

Research Article

Potential of Ceria-Based Catalysts for the Oxidation of Landfill Leachate by Heterogeneous Fenton Process

E. Aneggi,¹ V. Cabbai,¹ A. Trovarelli,² and D. Goi³

¹Department of Chemistry, Physics and Environment, University of Udine, Via del Cotonificio, 108-331100 Udine, Italy

²Catalysis Group, Department of Chemistry, Physics and Environment, University of Udine, Via del Cotonificio, 108-331100 Udine, Italy

³Civil Environmental Group, Department of Chemistry, Physics and Environment, University of Udine, Via del Cotonificio, 108-331100 Udine, Italy

Correspondence should be addressed to D. Goi, goi@uniud.it

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In this study, ceria and ceria-zirconia solid solutions were tested as catalyst for the treatment of landfill leachate with a Fenton-like process. The catalysts considered in this work were pure ceria and ceria-zirconia solid solutions as well as iron-doped samples. All the catalysts were extensively characterized and applied in batch Fenton-like reactions by a close batch system, the COD (chemical oxygen demand) and TOC (total organic carbon) parameters were carried out before and after the treatments in order to assay oxidative abatement. Results show a measurable improvement of the TOC and COD abatement using ceria-based catalysts in Fenton-like process and the best result was achieved for iron-doped ceria-zirconia solid solution. Our outcomes point out that heterogeneous Fenton technique could be effectively used for the treatment of landfill leachate and it is worth to be the object of further investigations.

1. Introduction

Landfill leachate is a liquid waste of primary environmental concern because of the quantity and quality of the harmful pollutants contained in it. There are a large number of various types of organic and inorganic substances, depending on the age and type of solid wastes located in the landfill. Leachate from sanitary landfills can be an important source of ground water contamination and for this reason it is collected from the bottom of the landfill to be treated; further, this highly contaminated liquid waste accumulates a great diversity of harmful pollutants. Some of them are particularly refractory and for this reason traditional wastewater treatment plants are not efficient in their abatement. Inorganic and organic content of leachate is characteristically related to environmental risk because of scarce biodegradation, severe bioaccumulation, and potential health damages [1, 2]. It is well known that conventional biological liquid waste treatments alone are unable to achieved complete removal of the leachate pollution over the life of the landfill.

In truth conventional biological processes are time consuming and low-efficiency methods to treat directly leachate, consequently physicochemical processes are frequently utilized to pretreat this liquid waste in order to reduce organic refractory before biological action in treatment plants units [3].

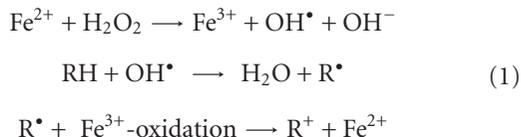
The most employed and studied methods in landfill leachate pretreatment are chemical or electrochemical coagulation [4], precipitation [5], and oxidation [6, 7]. Among these, a particular attention is given to oxidation techniques and especially to advanced oxidation processes (AOPs).

AOPs are methods able to convert nonbiodegradable organic pollutants into nontoxic biodegradable forms [8, 9], by the production of highly oxidizing hydroxyl radical species that promptly oxidize organic pollutants by a broad range of actions.

As a matter of fact oxidation by hydroxyl radicals species can be activated starting from H_2O_2 by intervention of transition metal salts (e.g., iron salts) [10], from ozone [11] or UV-light [12], leading to a more effective method to

decompose certain refractory contaminants of leachate. In particular, Fenton oxidation is a well-known AOP used as pretreatment of leachate worldwide [10].

The Fenton's reagent works at mild temperature and pressure generating hydroxyl radicals following the generally accepted structure of reactions:



This reaction is followed by other very complex oxidation reactions in which a lot of radical forms are generated and take part in the overall Fenton oxidation. The H_2O_2 can act both as a scavenger or initiator, all organics in liquid waste can participate in radical generation [10] and the ferric iron catalyzes and decomposes H_2O_2 to additional radical forms contributing to the oxidation [13]. Moreover, the reaction of ferrous iron forms ferric hydroxo complexes which can contribute to the coagulation capacity of the Fenton reagent [14]. The reactions including hydrogen peroxide and ferric ions or other transition metal ions are also reported as Fenton-like reactions [15, 16]; moreover, some new wet peroxidations, in which various catalysts are added with hydrogen peroxide to remove organic compounds by low temperature reactions, are presented as heterogeneous Fenton-like systems [17–19].

The Fenton process is one of the most interesting AOPs when it is used to treat or pretreat heavily contaminated liquid wastes, and a lot of full-scale applications are installed over the world. The main advantage is to reach treatment of liquid wastes at mild conditions of temperature and pressure, but the most important drawback is the production of a sludge which needs to be treated as well. It is also a recognized concept that Fenton process, at reasonable reagents concentration, cannot lead to the complete mineralization of all organic compounds and often only partial oxidation occurs even in assisted oxidations [20].

Leachate treatment by classic Fenton process was often studied to assay potential increase of the biodegradability or reduction of toxicity or color removal [21–23]. Recently, photo-Fenton [24] and electro-Fenton [25] processes have been investigated for landfill leachate treatment and several studies have been dedicated to heterogeneous Fenton treatment of phenolic [19, 26, 27] or industrial wastewater [28–31]. Heterogeneous process could be a promising alternative due to the more important drawback of classic Fenton, the large amount of iron required for the reaction that dramatically exceeds the legally quantity permitted for effluent discharge (<2 mg/L) and consequently requires a final waste management. At present, at the best of our knowledge, only one experience is reported about leachate treatment by heterogeneous catalytic Fenton-like systems [32], which can potentially be a promising way to activate radicals oxidizing species with minor sludge production. The experience reported in this paper tries to give a contribution to this theme.

The use of ceria-based materials in catalytic science is well established [33, 34]. Ceria is presently used in a large

number of industrial processes and it accounts for a large part of the rare earth oxide market. Undoubtedly, its major commercial application is in the treatment of emissions from internal combustion engines where ceria-based materials have been used in the past 30 years [35]. Its more important action in three-way catalysts (TWCs) is to take up and release oxygen following variations in the stoichiometric composition of the feedstream; however, several other processes also benefit from the use of cerium and its derivatives. Organosoluble compounds of cerium are used as fuel additives for diesel engines and industrial boilers to reduce carbon deposits after combustion. Cerium oxide is used also as a catalytically active component to oxidize the liquid portion of particulate present in diesel engine exhaust. CeO_2 is also used as an additive or a promoter in commercial applications such as fluid catalytic cracking, ammoxidation and dehydrogenation processes [33–37]. Moreover, in the last years several ceria-based catalysts were investigated for CWAO (catalytic wet air oxidation) [38–40] and CWOP (catalytic wet peroxide oxidation) [41–44] techniques. The main purpose of this work is to investigate doped ceria materials in the treatment of landfill leachate by a heterogeneous Fenton process.

2. Materials and Methods

2.1. Characterization and Sampling of Landfill Leachate. The leachate used in this study was drawn from an aged landfill near the city of Udine (northeast Italy); the landfill is not equipped with a recirculation system and it produces a stable leachate with high concentrations of COD and low BOD/COD ratio with a brown-green color. All the measures are carried out following the Standard Methods for the Examination of Water and Wastewater [45], COD was determined by colorimetric method utilizing a Hach Lange-DR 5000 spectrophotometer and quenching measurable residual H_2O_2 to prevent interference by addition of $\text{MnO}_{2(s)}$. Residual H_2O_2 was checked and determined to be zero by using test strips (Peroxide test sticks Quantofix, Sigma Aldrich). The TOC analyses were performed by a TOC-VCPN, Shimadzu analyzer.

2.2. Preparation and Characterization of the Catalysts. The catalysts, ceria (CeO_2 , CZ100), ceria-zirconia solid solutions ($\text{Ce}_{0.44}\text{Zr}_{0.56}\text{O}_2$, CZ44) and Fe-doped materials ($\text{Ce}_{0.85}\text{Fe}_{0.15}\text{O}_{1.925}$, CF and $\text{Ce}_{0.45}\text{Zr}_{0.40}\text{Fe}_{0.15}\text{O}_{1.925}$, CZF) were prepared by coprecipitation starting from nitrates. Precipitates were dried at 393 K and calcined at 773 K for 2 h. Fe-doped materials were also calcined at higher temperature (1073 K) to investigate the behavior of iron-phase in the system. Textural characteristics of all samples were measured according to the BET method by nitrogen adsorption at 77 K, using a Tristar 3000 gas adsorption analyzer (Micromeritics).

Structural features of the catalysts were characterized by X-ray diffraction (XRD). XRD patterns were recorded on a Philips X'Pert diffractometer operated at 40 kV and 40 mA using nickel-filtered Cu-K_α radiation. Spectra were collected using a step size of 0.02° and a counting time of 40 s per angular abscissa in the range 20° – 145° . The Philips X'Pert

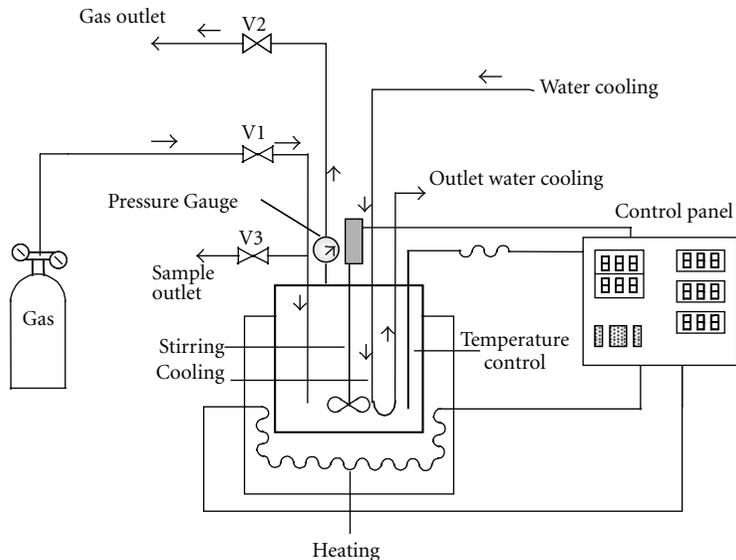


FIGURE 1: Schematic representation of the batch oxidation reactor used for tests.

HighScore software was used for phase identification. The mean crystalline size was estimated from the full width at the half maximum (FWHM) of the X-ray diffraction peak using the Scherrer equation [46] with a correction for instrument line broadening. Rietveld refinement [47] of XRD pattern was performed by means of GSAS-EXPGUI program [48, 49]. The accuracy of these values was estimated by checking their agreement against the values of the lattice constant, assumed to comply with the Vegard's law [50].

In order to evaluate the oxygen/storage capacity (OSC) of samples TGA, experiments in Ar/H₂ (5%) flow (total flow 100 mL/min) were carried out. Each sample was treated in N₂ atmosphere for 1 h at 553 K. Then, it was heated at a constant rate (10 K/min) till 673 K and kept at this temperature for 15 minutes, to eliminate the absorbed water. Finally, Ar/H₂ mixture was introduced while keeping the temperature at 673 K for 30 minutes. The observed weight loss is due to oxygen removal by H₂ to form water, and it can be associated to total oxygen storage capacity at that temperature [51, 52].

2.3. Catalytic Activity

2.3.1. Heterogeneous Fenton. A pressure vessel (Parr Instruments) equipped with a glass batch reactor with continuous stirring (400 rpm) (Figure 1) was used to carry out Fenton-like oxidative reactions. The experiments were conducted for 120 minutes at 343 K stirring 100 mL of leachate with 10 mg of catalysts and 5 mL of H₂O₂ (3%). At the end of the reaction (2 hours), samples were taken out and analyzed. Each experiment was repeated three times to obtain the reproducibility (error bars are included in figures).

3. Results and Discussion

3.1. Textural and Structural Characterization. The leachate selected to test oxidative Fenton-like process was characterized by a small concentration of iron in the raw mixture,

TABLE 1: Characterization of the landfill leachate used in this study.

Parameter	Unit of measurement	Values
pH	—	9
BOD ₅	mg O ₂ /L	60
COD	mg O ₂ /L	2500
BOD ₅ /COD	—	0.024
TN	mg N/L	1860
TOC	mg C/L	575
AOS	—	-2.52
ΔOD	mg O ₂ /L	0.38
Ammonia	mg NH ₄ ⁺ /L	2150
Chloride	mg Cl ⁻ /L	—
Color	PtCo unit	3600
Total iron	mg Fe/L	1.2
Nitrate	mg NO ₃ /L	—
Orthophosphate	mg PO ₄ ³⁻ /L	60
Sulfate	mg SO ₄ ²⁻ /L	—

a high pH value, a slight high value of COD and TOC if compared to average values of other old landfill leachate [53]. The main properties are described in Table 1.

Textural and structural characterization of all catalysts is reported in Table 2. Materials have surface area in the range 55–135 m²/g. Ceria-zirconia solid solutions (CZ44 and CZF) show higher surface area with respect to ceria-based samples (CZ100 and CF) due to the stabilization effect of zirconia.

The introduction of ZrO₂ significantly enhances textural properties, indeed, sintering in ceria-zirconia is less important in accordance with its better thermal resistance [54].

Doping ceria has a significant positive effect on the catalytic, oxygen storage/redox and thermal properties of catalysts. The introduction of Zr⁴⁺ induces a structural modification and this factor plays a key role in the redox

TABLE 2: Characteristics of catalysts used in this study and crystallographic parameters of modified ceria samples as obtained from Rietveld refinement and Vegard's law.

Sample	Composition	BET surface area (m ² /g)	Crystallite size (nm) ^a	Phase	Cell parameter	
					$a = b = c$ (Å)	From Vegard's law
CZ100	CeO ₂	53	7	Cubic	5.411 (1)	5.411
CZ44	Ce _{0.44} Zr _{0.56} O ₂	90	4.7	Cubic	5.281 (1)	5.285
CF	Ce _{0.85} Fe _{0.15} O _{1.925}	77	7.5	Cubic	5.396 (1)	5.263
CF (1073 K)	Ce _{0.85} Fe _{0.15} O _{1.925}	22	31.1	Cubic	5.408 (1)	5.263
CZF	Ce _{0.45} Zr _{0.40} Fe _{0.15} O _{1.925}	132	3.5	Cubic	5.295 (1)	5.163
CZF (1073 K)	Ce _{0.45} Zr _{0.40} Fe _{0.15} O _{1.925}	22	8.9	Cubic	5.292 (1)	5.163

^aCalculated with Scherrer formula from X-ray diffraction patterns.

behaviour of ceria-zirconia solid solutions. The substitution of Ce⁴⁺ with Zr⁴⁺ produces a contraction of the cell volume and induces stress in the structure and consequently structural defects that increase the oxygen mobility. It is important to point out that the oxygen mobility is increased if no modification in the structure of solid solution is observed. From these considerations, we noted that better performances are achieved for solid solutions with cubic symmetry and with a high level of Zr⁴⁺. Alternatively, a higher amount of ZrO₂ decreases the number of redox sites and consequently the activity of the system. There is an inverse relationship between the two effects; in order to obtain an active system it is important to balance the amount of structural defects and the amount of ceria. Literature data suggest that better results are obtained for compositions between CZ50 and CZ90 [55–58].

The structural features of all samples were analyzed by XRD.

In CeO₂-ZrO₂ system, several phases could be formed, depending on preparation conditions and concentration of single-oxide constituents [59]. In general, for a CeO₂ content <20 mol% a single-phase monoclinic cell is observed, while in CeO₂-rich compositions (CeO₂ > 70 mol%) solid solutions of cubic symmetry are formed. At intermediate levels, regions of tetragonal (*t*, *t'*, and *t''* phases) and cubic symmetry coexist in the phase diagram, their formation depending on the preparation method used. In our case, the Rietveld analysis of the diffraction profile of the materials has been carried out by opening the fitting to cubic, tetragonal and a mixture of the two.

As shown in Table 2, XRD measurements suggest that for binary ceria-zirconia samples with cerium content greater than 40 mol% the formation of a cubic fluorite lattice is favored, in accordance with the literature [60]. Thus, our ceria and ceria-zirconia solid solution crystallize in a cubic fluorite structure of *Fm3m* symmetry. In CZ44, no peak splitting that would indicate the presence of two phases could be detected, and therefore, the diffraction patterns demonstrate the formation of a single solid solution-like ceria-zirconia phase. This cannot exclude the presence of different arrangements of oxygen sublattice or the presence of a multiphase system at a nanoscale level, not detected by XRD. In fresh samples doped with Fe, XRD features allow to detect only the CeO₂ or Ce_{0.44}Zr_{0.56}O₂ cubic phase *Fm3m*, while Fe₂O₃ or other iron oxide phases are not visible

(Figure 2(a)). XRD peaks are broad and the values of crystallite size obtained according to Scherrer equation are about 7.5 nm for sample CF and 3.5 nm for sample CZF. In order to understand better the structural properties of Fe-doped system, CF and CZF catalysts were calcined at higher temperatures (1023 K).

After calcination, in the XRD profile of CF, peaks assigned to rhombohedral Fe₂O₃ (hematite) with *R-3c* symmetry are visible (Figure 2(b)).

The lack of peak due to iron oxide in fresh CF samples could indicate the formation of solid solution between Ce and Fe. However, a comparison between lattice parameters retrieved from Rietveld refinement and from Vegard law (values of cell parameter expected if all the iron contained were dissolved in the lattice) indicates that only a small percentage of iron is dissolved in ceria (Table 2).

After aging, the increase of cell parameter indicates a segregation of the iron eventually dissolved in the lattice with formation of weak signal due to crystalline Fe₂O₃. It is known that lower valence ions such as Fe³⁺ are extremely difficult to dissolve into the ceria lattice, especially when treating at high temperature [61]. Mutual dissolution of Ce and Fe into Fe₂O₃ and CeO₂ has been reported to exist in Fe-rich Ce/Fe mixed oxides prepared by coprecipitation [62].

For CZF, the value of cell parameter retrieved by Rietveld refinement is not in agreement with that computed from Vegard's law: the adding of a cation (Fe³⁺) with ionic radius smaller than Ce⁴⁺ and Zr⁴⁺ should produce a decrease in cell volume in the case of a solid solution. Conversely, we observe a value higher than expected indicating that Fe₂O₃ is probably deposited on the surface. Moreover, iron could be present as interstitial and/or extralattice or amorphous interparticle iron. As in the case of pure ceria, we cannot exclude that a small fraction of Fe is dissolved within ceria-zirconia framework.

3.2. Catalytic Activity. We investigated the heterogeneous process on different ceria-based catalysts performing reactions at 343 K for 2 hours, without any pH correction of the leachate (pH 9). Preliminary tests were carried out in order to verify the activity of catalyst and/or H₂O₂. In absence of catalyst and H₂O₂ (Figure 3), the abatement of COD and TOC, due only to the thermal treatment at 343 K, is small, respectively 1% and 14%.

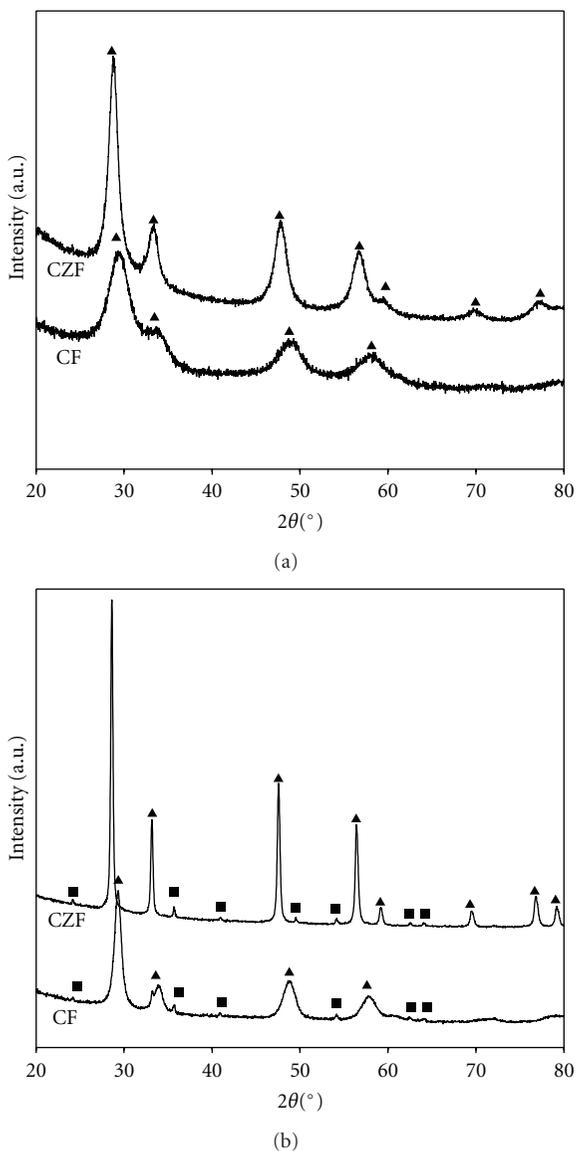


FIGURE 2: XRD profile for fresh (a) and aged (b) iron-doped samples (▲: CeO₂ and CeZrO₂; ■: Fe₂O₃).

As shown in the plot, the advantage of the addition, for the abatement of COD and TOC, of bare ceria is negligible. In absence of the catalyst, but with 5 mL of H₂O₂ (3%), a small improvement in the activity was observed due to the oxidation capacity of the hydrogen peroxide alone. This activity could be explained considering that the small amount of iron presented in the leachate (Table 1) can interact with H₂O₂ (Fe/H₂O₂ ratio was 1:687) catalyzing the formation of [•]OH radicals as in the homogeneous Fenton. When pure ceria and hydrogen peroxide were used in combination, the catalytic activity was further improved reaching an abatement of COD and TOC of 7% and 30%, respectively, confirming the positive synergic action of the two agents in the heterogeneous Fenton-like process. From these preliminary tests, we can conclude that ceria alone is not active and

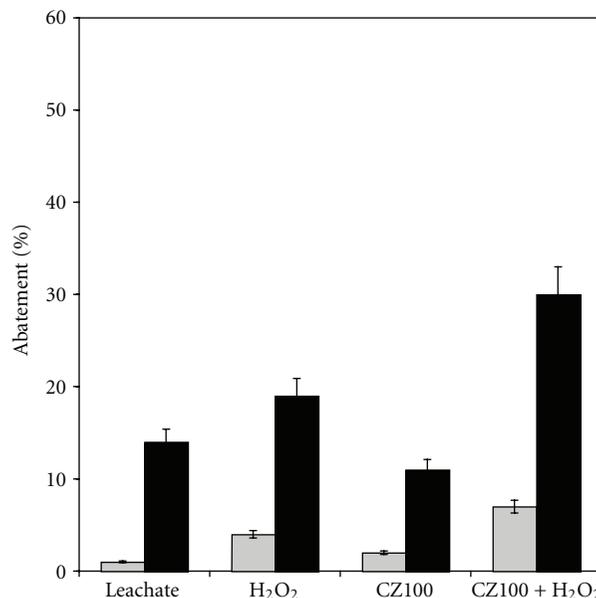


FIGURE 3: COD (light grey) and TOC (black) abatement for reaction with and without catalyst and H₂O₂ (reaction conditions: 10 mg of catalyst, 5 mL of H₂O₂, pH = 9, T = 343 K).

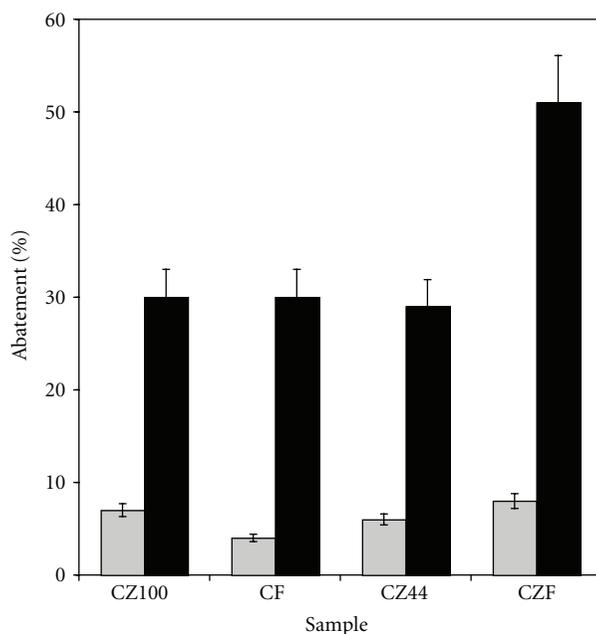


FIGURE 4: COD (light grey) and TOC (black) abatement for different catalysts (reaction conditions: 10 mg of catalyst, 5 mL of H₂O₂, pH = 9, T = 343 K).

a synergic action between catalyst and hydrogen peroxide is necessary to obtain higher performance.

After blank tests, the activity of the four ceria-based catalysts (CZ100, CZ44, CF, and CZF) was investigated and the results are shown in Figure 4.

Ceria and ceria-zirconia solid solutions show very similar results. The catalytic activity of ceria-based systems could

be attributed to the capacity of cerium oxide to decompose H_2O_2 , as reported in a previous study in which the decomposition of hydrogen peroxide, with formation of radical species, in an aqueous suspension of CeO_2 was investigated [63]. The mechanism for H_2O_2 decomposition in the presence of water-oxide interfaces is still not completely elucidated, but it was suggested that it occurs on the surface with OH or HO_2 radicals production.

The catalytic activity of cerium oxide is correlated with its oxygen storage capacity. One of the most important roles of CeO_2 in catalytic redox reactions is to provide surface active sites [64] and to act as an oxygen storage/transport medium by its redox cycle between Ce^{4+} and Ce^{3+} . That is, the presence of surface active oxygens from one side and the oxygen storage capacity from the other are among the most important factors to be considered. These, in turn, are strongly influenced by surface area and surface/bulk composition.

As pointed out previously, doping ceria with Zr^{4+} increase, the oxygen mobility, but a higher amount of ZrO_2 decreases the number of redox sites and consequently the activity of the system. In order to explain the activity of the two systems, we need to take into account the right combination of surface area and composition.

For this reason, it is important to correlate overall activity with total available surface active oxygens, TSAO (which are linearly dependent on the amount of ceria) and total oxygen storage capacity, OSC (which generally shows a volcano-type relation with composition). The number of *total surface oxygens* (TSO) has been estimated according to Madier et al. [65] starting from the structure and the molar composition of the oxide considering the exposure of (100), (110), and (111) surfaces and assuming that Zr atoms do not participate in the redox process. The number of *total surface available oxygens* (TSAO) represents a fraction of total surface oxygens considering that only one atom out of four is involved in the Ce^{4+} - Ce^{3+} redox process [65–67]. OSC data collected according to the method described in the experimental. Results are reported in Table 3.

Even though CZ100 has a lower surface area, pure ceria and CZ44 show almost the same value of TSAO (225 $\mu\text{mol O/g}$ and 182 $\mu\text{mol O/g}$, resp.). A more pronounced difference was found in OSC (1669 $\mu\text{g O}_2/\text{g}$ and 3721 $\mu\text{g O}_2/\text{g}$ for CZ100 and CZ44, resp.) that takes into account surface and bulk oxygens. In both catalysts, the surface area is quite high, consequently the abstraction of oxygen involves mainly surface sites, with little or no participation of the bulk in the reaction. Therefore, the more important factor is the availability of surface oxygen. In our materials (CZ100 and CZ44), the availability of surface oxygen is almost the same; therefore the two systems, CZ100 and CZ44, exhibit a very similar catalytic activity in the treatment of landfill leachate.

For CZF, the simultaneously presence of iron and zirconia significantly increased the abatement of TOC (51%) but has no significant effect on COD.

CF sample is characterized by the formation of cubic ceria-like solid solution where Fe cations are dissolved within ceria structure. In this case, the interaction takes place

TABLE 3: TSAO and OSC for CZ100 and CZ44.

Sample	TSAO ($\mu\text{mol O/g}$)	OSC ($\mu\text{g O}_2/\text{g}$)
CZ100	225	1669
CZ44	182	3721

through the sharing of oxygen anion defined by the Fe–O–Ce bonds formed in the Fe-doped CeO_2 lattice [62].

In CZF sample, the lack of these interactions due to the lower amount of ceria and consequently to the lower amount of Ce-Fe-O entities formed in the system, can explain the different behavior of this catalyst. Indeed, in this case, a higher amount of Fe (due to weaker interaction with Ce and to the amorphous Fe_2O_3 phase on the surface) is available for the reaction with the leachate.

Our research pointed out the good activity of ceria-based heterogeneous treatment and we can conclude that ceria based catalyst is a very promising class of materials for this kind of application.

Further studies will be dedicated to a better understanding of the mechanism of reaction of ceria-based catalyst and to the optimization of the reaction conditions and catalytic stability.

4. Conclusions

Our study shows that the heterogeneous Fenton process could be successfully used in the treatment of landfill leachate substituting homogeneous treatment. Promising results were obtained in leachate oxidation by a heterogeneous Fenton-like process over ceria-based catalysts with an abatement of TOC higher than 50%.

This is just a first investigation into the potentiality of heterogeneous reaction, but the results appear encouraging. In heterogeneous reactions, several variables are involved and need to be completely understood for a good optimization of the catalyst. Further studies will be dedicated to a better understanding of the mechanism of reaction of ceria-based catalysts and the role of iron and zirconia in the reactions and leaching. Moreover, we need to optimize the reaction conditions, such as pH, temperature, and catalyst/peroxide ratio. Additional investigations should be performed in order to deeply explore a promising technique such as heterogeneous Fenton. At the moment, several aspects need to be investigated in more detail, but the results open a new field of research and point out a very interesting class of catalyst that could be used for landfill leachate treatment and worthy to be the subject of further investigations.

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