leachate. The effect of temperature on the extent of Fenton-like oxidation is reported in Figure 4C.

When the leachate is treated at 20 °C, only 28% of the organics are mineralized. A progressive increase in process efficacies has been observed while stepwise increasing the reaction temperatures from 30 to 70 °C. These results indicate that when a higher reaction temperature is used, a higher amount of energy is available for the transformation of oxidant into oxidizing species^{67,68} and thus a higher abatement of organics is obtained,⁶⁹ which is in agreement with the Arrhenius law.⁷⁰ Figure 5 shows the combined effect of time

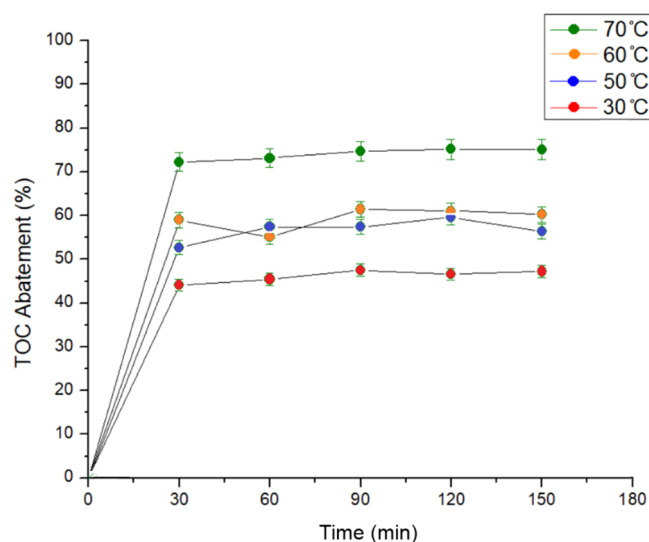


Figure 5. TOC abatement as a function of time over temperature (reaction conditions: pH 3, SSW particle size—100 μm , catalyst dose—1 g/L, H_2O_2 dose—40 mL/L (3%), and temperature 30–70 °C).

over temperature. The reaction is fast and the highest TOC abatement is achieved in the early 30 min and additional reaction times did not increase the process efficiency significantly, independently of the temperature of reaction.

The effects of different sizes of steel scale over time have also been investigated, and again, the reaction is very fast and occurs in the first 30 min and then the TOC removal remains almost stable (Figure S6).

3.8. Steel Scale Recycling. To better understand the recyclable nature of the steel scale, it was recovered and reused without modification in subsequent Fenton-like oxidation reactions by monitoring TOC abatement and residual H_2O_2 (Figure 6).

It has been noticed that the freshly employed SSW afforded maximum TOC abatement of 75%. Moreover, only 12% of the

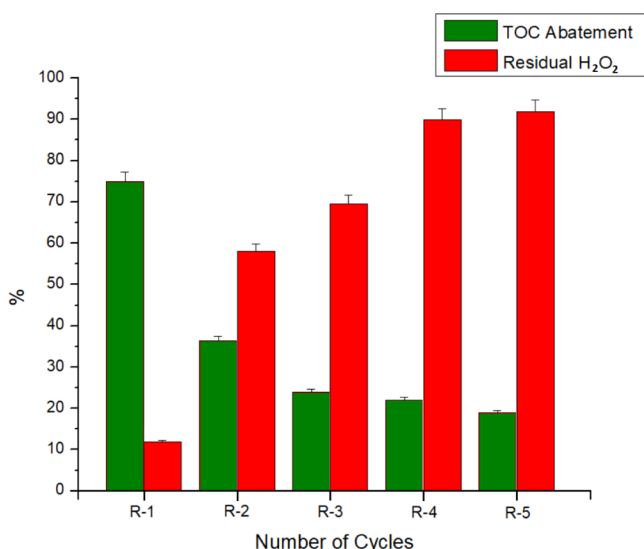


Figure 6. Effect of SSW recycling on TOC abatement efficiencies and H₂O₂ utilization (reaction conditions: pH 3, steel scale particle size—100 μ m, catalyst dose—1 g/L, H₂O₂ dose—40 mL/L (3%), temperature—70 $^{\circ}$ C, and reaction time—150 min).

employed H₂O₂ was found at the end of the reaction. The TOC abatement sharply dropped to 36% in the second application and 58% of the oxidant remained intact. Similarly, the catalytic ability of SSW was progressively decreased after every recycle and in the fifth application only 19% of the TOC was removed, while 92% of the H₂O₂ persisted at the end of Fenton-like oxidation.

These results clearly suggest that fresh SSWs are more active in the formation of OH \cdot radicals, achieving a higher process efficiency. The loss of activity after use is closely related to the morphology change observed with SEM analysis and the progressive loss of iron. As noted above, after reaction, the SSW showed a more heterogeneous morphology with numerous cavities on the solid surface (Figure 2), indicating that part of the solid composite has been lost during the oxidation reaction. In addition, it is important to consider also the tendency of iron catalysts to form stable complexes with the degradation products^{71,72} and the mere deposition of organics and inorganics onto the SSW particles that can hinder its catalytic ability (Figure 7). Since the number of available active sites keep on decreasing in every cycle, the degree to which H₂O₂ can form OH \cdot also decreases, ultimately reducing

the efficiency of the Fenton-like process. The formation of cavities on the solid surface during the catalytic treatment can induce deposition of organic compounds/degradation products, negatively affecting the recycling of the material in subsequent catalytic cycles. Due to the low cost of the SSW and its wide availability, it is not useful to investigate its regeneration because it is certainly more expensive and less environmentally friendly than the use of new SSW.

Summarizing, the oxidation process over SSW is optimal when the oxidant and catalyst are used at 1.2:1 ratio under acidic conditions (pH 3) and 70 $^{\circ}$ C. At optimal conditions, SSW successfully removed nearly 75% of the recalcitrant organic loading from landfill leachate.

These results are important from a circular economy perspective because a solid waste (SSW), which is produced in huge quantity all over the world, can be used as an efficient catalyst in a highly polluted liquid waste treatment process, changing its profile from a waste to a catalyst. Precisely, in the light of this vision of reusing a waste, deactivation after a single use must not to be seen as a great problem; in fact, as the available quantities of SSW are extremely high and their cost may be assumed close to zero, the process must be considered advantageous even without any recovery and subsequent reuse.

4. CONCLUSIONS

This study has shown promising results of SSW as a heterogeneous Fenton-like catalyst for the treatment of an extremely polluted liquid waste. Abatement of 75% has been achieved for landfill leachate, highlighting the oxidation capacity of SSW for the abatement of organics and opens new a perspective for more sustainable processes and for a low-cost treatment of several wastewater streams.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.1c01901>.

Additional figures and tables: SEM micrographs of SSW before and after application in Fenton-like oxidation, scheme of agglomeration behavior of various particle sizes of SSW, effective utilization of H₂O₂ over variable steel scale doses, effect of pH on transformation and utilization of oxidant, landfill leachate before and after the Fenton-like process, metallic composition of steel scale, and landfill leachate (PDF)

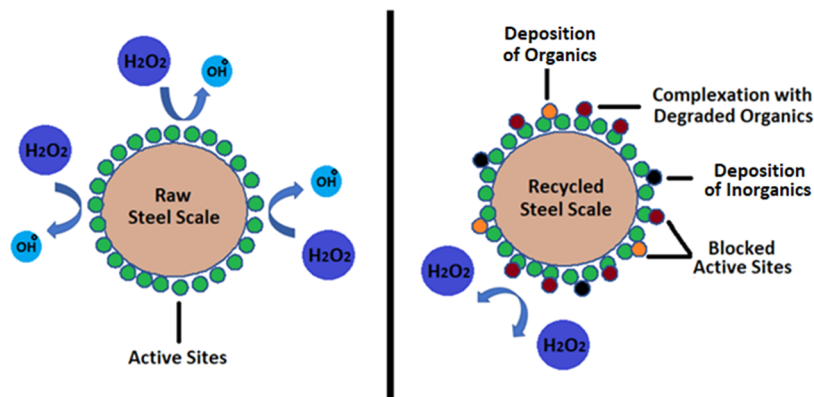


Figure 7. Catalytic inactivity of SSW after recycling.

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Notes

The authors declare no competing financial interest.

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