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Catalytic Combustion of Tannery Sludge in a Rotating Reactor

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Abstract

This work is focused on the catalytic combustion of tannery sludge by using ferrites and CeO_2 in a stainless steel fixed bed reactor in comparison with the same system set in rotation.

The presence of catalysts determined an increase of the reactivity with respect to the sludge alone. CeO_2 catalyst enhanced mainly the reaction rate associated to the combustion of volatiles while it is not active in the combustion of the char. On the contrary, both $LaFeO_3$ and $LnFeO_3$ perovskites have accelerated the latter step. In the case of sludge alone, passing from the fixed to the rotating reactor, the mass of carbon burned increased from 18 wt% to 31 wt% indicating that the related effect is the promotion of mass transfer rates among the different phases. Moreover the ratio CO/CO_2 widely decreased in the rotating system demonstrating that the enhanced oxygen mass transfer from gas to sludge particle surface determined an improvement of the combustion process since the selectivity to CO_2 is enhanced.

Keywords: Catalytic combustion; Tannery sewage sludge; Rotating reactor

Introduction

In the wastewater treatment system, the sewage passes through a series of treatment steps that use physical, biological, and chemical processes to remove pollutants from water. Many different treatment processes of industrial wastewater effluents are studied [1-13].

In any case, the final products are the purified water and sludge. Common disposal processes for sewage sludge from tannery wastewater are land-filling and thermal conversion (combustion, incineration, pyrolysis). The most used thermal processes are carried out without the presence of catalysts. For municipal sludge, several catalysts were tested, such as TiO_2, Al_2O_3, Fe_2O_3, $MnO_2/CuO/CaO$. Only in the case of MnO_2/KOH, it has been found a clear demonstration that, with the addition of catalysts, the ignition of MSW is enhanced [14].

The influence of catalysts was also investigated in the thermal incineration of industrial sludge. In this case K_2CO_3, NaCl and Al_2O_3 were used. The catalytic performance of K_2CO_3 was better than NaCl and Al_2O_3 [15].

Very recently, we worked on the thermal treatment of tannery sewage sludge using CeO_2 as catalyst and studying the influence of catalyst loading by thermogravimetric analysis coupled with mass spectrometry (TG-MS). The catalyst mixed with the dried sludge improved either the selectivity of the sludge combustion process, reducing the emission of cyclic and aromatic substances, either the combustion peak temperature, yielding a higher oxidation rate of the sludge organic fraction [16].

Moreover by adding the catalysts in the step of sludge formation, i.e. immediately after the addition of flocculants into the coagulation-flocculation step of tannery wastewater, the combustion peak of the sludge organic fraction occurred at lower temperature, about $300°C$, while in the absence of catalyst the onset was at about $525°C$). This points out to a significant improvement of the oxidation process due to the catalytic material [17]. The reaction occurs in a solid-solid-gas system and to this purpose, it is necessary to improve the contact among the solid phases. A way to obtain an improved physical contact among the sludge particles and catalysts during the combustion is to place in rotation the reactor. So, this work was focused on the catalytic combustion of tannery sludge by using ferrites and CeO_2 in a stainless steel fixed bed reactor in comparison with the same reactor set in rotation.

Experimental

Materials and characterization methods

Tannery sewage sludge samples were supplied by an Italian tannery wastewater treatment plant. Sludge conditioning was accomplished by preliminary sample milling. In particular sludge was dried in a stove at $80°C$ for 8 hours and then pounded in an electric mortar to a size between 180-250 micron.

Dried sludge was characterized by different techniques. Moisture content was evaluated by gravimetric analysis of samples before and after an isothermal treatment at $100°C \pm 2°C$ up to constant weight. Total ashes percentage was obtained by weighing the inorganic residue after isothermal treatment at $550°C$ for 8 hours. Finally, the organic matter was calculated by difference with the moisture and inorganic matter content in the samples. The mineral content was analysed by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry) Liberty Series II Varian with axial torch after sludge acidic digestion. The organic fraction of sludge was analysed by GC-

MS after solvent extraction (hexane). By cool-on-column injector the sample was introduced into GC column (Restek Rtx-5ms, 5% diphenyl and 95% dimethyl polysiloxane, 0.25 mm ID, 30 meter), then the separated compounds were analysed by a Quadrupole Mass Selective Detector (HP 5973). For the analysis of volatile compounds a Purge and Trap (P&T) device was used to introduce samples into the GC-MS, equipped with a GC column (Restek Rtx-624, 6% cyanopropylphenyl and 94% polysiloxane, 0.25 mm ID, 60 meter) via split/splitless inlet system.

CeO_2, $LaFeO_3$ and $LnFeO_3$ (Ln=Ce, La, Nd, Pr, Sm) as catalysts were mixed with sludge by gently grinding in an agate mortar to obtain a contact between the two solid phases. The obtained samples are named Cex, Lay and Lnz, where where x, y and z represent the weight percentage of CeO_2, $LaFeO_3$ and $LnFeO_3$ in the mixture catalyst-sludge, respectively. The catalyst loading was in the range 3-6 wt%. Physico-chemical characterization of sludge and catalysts was performed by different techniques. Specific surface areas were obtained by N_2 adsorption measurement at $-196°C$ with a Costech Sorptometer 1042 after pre-treatment at $120°C$ for 1 h in He flow (99.9990%). X-ray diffraction (XRD) was carried out using the X-ray microdiffractometer Rigaku D-max-RAPID.

TG-MS analyses were performed in air flow by a thermogravimetric analyzer (SDTQ600, TA Instruments) studying the evolved gas by a mass detector in the range m/z=29-209 (Pfeiffer Vacuum Benchtop Thermostar). Measurements were carried out on about 30 mg of sample in 100 (stp) cm^3/min air flow (chromatographic grade) at $10°C$/min heating rate, in the temperature range 20-1000°C. The parameters used for the evaluation of the catalytic activity from thermal analysis (TG-MS) were the maximum value of the first derivative of weight loss with respect to time (DTG_{max}), to describe the rate of conversion for the combustible matter, and the value of peak temperature (T_{max}) associated to DTG_{max}. The emission of aromatic substances was monitored by analyzing the mass fragment m/z=78, characteristic of benzene.

Stainless steel reactor for constant temperature oxidation

A microreactor was employed in order to evaluate the reactivity of the mixture sludge-catalyst. The microreactor comprises a 500 mm length, 17 mm ID stainless steel tubular flow reactor, heated by an electrical furnace. Oxidation tests at constant set temperatures were carried out in air flow. ABB continuous analyzers determined exhaust gas concentrations: URAS 14 (for CO, CO_2 and SO_2 concentrations) and MAGNOS 106 (for oxygen). Signals from the analyzers were sent to a personal computer for data processing. Samples to be tested were previously diluted with quartz particles to avoid local raise of temperature during the tests. The diluted mixture was loaded to the reactor, filling about 3 cm in length of its central zone. The test started raising the temperature to the desired value (T=350°C) in static air. Then the air stream was fed to the reactor, starting the oxidation. The feeding air flow rate was 30 L/h (STP). Operating pressure was 1 atm. The initial mass of the sample was about 70 mg. In the case of tests with rotating reactor, the rotating rate was equal to 3 rpm.

Results and Discussion

Sludge and catalysts characterization

The analytical results obtained for furnished sludge are shown in Table 1.

Characteristic	Unit	Content
Moisture and volatile matter at 102°C	wt%	17.8
Inorganic substances residue at 550°C	wt%	24.0
Organic substances	wt%	58.3
pH	pH	7.10
Al	mg/Kg	3664
Cr	mg/Kg	33119
Fe	mg/Kg	14414
Cr VI	mg/Kg	<4
Cu	mg/Kg	54
Zn	mg/Kg	728
Mn	mg/Kg	142
Polycyclic aromatic hydrocarbons (PAHs)	mg/Kg	<0.5
Aromatic solvents	mg/Kg	0.09
Phenols	mg/Kg	623.2
Benzoalkanes	mg/Kg	1418
Non-aromatic light hydrocarbons (C<12)	mg/Kg	1.3
Non aromatic heavy hydrocarbons (C>12)	mg/Kg	3150

Table 1: Results of analytical tests on sludge.

The sample is mainly constituted by water (the portion loss at 102°C), organic matter and inorganic matter (residue at 550°C).

The abundance of chromium in the sludge depends of the initial composition of wastewater, as they are collected and equalized, i.e. from the prevalent tanning process in the relative industrial district. The presence of Al and Fe is mainly due to the use of $Al_2(SO_4)_3$ as coagulant agent for wastewater, although it may derive, in small quantities, also from the tanning industry.
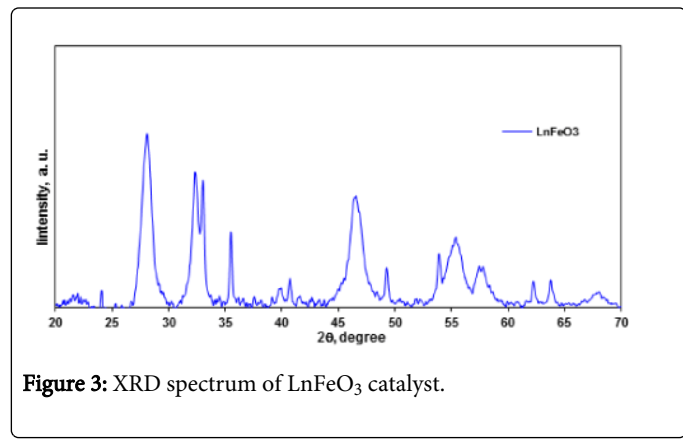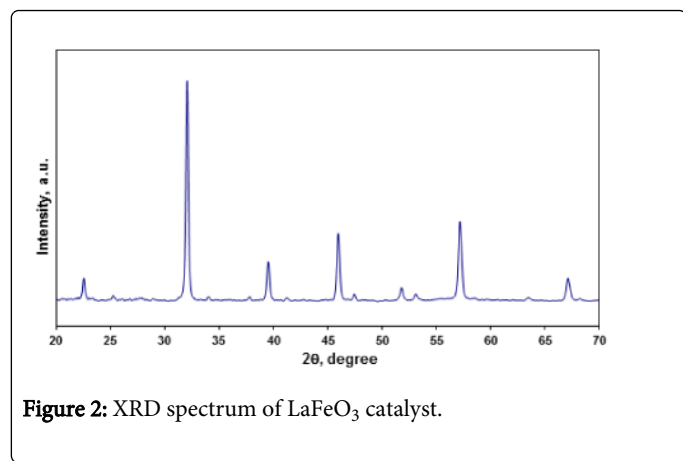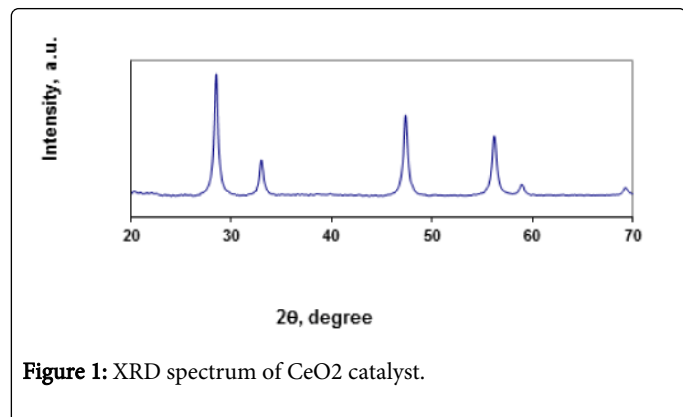
The values of specific surface area for sludge and catalysts are reported in Table 2.

Sample	Specific surface area, m^2/g
CeO_2	80
$LaFeO_3$	6
$LnFeO_3$	3.3

Table 2: Values of specific surface area for catalysts.

The surface area of CeO_2 is strongly higher. Consequently, the latter would seem able to make good contact with the sludge. XRD analysis carried out on CeO_2 and $LaFeO_3$ (Figure 1 and Figure 2) revealed the presence of only the signals due to the crystalline structure of the two substances. Since the catalyst $LnFeO3$ is a solid that includes several rare earth elements (La, Ce, La, Nd, Pr, Sm), the XRD peaks are not easy to attribute. From Figure 3 the diffraction patterns of the sample $LnFeO_3$ are clearly related, to those of La, Ce, Nd, Pr, Sm ferrites,

Fe_2O_3 and Fe_3O_4 [18]. Finally, the signals obtained for values of 2 teta equal to 32.1 and 55.5, are likely due to CeO_2 present in the structure of the sample analyzed.

Figure 1: XRD spectrum of CeO2 catalyst.

Figure 2: XRD spectrum of $LaFeO_3$ catalyst.

Figure 3: XRD spectrum of $LnFeO_3$ catalyst.

| Sample	T_{max}, $^\circ$C	Aromatic compounds emission, I^*/mg
Sludge	457	2.51*10-11
Ce3	304	8.71*10-12
Ce4	285	8.92*10-12
Ce6	308	n. d.
La3	318	n. d.
La4	310	n. d.
La6	432	n. d.
Ln3	324	n. d.
Ln4	324	n. d.
Ln6	315	n. d.

Table 3: Values of T_{max} and aromatic compounds emission for sludge and catalysts.

I^*: integral of mass fragment m/z=78 profile as a function of run time; n.d: not detectable.

As general remarks on TG-MS results, the addition of catalytic material to dried sludge determined effects either with regard to the selectivity of the process, by reducing the emission of aromatic substances, either with respect to the operating conditions, resulting in lower values of T_{max}. Table 3 summarizes the results obtained from the analysis carried out on all samples in terms of T_{max} and the amount of aromatic compounds emitted, evaluated by the integral (I^*) of the signal associated to the mass fragment m/z=78 as a function of run time. T_{max} decreased from 457°C for sludge alone to about 285°C for a CeO_2 loading of 5 wt%. The amount of aromatic compounds emitted during the combustion decreased to zero for a CeO_2 loading of 6 wt% and for all the mixtures containing $LaFeO_3$ and $LnFeO_3$ catalysts.

Constant temperature oxidation tests

For all the samples, during the combustion tests in the reactor, there was the emission of CO_2, CO and SO_2. The behaviour of CO_2 produced from the oxidation of sludge in the absence of catalyst is depicted in Figure 4.

Figure 4: Behavior of CO_2 produced during the oxidation of sludge in the absence of catalyst.
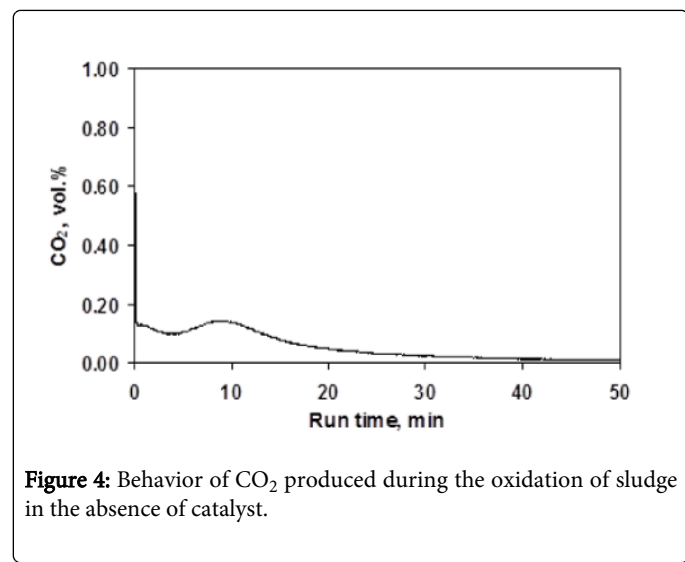
Two main stages in the behaviour of CO_2 can be distinguished; the first, with high intensity, occurring in the first five minutes of reaction, is due to the combustion of volatiles, while the second, lower in intensity, is associated to the char combustion. From these data it is possible to observe that gas-phase combustion of volatiles is the dominant reaction in sludge combustion [19] while char combustion is the slowest reaction step [20]. Because of the surface flux of water

and volatiles, a probable prevention to the transfer of oxygen towards the exhaust char pellet, occurs [21]. A similar behaviour was obtained for all the samples.

Table 4 summarizes the results obtained as a function of type and catalyst loading in terms of percentage of carbon burned (%C), evaluated with respect to the total weight of sludge loaded in the reactor. The mass of carbon burned was calculated by the integration of the signal associated to the CO and CO_2 produced as a function of run time.

The amount of carbon burned increased from 18 to 25.6 wt% by increasing CeO_2 loading. The highest value of %C was obtained in presence of $LaFeO_3$ and $LnFeO_3$ catalysts. In particular it increased up to 32 wt%, significantly higher with respect to 18 wt% of the sludge alone.

These results clearly indicate that the presence of catalyst enhanced the combustion process allowing to burn a higher amount of organic substances contained in the sludge.

| Catalyst	Percentage of carbon burned, wt %
Sludge	18.0
Ce3	18.3
Ce4	18.9
Ce6	25.6
La3	30.4
La4	32.0
La6	29.1
Ln3	31.9
Ln4	30.4
Ln6	30.5

Table 4: Percentage of carbon burned evaluated with respect to the total sludge weight loaded in the fixed bed microreactor.

The results are also analysed considering the reactivity defined as the rate of change of the carbon conversion degree dX/dt (where $X=(m_0-m)/m_0$, m and m_0 being the current and the total mass of carbon that can be burnt, respectively) as a function of X [22].

The behaviour of dX/dt for sludge, Ce3, La3 and Ln3 is shown in Figure 5a and 5b. In all cases, the presence of catalysts determined an increase of the reactivity with respect to the sludge. Ce3 sample presented the highest dX/dt up to X=0.24 in which the combustion of volatiles occurs.

Figure 5b shows the profiles of dX/dt as a function of X in the range 0-0.2 for the same samples.

For X higher than 0.24, the reactivity of Ce3 sample is negligible, underlining that CeO_2 catalyst enhanced mainly the reaction rate associated to the combustion of volatiles and that it is not active in the combustion of the char. On the contrary, both $LaFeO_3$ and $LnFeO_3$ accelerated also the latter reaction. In fact the two perovskites showed reactivity higher than sludge alone and allowed to burn all the organic fraction of the sludge.
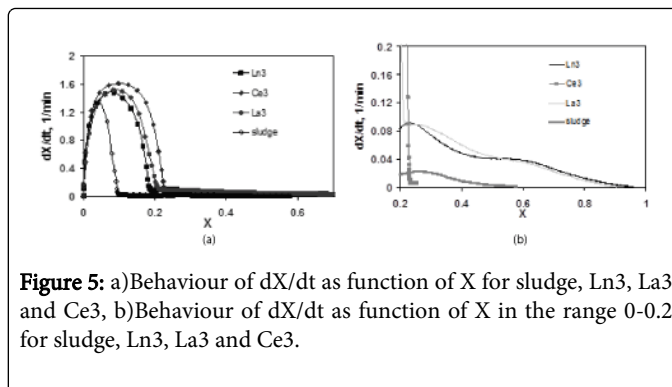
Figure 5: a)Behaviour of dX/dt as function of X for sludge, Ln3, La3 and Ce3, b)Behaviour of dX/dt as function of X in the range 0-0.2 for sludge, Ln3, La3 and Ce3.

In Figure 6a and 6b, the reactivity of sludge alone obtained with fixed bed in comparison with the rotating system, is reported.

Passing from the fixed to the rotating reactor, both the reactivity associated to the combustion of volatiles (Figure 6a) and that one of char combustion (Figure 6b) was markedly enhanced. Moreover the mass of carbon burned, increased from 18 wt% to 31 wt% and the ratio CO/CO_2 decreased from 0.33 to 0.17 indicating that the rotation system enhanced the oxygen mass transfer rate from gas to sludge particle surface. An improvement of the combustion process is so determined.
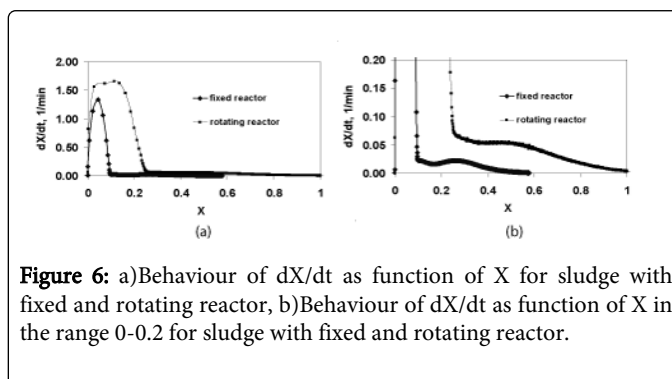
Figure 6: a)Behaviour of dX/dt as function of X for sludge with fixed and rotating reactor, b)Behaviour of dX/dt as function of X in the range 0-0.2 for sludge with fixed and rotating reactor.

In the presence of CeO_2 catalyst, neither the reactivity nor the ratio CO/CO_2 show significant differences passing from fixed to rotating reactor. An important influence was instead obtained in presence of $LaFeO_3$ catalyst with a content of 4 wt% (Figure 7a and Figure 7b). In this case, the reactivity of the sample was enhanced (Figure 7a) and in particular also the combustion rate of the char is higher when the rotating reactor was used, confirming that the mass transfer rate was increased with respect to the case in which the fixed bed was used.

Conclusions

In the present study the combustion of tannery sewage sludge was evaluated in the absence and in the presence of cerium oxide or perovskites in a stainless steel fixed bed reactor. The oxidation profiles evidenced two main stages. The first occurring in the initial time of the reaction, due to the combustion of volatiles, while the second associated to the char combustion. The presence of catalysts determined an increase of the reactivity with respect to the sludge alone. CeO_2 catalyst enhanced mainly the reaction rate associated to the combustion of volatiles while it is not active in the combustion of the char. On the contrary, both $LaFeO_3$ and $LnFeO_3$ perovskites also accelerated the latter step. Passing from the fixed to the rotating

reactor, the mass of carbon burned, increased, while the ratio CO/CO_2 decreased from 0.33 to 0.17 indicating that the rotation system enhanced the oxygen mass transfer rate from gas to sludge particle surface determining an improvement of the combustion process.

Catalytic thermal conversion presents many advantages, such as reduction of disposed solid mass and volume and energy recovery from the organic sludge fraction, determining lower disposal costs.
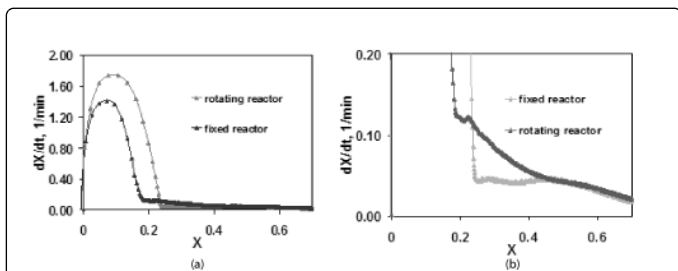
Figure 7: a) Behaviour of dX/dt as function of X for La4 with fixed and rotating reactor, b) Behaviour of dX/dt as function of X in the range 0-0.2 for La4 with fixed and rotating reactor.

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