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Enhanced Thermal Treatment of Tannery Sewage Sludge

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Thermal conversion of sewage sludge presents several advantages, such as the reduction of mass and volume of solid waste and energy recovery from the organic sludge fraction, resulting in lower disposal costs with respect to landfilling. In this work, the combustion behaviour of a dried tannery sewage sludge was compared in the absence and in the presence of a catalyst, investigating the role of catalyst loading. The catalyst mixed with the dried sludge improves 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. By adding the catalysts in the step of sludge formation, i.e. immediately after the addition of flocculant into the coagulation-flocculation step of tannery wastewater, the combustion peak of the sludge organic fraction occurred at about 300 K lower than in the absence of catalyst (about 798 K), pointing out to a significant improvement of the oxidation process due to the catalytic material.

1. Introduction

Wastewaters from the tanning industry are typically collected to be treated in centralized plants. Pollutants are removed generating sludge as main product of purification. Although influenced by the operating conditions of the treatment, the sewage sludge usually consists of organic and inorganic substances (Tian et al. 2002; Paranaudeau et al. 2007; Fonts et al. 2009). For the sludge disposal the solution till now implemented is the landfill, however, this solution is clearly unsatisfactory, both for the difficulty of finding suitable sites and for its limited capacity**.** Furthermore, landfill involves immobilization of materials that might often be reused, as recently proposed for production of inert materials such as bricks, expanded clay, or biogas generation. Other proposals, such as the use in agriculture or incineration, though represent more immediate and realistic applications are poorly implemented. The reuse is also limited by bad odours generation, difficulty in handling and transfer costs (Magalhaes et al. 2008). In line with recent findings, incineration with energy recovery can constitute an interesting alternative to the accumulation in landfills. Thermal systems are used today to treat municipal solid waste, the most related to non-catalytic sewage sludge thermal

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treatment, typically grouped into three categories: mono-incineration, co-combustion and alternative thermal processes such as non-catalytic wet oxidation of sludge (Werther and Ogata, 1999). The influence of catalysts on the combustion of solid sludge was studied for the civil sector. In particular, the most active catalyst was found to be MnO_2 supported on KOH, but it produced only 10 % increase in burning rate than in the absence of catalyst (Boxiong et al. 2006). We have recently shown that mixing a selected catalyst to tannery sewadge sludge caused several positive effects, both as regards the selectivity of the process, reducing the emission of cyclic and aromatic substances, both in terms of operating conditions, decreasing the combustion temperature and increasing the sludge oxidation rate (Ciambelli et al. 2009). An additional process step is required for sludge catalytic combustion, due to the need of optimising the procedure to obtain an effective mixture catalyst - dried sludge. In this work, the combustion behaviour of a dried tannery sewage sludge was compared in the absence and in the presence of catalyst, evaluating the influence of catalyst load. In order to avoid the mixing step, it was verified the possibility of adding the catalysts directly into the coagulation-flocculation process, responsible of the sludge formation.

2. Experimental

Samples of dried tannery sludge and wastewater were furnished by an Italian tannery wastewater treatment plant. Dried sludge was characterized by different techniques. The moisture content was evaluated by gravimetric analysis of samples before and after isothermal treatment at 373 ± 2 K up to constant weight. The total ashes percentage was obtained by weighing the inorganic residue after isothermal treatment at 823 K for 8 h. Finally, the amount of organic matter was calculated by subtracting the moisture and inorganic matter content in the samples. The mineral content was analyzed 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 analyzed by GC-MS after solvent extraction (hexane). By cool-on-column injector the sample was introduced into GC column (Restek Rtx-5 ms, 5 % diphenyl and 95% dimethyl polysiloxane, 0.25 mm ID, 30 m in length), then the separated compounds were analyzed 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 m in length) via split/splitless inlet system. To measure the combustion profile, dried sludge underwent to air flow simultaneous TG/DSC thermal analysis (SDTQ600, TA Instruments), studying the evolved gas by a mass detector (MS) in the range m/z = 15-103 (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 K/min heating rate in the temperature range 293-1273 K. A catalytic additive (UNISASSIP, material under patent procedure) was used to improve the combustion of the tannery sewage sludge. The optimal catalyst loading was determined by TG-MS analysis on catalyst-sludge mixtures prepared by gently grinding in an agate mortar to get an effective contact between the two solid phases (catalyst and dry sludge). The coagulation/flocculation process was carried out in our laboratory on a tannery wastewater using $Ca(OH)_2$ and $Al_2(SO_4)_3$ as coagulant agent to allow the precipitation of suspended substances. An anionic flocculant was added to the system. The obtained sludge was dried at 393 K. To study the effect of the presence of catalyst, the same procedure was performed adding the powder catalyst immediately after the addition of flocculant. The amount of added catalyst was similar to the optimal loading found in the previous tests. Sludge samples obtained in the coagulation/flocculation process with and without catalyst were analyzed by TG-MS technique.

3. Results and discussion

3.1 Sludge composition

Table 1 Results of analytical tests on sludge

Characteristic	*Unit*	*Wet basis*	*Dry basis*
Moisture and volatile matter at 376 K	wt%	8.5	-
Inorganic substances residue at 823 K	wt%	30	32
Organic substances	wt%	62	68
pH	pH unit	6.8	6.8
Al	mg kg^{-1}	15685	17143
Cr	mg kg^{-1}	18962	20723
Fe	mg kg^{-1}	6550	7159
Cr VI	mg kg^{-1}	< 0.02	< 0.02
Cu	mg kg^{-1}	69	75
Zn	mg kg^{-1}	1559	1703
Mn	mg kg^{-1}	72	79
Total oils and fats	mg kg^{-1}	160940	175891
Alcohols and fatty acids	mg kg^{-1}	5.110	5.554
Polycyclic aromatic hydrocarbons (PAHs)	mg kg^{-1}	2.6	3.0
Aromatic solvents	mg kg^{-1}	1.8	2.0
Chlorinated solvents	mg kg^{-1}	1.3	1.0
Carbonylic compounds	mg kg^{-1}	3150	3443
Phenols	mg kg^{-1}	812	887
Benzoalkanes	mg kg^{-1}	952	1040
Chlorinated alkanes with long chain	mg kg^{-1}	-	-
Organic nitrogen compounds	mg kg^{-1}	521	569
Non-aromatic light hydrocarbons (C<12)	mg kg^{-1}	12	14
Non aromatic heavy hydrocarbons (C>12)	mg kg^{-1}	7940	8678

The analytical results obtained for the dried sludge are shown in Table 1. The dried sludge is mainly constituted by water (the portion loss at 376 K) and organic matter, while the inorganic matter (residue at 823 K) is present in a smaller percentage. The pH values are around the neutrality (about 6.8). With regard the organic matter, the sludge is predominantly constituted of fatty substances and non aromatic hydrocarbons (C>12), according to the materials used during the tanning process. Aromatic solvents are present in very small quantities, together with other kinds of aromatic compounds, such as benzoalkanes, used as surfactants for fatliquoring mixtures, waxes and other finishing compounds in the leather processing. Non-aromatic hydrocarbons (C<12) are detected in low amounts. The most representative components of the inorganic fraction are trivalent chromium (Cr^{3+}), aluminum (Al) and iron (Fe). The abundance of chromium in the sludge depends of the initial composition of wastewater, as they are collected and equalized from the prevalent tanning process in the relevant industrial district. The presence of Al and Fe is mainly due to the use of sulphate and /or chloride salts of these elements as coagulant agents for tannery wastewater, although Al presence may derive in small quantities also from the tanning industry.

3.2 TG-MS analysis

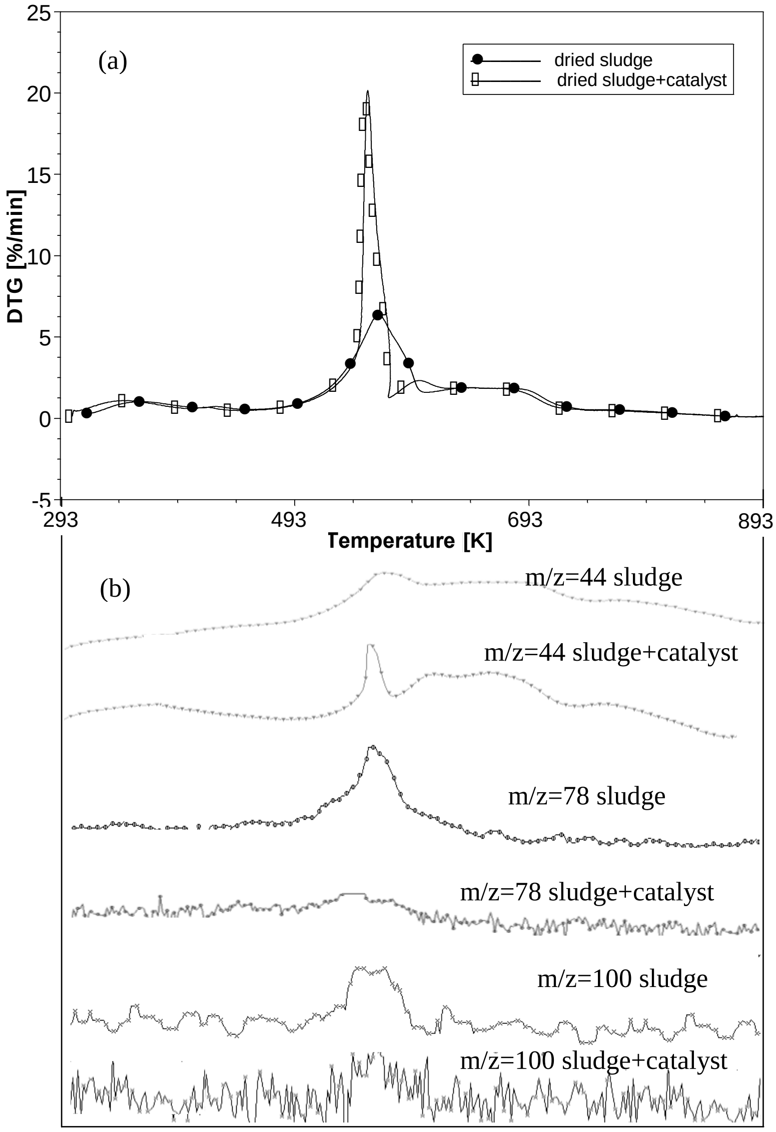

Figure 1 DTG behaviour (a) and MS spectrum (b) of dried sludge and dried sludge + catalyst

The selected parameters from thermal analysis tests were the first derivative maximum value 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 addition of catalyst to dried sludge caused a dramatic improvement of the combustion performance: T_{max} decreased from 565 K for sludge alone (Figure 1-a) to about 537 K in the presence of 5 wt% of catalyst. Moreover, DTG_{max} strongly increased, from 6 %/min in the absence of catalyst to about 20 %/min for catalyzed process. It is worthwhile to note that in the sludge catalytic combustion an evident decrease of the amount of released cyclic compounds and aromatics (m/z = 100 and 78, respectively) was found, since they were selectively oxidized to CO_2 (m/z=44) (Figure 1-b). Thus, catalyzed sludge combustion caused positive effects either with regard to the selectivity of the process, by reducing the emission of cyclic and aromatic substances, either with respect to the operating conditions, resulting in lower values of T_{max} and higher DTG_{max}. With the aim of finding the optimal catalyst loading, mixtures at different catalyst amount were prepared by gently grinding and tested by TG-MS analysis.

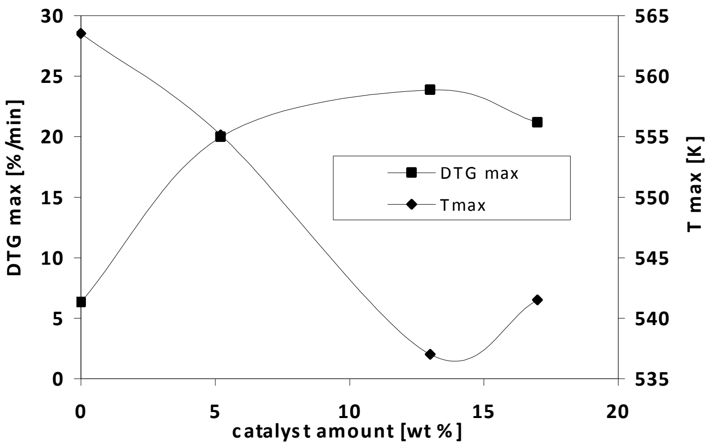

Figure 2 T_{max} and DTG_{max} obtained by gently grinding as a function of catalyst amount

In Figure 2, T_{max} and DTG_{max} values are reported as function of catalyst loading. The optimum was found at 13 wt% of catalyst, by evinced from the minumum of $T_{max.}$ Moreover, at the same catalyst content, DTG_{max} strongly increased from 6%/min in the absence of catalyst to about 24 %/min for the catalyzed process. At this optimal loading value the catalyst was added into the wastewater coagulation-flocculation process carried out in our laboratory through the following steps: i) addition of $Al_2(SO_4)_3$ (800 g m^{-3}) to the untreated wastewater (volume: 0.600 dm^3; pH=4.28); ii) addition of $Ca(OH)_2$ until reaching a pH value of 7; iii) addition of flocculants agent (4 g m^{-3}); insertion of catalyst into the process; iiii) drying at 393 K. The results of thermogravimetric analysis (DTG) of coagulation-flocculation sludge samples obtained with and without the catalyst vs temperature are reported in Figure 3. The main combustion stage was found between 753-873 K and 428-633 K for uncatalyzed and catalyzed process, respectively. Although in the presence of catalyst DTG_{max} is lower, the combustion of the organic content occurred at T_{max} ~573 K with respect to that obtained without catalyst (about

798 K), pointing out to an obvious improvement of oxidation process operated by the effective dispersion of the catalytic material inside the sludge.

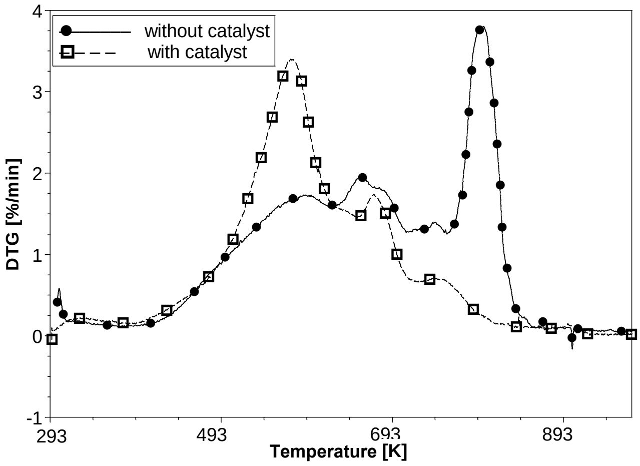

Figure 3 DTG behaviour of sludge samples obtained in the coagulation-flocculation process with and without the catalyst.

4. Conclusions

The addition of catalysts directly to the coagulation-flocculation process of tannery wastewater results in a good and effective dispersion of catalyst, improving sludge combustion and avoiding an additional mixing step. The catalytic sludge combustion caused positive effects, either with regard to the selectivity of the process by reducing the emission of cyclic and aromatic substances, either with respect to the operating conditions, lowering the temperature for the combustion of the sludge organic fraction.

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