

PRE-TREATMENT OF INDUSTRIAL LANDFILL LEACHATE BY FENTON'S OXIDATION

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ABSTRACT

Biological treatment (aerobic and anaerobic) of industrial landfill leachate is limited by the presence of toxic contaminants (e.g., heavy metals) and recalcitrant (biopersistent) organics (e.g., polyphenols, pharmaceuticals, cosmetics, etc.,), hindering viable conditions for biomass proliferation in biological reactors, with difficulties in meeting concentration limits imposed by applied regulations.

Fenton's oxidation by the use of Fe^{2+} - H_2O_2 - H^+ mixture may be used as a pre-treatment of industrial landfill leachate for preliminary abatement of the organic load and to improve biodegradability ($\text{BOD}/\text{COD}>0.4$) to favour biological oxidation in conventional wastewater treatment plants.

Leachate from Grottaglie (S.E. Italy) non-hazardous landfill ($\text{pH } 8.6$; $\text{COD}=11.000 \text{ mg l}^{-1}$; $\text{BOD}_5=2.400 \text{ mg l}^{-1}$; $\text{NH}_4\text{-N}=2.900 \text{ mg l}^{-1}$; conductivity= $60.000 \mu\text{s cm}^{-1}$) was laboratory tested in different operative conditions, i.e., initial pH, $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ratio, concentrations and reaction time. The oxidation reaction was monitored by equilibrium pH and residual COD and BOD_5 concentrations.

Best operative conditions were obtained at pH 3, $\text{Fe}^{2+}=700 \text{ mg l}^{-1}$, $\text{H}_2\text{O}_2=9,900 \text{ mg l}^{-1}$ ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio~13w/w), reaction time=2h. Following the oxidation reaction, solution pH was neutralized by the addition of $\text{Ca}(\text{OH})_2$ or NaOH (120 meq l^{-1}) for further abatement of target parameters by precipitation/sorption.

Preliminary technical/economical evaluation of possible process schemes is also given in the paper.

KEYWORDS: advanced oxidation, industrial landfill leachate, Fenton's reagent

1. INTRODUCTION

The main feature of current EU regulations on solid waste management (91/156 CE and EU 91/689 CE) is essentially based on "recovery, recycling and reuse" criteria. Nevertheless landfilling is still the most important technology for solid waste management. In the average, 60% of municipal solid wastes (MSW) produced, and even a larger fraction of industrial solid wastes (ISW), are still disposed-off in controlled landfilling [1].

Leachate formation, i.e., the liquid waste formed after weathering (rain, snowfalls) on the solid wastes, beyond the fraction released by intrinsic humidity and fermentation of solid wastes, is the main environmental impact during landfilling operation. The composition of such effluents

is variable depending on type, origin and composition of the wastes, the structure, management and the "age" of the landfill [2,3]. Above considerations are strictly applicable to MSW leachate, the problem is amplified in reference to ISW leachate being the origin of the landfilled solids diversified depending on the productive activity of origin.

Treatment of such highly concentrated wastewater is based on physico-chemical methods, i.e., chemical co-precipitation of heavy metals coupled to sorption of bulk COD on cheap coagulants ($\text{Ca}(\text{OH})_2$, polyelectrolytes) [4], or, in more advanced configurations, by the use of biosorbents such as lignocellulosic residues from the agri-food industry (olive-oil milling, winery, etc.). In this latter case biosorbents are used "once through" and the exhausted materials, containing massive quantities of contaminants, are disposed-off in the same landfill [5]. The use of more expensive sorbents such as activated carbon, adsorbent resins is possible with related economic implications. Alternatively, landfill leachate may be evaporated, incinerated or, in arid-semiarid areas, it may be re-circulated on the waste thus taking advantage of the evaporation favoured by the dry climatic conditions. Odour emissions is however the main limit of the operation [6].

Application of conventional biological treatment to reference liquors is limited by the presence of toxics (e.g., heavy metals) and/or recalcitrant organics (pharmaceuticals, polyphenols, endocrine disrupters) [7]. More than the generalised bio-toxicity, the technological problem is related to biorefractory nature of the organic matter due to the presence of high molecular weight substrates. Possibly, the autothrophic biomasses mediating hydrolysis of organic macromolecules are more sensitive to the mentioned toxicity and generalised non-viable conditions for biomass proliferation in the biological reactors.

Growing interest is lately focussed on the Advanced Oxidation Process (AOP) of landfills leachate with a multipurpose goal associated with: a) abatement of refractory COD load, with related enhancement of biodegradation after raising of the BOD_5/COD ratio; b) simultaneous removal of toxic contaminants by sorption-coprecipitation [8].

AOP are based on the formation of hydroxyl radicals (OH^\bullet), an extremely strong oxidant resulting from several reactions such as the synergistic action of two oxidants: $\text{O}_3+\text{H}_2\text{O}_2$; a catalyst and an oxidant: $\text{Fe}^{2+}+\text{H}_2\text{O}_2$ (the Fenton's reagent); a photocatalyst and an oxidant: $\text{TiO}_2+\text{H}_2\text{O}_2$; irradiation plus oxidation: $\text{UV}+\text{O}_3/\text{H}_2\text{O}_2$; etc., [9,10].

Generally speaking, full scale application of the Fenton's reagent does not requires supplementary operative costs beyond chemicals strictly needed for the oxidation reaction. In acidic media hydroxyl radicals are very efficiently formed for technical purposes. Chemicals are cheap, process layouts simple.

For proper design and control of full scale installations a basic knowledge of process principles and operative condition is needed. In the present paper, through laboratory experiments carried-out on the real leachate from Grottaglie (S.E. Italy) industrial landfill, is evaluated the influence of process operative parameters (pH, initial chemicals concentration and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ratio) on BOD_5/COD ratio for enhancement of conventional biological treatment of the resulting liquids.

2. GROTTAGLIE INDUSTRIAL LANDFILL

Grottaglie landfill site is located in the Apulia Region (S.E. Italy), 4 km south of the town. It is classified as a former 2nd Category type B installation, for "special-non-hazardous" industrial wastes according to the Italian legislation [11].

Fig.1 shows a schematic view of the installation including two lots, with capacities exceeding 330,000 m³ (lot no.1) and 1,500,000 m³ (lot no.2) and surface 15,000 m² (lot no.1), 28,000 (lot no.2, basin A) and 23,000 m² (lot no.2, basin B). A 3rd lot is underway and will be soon in operation.

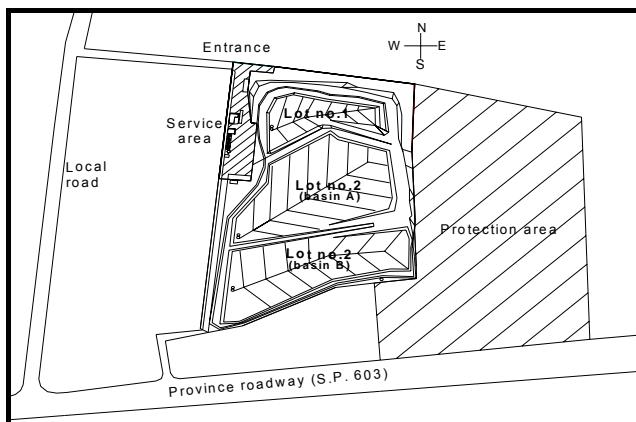


Figure 1. Layout of the Grottaglie industrial landfill

The annual leachate production (2003) for lot no.1 exceeded 7,600 m³. The average composition is shown in Tab.1.

Table 1. Average composition of the leachate produced at Grottaglie landfill

Parameter	Concentration (mg l ⁻¹)	Parameter	Concentration (mg l ⁻¹)
COD	13,500	Al	0.5
BOD ₅	3,000	Cr _{tot}	3
BTEX	< 5	Cr(VI)	< 0.5
Organic solvents	< 3	Ni	0.5
N-NH ₄	5,500	Pb	0.5
Oil-grease	< 10	Hg	< 0.5
Dry residue (105°,600°C)	545, 285	Cu	0.5
Suspended solids	700	Sn	< 0.5
Chlorinated organics	< 5	Cd	< 0.5
pH	8.5	Te	< 0.5
BOD ₅ /COD	0.22	Fe	5
Conductivity	60,000 μS cm ⁻¹	Zn	< 0.5

3. EXPERIMENTAL

Test leachate was characterised by the following relevant parameters: pH 8.7; COD = 10,915 mg l⁻¹; BOD₅ = 2,400 mg l⁻¹; N-NH₄ = 2,880 mg l⁻¹; Cr(III) = 9.8 mg l⁻¹; Conductivity = 58,700 μS/cm; and a BOD₅/COD ratio as low as 0.22.

The leachate sampled at the landfill was preliminarily neutralised at pH 3.2 by the addition of H₂SO₄ (98% w/v). The amount of the added acid was pre-determined by separate titration.

To optimise operative H₂O₂/Fe²⁺ ratio, in a first set of experiments the acidic leachate (pH 3.2) was contacted with arbitrary amounts of H₂O₂ (i.e., 9,900 and 5,280 mg l⁻¹ respectively), from stock solution (30% w/v), followed by increasing amounts of Fe²⁺ from a stock solution (FeSO₄·7H₂O 25% w/v). After 2h contact time, stirring was stopped and the solution allowed to settle (1h). The supernatant solution was analysed for residual COD, BOD₅ and Cr(III). Alternatively, at the end of the oxidation reaction and settling the mixture was added with Ca(OH)₂ slurry or 5M NaOH till neutralisation; a cation polyelectrolyte (Dryfloc 652 from Nymco Waters, Milan, Italy) was also added (3 mg l⁻¹) to favour clarification and metals co-precipitation.

In a second set of experiments, constant the H₂O₂/Fe²⁺ ratio previously optimised, were carried-out tests at increasingly higher concentrations to verify the influence of potential limitations on the oxidation reaction operated by the chemicals addition to the liquid phase. In this case also, the oxidation reaction was completed by the neutralisation step using the mentioned alkalisng agents and polyelectrolyte.

A final experiment was carried-out in a gas tight system for collection and quasi-quantitative characterisation of different outcoming products, i.e. gas, liquid, solid, resulting from the oxidation reaction.

4. RESULTS AND DISCUSSION

Fig.2 shows COD abatement (residual fraction in the liquid-phase) after optimisation of the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio, for tests carried-out at 9,900 and 5,280 $\text{mgH}_2\text{O}_2 \text{ l}^{-1}$ respectively. In spite of different initial amounts of hydrogen peroxide dosed, the curves converge to steady values of residual COD after dosage of about 400 and 700 $\text{mgFe}^{2+} \text{ l}^{-1}$, corresponding to a constant ratio in the range 14 w/w.

By assuming the following reactions presiding the Fenton's oxidation process:

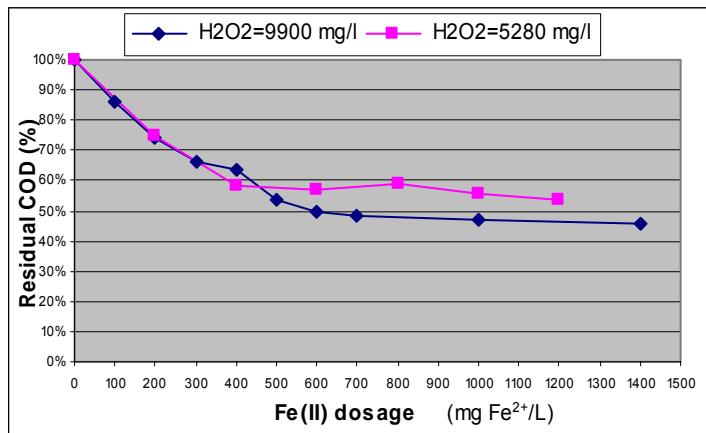
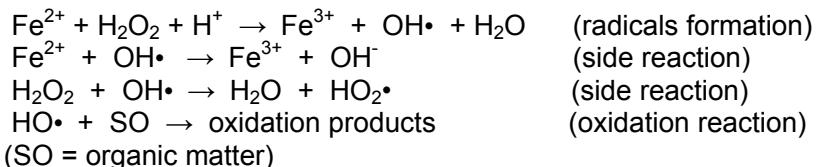


Figure 2. Fractional abatement of COD Vs. Fe^{2+} dosage for Grottaglie leachate

any excess dosage of chemicals should theoretically lead to a sensible reduction of free hydroxyl radicals (see side reactions above) thus inducing a minimum in the residual COD Vs. Fe^{2+} curve at the optimal ratio, followed by immediate raising due to depletion of $\text{OH}\cdot$ with corresponding sensitive reduction of the COD abatement. This is actually not verified in Fig.2 and, accordingly, some other oxidation reaction mechanism(s) should be postulated for the reference Fenton's process, based on a more accurate chemical characterisation of the leachate.

Fenton's oxidation of the Grottaglie leachate leads to ~50% abatement of the initial COD and 63% enhancement of the effluent biodegradability (BOD_5/COD ratio from 0.22 to 0.36) not too far from the indicated minimum figure (0.4) for efficient implementation of the aerobic biological treatment.

The addition of alkalis (lime slurry or caustic soda) and coagulation adjuvant (cationic polyelectrolyte) improves sensibly the quality of the oxidised liquid, in terms of reduced toxicity, after abatement of 40-70% trivalent chromium by using caustic or lime respectively, thus inducing sensible advantages to biological treatment to follow.

Based on the above results the following process scheme (Fig.3) may be proposed for potential upscaling of the Fenton's oxidation of the Grottaglie leachate.

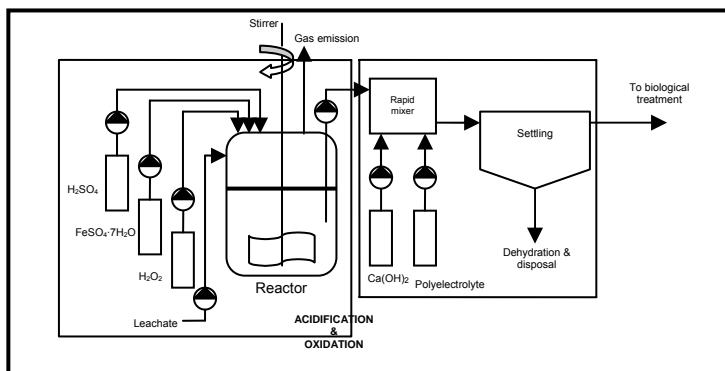


Figure 3. Schematic flow-sheet of the proposed Fenton's oxidation of Grottaglie leachate

Preliminary economic evaluation of the process indicates a tentative figure in the range of 9 € m^{-3} for the overall running costs of the process, including chemicals, power and maintenance. The figure appears definitely competitive as an "off-site" treatment of the landfill leachates based on conventional technologies, whose operative costs may exceed $20\text{-}30 \text{ €/m}^3$ depending on the final COD concentration.

5. CONCLUSION

A laboratory investigation was carried-out to verify potentialities of AOP (Fenton) pre-treatment of an industrial landfill leachate, with the aim of improving its biodegradability in view of conventional biological treatment to follow. To this aim the real leachate from Grottaglie landfill was tested under different operative conditions (i.e., initial pH, H_2O_2/Fe^{2+} ratio, addition of coagulants, final neutralisation). Possible layouts for process upscale are now open for development at a larger scale which is underway.

As a consequence of the present work the following main conclusions may be drawn:

- COD abatement ranging 50% of the initial figure is obtained, by the adoption of a H_2O_2/Fe^{2+} ratio exceeding 14 w/w;
- Enhancement of leachate biodegradation exceeding 60% (BOD_5/COD from 0.22 to 0.36) close to the threshold value set at 0.4
- Final clarification of the oxidised effluent by the use of cheap coagulants/precipitating agents [i.e., $Ca(OH)_2$, $NaOH$] and adjuvants (cationic polyelectrolytes) reduces final toxicity of the effluent after sensible reduction (70%) of the residual Cr(III) concentration
- Based on a preliminary technical/economic evaluation, O&M costs of the proposed process layout is in the range $9\text{-}10 \text{ € m}^{-3}$, a figure highly competitive with conventional treatments costs (e.g., inertisation) in the same landfill.

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