ECOTERRA
Journal of Environmental Research and Protection

An alternative to the treatment of leachate contaminated soil

[1]Irina A. Istrate, [2]Tiberiu Apostol, [2]Adrian Badea

[1] University "Politehnica" of Bucharest, Faculty of Biotechnical Systems Engineering, Bucharest, Romania; [2] University "Politehnica" of Bucharest, Department of Producing and Using Energy, Bucharest, Romania. Corresponding author: I. A. Istrate, ia_istrate@yahoo.com

Abstract. This paper presents an alternative to the problem that appears in almost all the landfills where the leachate collection is not done in a proper manner. In this research the efficiency of electric field based treatment is studied. The experimental test used the leachate obtained from a municipal solid waste landfill. For the present paper the main objective was to verify if the electrochemical treatment can be applied for the reduction of COD, BOD, ammonia nitrogen, total suspended solids and to observe if due to the usage of stainless steel electrodes for this treatment we could encounter hexavalent chromium in the liquid sample. The results obtained may be considered to be satisfactory, particularly if we consider how simple it is to apply this technology. In order to use this type of technology, the applicability of this technique to a specific industrial refluent must be supported by some preliminary studies were the treatment efficiency should be estimated.
Key Words: electro-oxidation, landfill leachate, BOD_5, COD.

Introduction. Since Romania has entered the European Union in 2007, had to align to all European regulations, including the ones related to landfilling. Also the care to the environment in a landfill must be at a higher level in order to have a very low negative influence on the environment. Laboratory studies to determine the effectiveness of various biological, physical and chemical treatment processes on sanitary landfill leachates have been investigated since the early 1970s (Boyle & Ham 1974; Ho et al 1974). Biological treatment processes, including anaerobic and aerobic processes, are quite effective for leachate generated in the early stage with a high BOD5/COD (Ehrig & Stegmann 1992). However, they generally fail to treat a leachate with a rather low BOD_5/COD, or high concentrations of toxic metals.

Leachate produced by municipal solid waste (MSW) landfills is a refluent that contains a high level of organic and inorganic pollutants that come from biological and physical-chemical processes within the controlled landfills. Leachate treatment is difficult, for a number of reasons (Pi et al 2009): the high concentrations of organic and inorganic pollutants; the variability of the characteristics of the refluent, over time, following the dynamics of the biological degradation processes of the waste in the landfill (quality fluctuation) and following those of the precipitations and of other hydrological balance terms (surface runoff, evapo-transpiration, field capacity of the landfill, etc.) (quantitative fluctuation).

In light of these difficulties, the possible alternatives available for the treatment are the ones classified as onsite treatments that may be grouped as follows (Rada et al 2013):

- complete treatment, intended to achieve the standards for discharging directly into surface waters;

- pretreatment, intended to reduce the quantity and/or polluting load of the leachate, which will subsequently be treated in an off-site plant and/or dumped into the sewage system.

The conventional municipal landfill is considered suitable for most climates, normally producing a highly contaminated leachate and a significant amount of landfill

gas. Leachate generation in landfills is affected by several parameters, including water content in waste, precipitation, evaporation, biochemical reaction of organic waste, operational mode, and even groundwater inflow.

In the last twenty years, several plants have been built for pretreating special refluents in medium-large treatment plants, that take in significant quantities of leachate, which, after a pretreatment that is generally chemical-physical (sifting, chemical precipitation of metals, etc.) and, in some cases, biological (activated sludge process, also combined with an ultra-filtration process – Membrane BioReactor, MBR), allow feeding the treated refluents into the water line of a municipal purification plant.

The treatment that allows discharging into the sewage system is greatly conditioned by the discharge limits set by existing provisions and regulations.

Generally speaking, in the case of mature leachates from MSW landfills, the greatest problems in achieving the levels set by the regulations for discharging into the sewage system are essentially the result of the high concentration of ammonia, which is associated with the low biodegradability of the leachate COD (Rada et al 2013).

In order to remedy this problem, a lot of research has been done over the last ten years to identify innovative solutions for the treatment of liquid waste that contains high concentrations of refractory organic compounds and of ammonia nitrogen.

Two types of treatment are of particular interest: chemical electro-oxidation; innovative biological removal.

In the last ten years, a number of unconventional biological processes have emerged (SHARON, Single Reactor High activity Ammonia Removal Over Nitrite; ANAMMOX, ANaerobic AMMonium OXidation, and CANON, Completely Autotrophic Nitrogen removal Over Nitrite), which are normally used when there are high ammonia nitrogen concentrations present (Rada et al 2013; Van Dongen et al 2001; Notenboom et al 2002; Sliekers et al 2003; Khin 2004), and which have a number of applications in full-scale plants (Mulder 2006).

Electric field based treatment – electro-oxidation. In this experimental investigation, our priority was to study the treatability of the leachate using electro-oxidation, because of the simplicity of the plant and of its management.

Electrochemical treatments consist of applying a voltage that is constant over time (a potentiostatic process) to the refluent being treated, or alternatively, of passing a current that is constant over time (a galvanostatic process) through it. The electrolytic cell is the reactor, in which this process takes place. As the continuous current flows, the negative electrode (cathode) gives electrons to chemical species which diminish; in contrast, the positive electrode (anode) receives electrons from chemical species, which become oxidized (Rada et al 2013).

Both of these processes encourage partial (conversion to more easily biodegradable compounds), or total electrochemical oxidation reactions (conversion to CO_2 and H_2O) of the pollutants. The choice of the electrode materials, the process voltages and currents, and the reaction time are decisive factors in the effectiveness of the process. Chemical electro-oxidation may be done in two distinct ways: indirect or direct electro-oxidation (Bashir et al 2009; Zhao et al 2009).

A second type of indirect electro-oxidation leads to the production of hydrogen peroxide H_2O_2, which also has a strong oxidizing effect on recalcitrant organic substances; by adding bivalent iron, Fe^{2+} (electro-Fenton), the reaction may be further enhanced (Do et al 1996; Deng et al 2008).

Another example of indirect electro-oxidation is what occurs in the presence of metal ions (Ag^{2+}, Fe^{3+}, Co^{3+}, Ni^{2+}) in a solution. These ions act as “mediators” and are oxidized onto the anode, passing from a low valence to a higher valence, thereby becoming much more reactive. In this way, they attack the organic compounds present in the solution and form hydroxyl radicals, which, in turn, are able to oxidize organic compounds. Many studies have demonstrated the efficiency of the electrochemical technology in removing pollutants of various kinds (Rada et al 2013; Bashir et al 2009; Li et al 1999; Szpyrkowicz 2005; Cabeza 2007; Mohan 2007; Deng 2007). Several experiments have been carried out to treat leachate by electro-Fenton, COD removal

yields of even greater than 85% were obtained and high yields also for the removal of nitrogen (Lin et al 2000; Zhang et al 2006; Atmaca et al 2009; Mohajeri et al 2010).

For the present paper the main objective was to verify if the electrochemical treatment can be applied for the reduction of COD, BOD, ammonia nitrogen, total suspended solids and to observe if due to different oxidative conditions for this treatment we could encounter hexavalent chromium in the liquid sample (taking into account that in soil we have Cr^{III} and by applying electrooxidation we could encounter the possibility to have Cr^{VI}).

The main charactheristics of the experimental setup used for the research, are presented in Figure 1 and the schematic diagram of the experimental apparatus used in the tests in Figure 2. The experimental setup used in this case had a capacity quite small but the construction principle can be extanded to a larger volume.

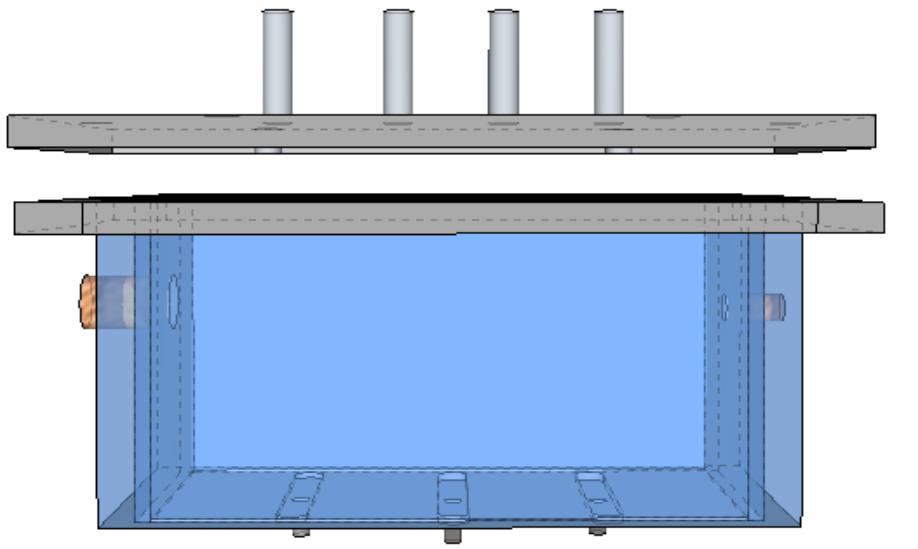

Figure 1. The experimental setup used for the research related to leachate treatment.

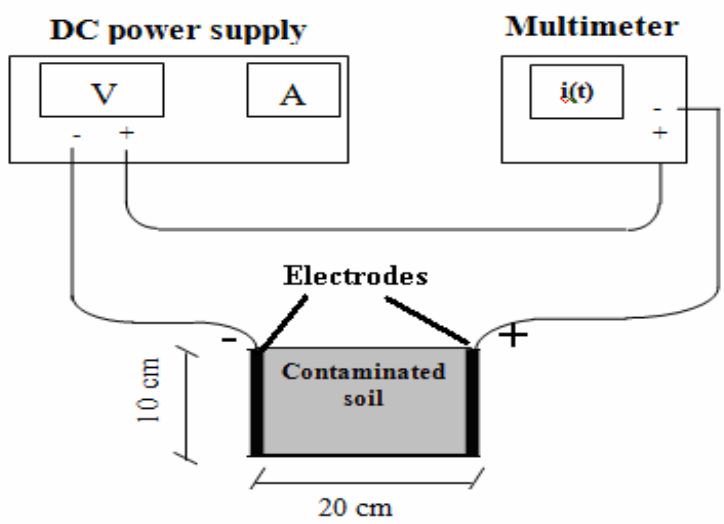

Figure 2. Schematic diagram of the experimental apparatus used in the tests (Rada et al 2013).

Experimental research. An understanding of the characteristics of landfill leachate is needed to interpret the variable performance found when treating leachates with electrochemical oxidation (Deng et al 2007).

Typical characteristics of landfill leachate are listed in Table 1. Organic compounds and ammonia nitrogen in landfill leachate are two principal chemical characteristics of environmental concern. Organic contaminants in leachate are described mainly using global

parameters such as chemical oxygen demand (COD), 5-day biochemical oxygen demand (BOD_5), and total organic carbon (TOC).

Table 1

Characterization of the leachate

Parameter	*Unit*	*Leachate*
pH	-	7.87
Conductivity	mS/cm	31.800
p-Alcalinity	Mmol/L	< 0.2
COD	Mg/L	7340
BOD_5	Mg/L	1250
Hydrocarbons	Mg/L	11 540
Ammonia nitrogen	mg L^{-1} $N(NH_4)$	1720
Nitrite	mg L^{-1} $N\text{-}NO_2$	< 0.1
Nitrate	mg L^{-1} $N\text{-}NO_3$	< 1.0
Total suspended solids	mg L^{-1}	311
Arsenic	mg L^{-1}	0.322
Beryllium	mg L^{-1}	0.900
Cadmium	mg L^{-1}	0.040
Cobalt	mg L^{-1}	0.110
Nickel	mg L^{-1}	0.050
Lead	mg L^{-1}	< 0.001
Total chromium	mg L^{-1}	9.40
Hexavalent chromium	mg L^{-1}	< 0.01

In young landfills (typically < 1–2 yr old), leachate is characterized by a high COD (typical 18,000 mg/L) and a high BOD_5/COD (typical > 0.6). In contrast, leachate in old landfills (typically > 5–10 yr old) is characterized by a relatively low COD (typical 100–500 mg/L), and a low BOD_5/COD (typical < 0.3). In our case it can be noticed that COD is less than half the value for the young landfills and the ratio BOD_5/COD is < 0.16.

Even thought the experimental research involved the development of several tests that had the same main charactheristics, in this paper only the results obtained after one test will be presented. The main parameters of the tests were: the treatment period was of 7 days, with a specific voltage that varied between 0.5 and 1 V cm^{-1}. During the first hours of treatment, it was decided that a voltage of 1.5 V cm^{-1} should be applied, but, given that, already after the first 30 minutes, the current value was greater than 2.5 A, the voltage was reduced eventually to 0.5 V cm^{-1}. This voltage was kept constant for the first 4 days of treatment, after which, it was increased to 1 V cm^{-1} in the second part of the treatment, because we found that the current tended to fall to a constant value, which, in the case in question, did not exceed 150 mA. The trend of the current monitored during the test is shown in Table 2. The amount of energy consumed was around 300 kWh m^{-3} (0.30 kWh L^{-1}).

The pH value increased slightly by the end of the treatment: from its initial value 7.87 to a final value 7.98. A review of previous experiments does not allow a conclusion on whether increasing or decreasing pH favors COD removal in electrochemical oxidation of landfill leachate (Deng et al 2007). The electrical conductivity fell from the initial value of 31.8 mS cm^{-1} to 15.15 mS cm^{-1} (after 7 days of treatment).

We can see a modest removal of COD and BOD after the first 3 days of treatment; this removal went on to improve by the end of the treatment (from 25% to 70% for COD, and from 30% to 60% for BOD). The test presented in this article refers to the one with higher results.

Table 2

Characterization of the leachate after the test with higher result

Parameter	*Unit*	*Leachate*
pH	-	7.98
Conductivity	mS/cm	15.150
p-Alcalinity	Mmol/L	< 0.2
COD	Mg/L	2936
BOD_5	Mg/L	375
Hydrocarbons	Mg/L	5770
Ammonia nitrogen	mg L^{-1} $N(NH_4)$	1376
Nitrite	mg L^{-1} $N\text{-}NO_2$	< 0.1
Nitrate	mg L^{-1} $N\text{-}NO_3$	< 1.0
Total suspended solids	mg L^{-1}	513

In view of the national maximum value for discharging into the sewage system that are significant lower than the ones obtained for the leachate, it is necessary to apply the treatment for at least another 14 days (in addition to the 7 already tested).

An interesting phenomena observed also in other papers (Rada et al 2013) was the sedimentation that represented around 20% of the total treated volume. This can be due also to the corosion of electrodes which were subjected to a relative high current. The behavior of anode materials is a major experimental concern during electro-oxidation of wastewater. During electro-oxidation of leachate, the effect of cathode materials has not been extensively investigated, although they may have a considerable influence on electro-oxidation of organic compounds (Deng et al 2007). The increase in the suspended solids was due also to electro-flocculation phenomena, caused after iron ions were released into the solution.

For ammonia nitrogen, we can see a modest final removal, of only 20.07%. Compared with others research in our case it was not observed the increasing of the nitrate quantity which would have indicated a transformation of ammonia nitrogen.

In this case, the total suspended solids did not register any removal, but an increase by nearly 13% after the 7-day treatment. This was due, in part, to the phenomena of corrosion of the steel plates, with a subsequent release of suspended matter, and, in part, to electro-flocculation phenomena, produced following the release of iron ions into the solution.

One interesting value measured in the initial analysis is the hydrocarbons wuantity that exceeded the legal limits by five times. After the applied treatment the removal percentages regarding this value reached up to 50%.

Electrochemical oxidation of landfill leachate under appropriate conditions can remove most COD and almost all ammonia, and also significantly remove color. During electro-oxidation, reduction of pollutants appears to be primarily due to indirect oxidation. Pretreatment methods, anode materials, pH, current density, chloride concentration and electrolytes added all influence removal efficiencies of pollutants and energy consumption. Two drawbacks of electro-oxidation may limit its wide application for landfill leachate treatment: high energy consumption, and potential for formation of chlorinated organics. Especially because of its expensive operating costs compared with other available technologies (for example, biological processes), electro-oxidation will be favored as a finishing step in a combined process or an auxiliary unit in emergency situations, instead of a full treatment for landfill leachate (Cossu et al 1998; Deng et al 2007).

Conclusions. The effects of a number of operating factors on electrooxidation of leachate have been investigated, including pretreatment, anode materials, pH, current density, concentration, as well as electrolytes added. These factors variously influence pollutant removal efficiency, current efficiency and energy consumption.

Tests were carried out on a laboratory scale, on a number of samples of landfill leachate, in order to verify whether the technique of electro-oxidation could be applied for its treatment.

The yields obtained may be considered satisfactory, particularly if we consider how simple it is to apply this technology. As with all processes for treating refluent water, the applicability of this technique to a specific industrial refluent must be supported by preliminary feasibility studies that estimate its effectiveness and that optimize the project parameters. In order to achieve the discharging limits for COD, but particularly those for nitrogen, electro-oxidation is not sufficient on its own, and other treatments must be applied.

One of the problems found in similar tests was the presence of a higher value at the end of the treatment than at the beginning, for some metals, which may be primarily, albeit in part, associated with corrosion of the electrodes. For our research it was not the case. Eventhought this aspect should be taken into account when this technology is used.

Electrochemical oxidation is a promising and powerful technology, especially for low BOD_5/COD or high toxic landfill leachate where biological processes suffer. Future work is expected to clarify the influence of pH, and the risk of formation of chlorinated organics during electro-oxidation of landfill leachate. Additionally, development of material science for more economical and effective electrodes is expected to improve the application of electro-oxidation of landfill leachate. Also tests on different scales will be performed in the future in order to better establish if this technology is indeed a good alternative.

Acknowledgements. This work was supported under FSE – European Structural Funds POSCCE-A2-O2.1.1, REMOVED ID1679, SMIS-CSNR: 47475, Nb. 549/02.09.2013 (2013-2015).

References

Atmaca E., 2009 Treatment of landfill leachate by using electro-Fenton method. Journal of Hazardous Materials 163(1):109-114.

Bashir M. J. K., Isa M. H., Skutty R. M., Awang Z. B., Aziz H. A., Mohajeri S., Farooqi I. H., 2009 Landfill leachate treatment by electrochemical oxidation. Waste Management 29:2534-2541.

Boyle W. C., Ham R. K., 1974 Biological treatment of landfill leachate. Journal Water Pollution Control Federation 46(5):860–872.

Cabeza A., Urtiaga A. M., Ortiz I., 2007 Electrochemical treatment of landfill leachates using a boron-doped diamond anode. Ind Eng Chem Res 46:1439–1446.

Cossu R., Polcaro A. M., Lavagnolo M. C., Mascia M., Palmas S., Renoldi F., 1998 Electrochemical treatment of landfill leachate: oxidation at Ti/PbO_2 and Ti/SnO_2 anodes. Environmental Science and Technology 32(22):3570–3573.

Deng Y., Englehardt J. D., 2007 Electrochemical oxidation for landfill leachate treatment. Waste Management 27:380–388.

Deng Y., Englehardt J. D., 2008 Hydrogen peroxide-enhanced iron-mediated aeration for the treatment of mature landfill leachate. Journal of Hazardous Materials 153(1-2):293-299.

Do J. S., Yeh W. C., 1996 Paired electro-oxidative degradation of phenols with in situ generated hydrogen peroxide and hypochlorite. Journal of Applied Electrochemistry 26(6):673-678.

Ehrig H., Stegmann R., 1992 Biological process. In: Landfilling of waste: leachate. Christensen T. H., Cossu R., Stegmann R. (eds), Elsevier Applied Science, London and New York.

Ho S., Boyle W. C., Ham R. K., 1974 Chemical treatment of leachate from sanitary landfills. Journal Water Pollution Control Federation 46(7):1776–1791.

Khin T., Annachhatre A. P., 2004 Novel microbial nitrogen removal processes. Biotechnology Advances 22:519-532.

Li X. Z., Zhao Q. L., Hao X. D., 1999 Ammonium removal from landfill leachate by chemical precipitation. Waste Management 19:409-415.
Lin S. H., Chang C. C, 2000 Treatment of landfill leachate by combined electro-Fenton oxidation and sequencing batch reactor method. Water Research 34(17):4243-4249.
Mohajeri S., Aziz H. A., Isa M. H., Zahed M. A., Adlan M. N., 2010 Statistical optimization of process parameters for landfill leachate treatment using electro-Fenton technique. Journal of Hazardous Materials 176(1-3):749-758.
Mohan N., Balasubramanian N., Ahmed Basha C., 2007 Electrochemical oxidation of textile wastewater and its reuse. Journal of Hazardous Materials 147(1-2):644-651.
Mulder J. W., Duin J. O. J., Goverde J., Poiesz W. G., Van Veldhuizen H. M., Van Kempen R., Roeleveld P., 2006 Full-scale experience with the SHARON process through the eyes of the operators. Proceedings of WEFTEC 06, October 21-25, Dallas Convention Center Dallas, TX, USA.
Notenboom G. J., Jacobs J. C., Van Kempen R., Van Loosdrecht M. C. M., 2002 High rate treatment with SHARON process of waste water from solid waste digestion. IWA 3rd International Symposium Anaerobic Digestion of Solid Wastes, 18-20 September 2002, Munich, Germany.
Pi K. W., Li Z., Wan D. J., Gao L. X., 2009 Pretreatment of municipal landfill leachate by a combined process. Process Safety and Environmental Protection 87(3):191-196.
Rada E. C, Istrate I. A, Ragazzi M., Andreottola A., Torretta V., 2013 Analysis of electro-oxidation suitability for landfill leachate treatment through an experimental study. Sustainability 5(9):3960-3975.
Sliekers A. O., Third K. A., Abma W., Kuenen J. G., Jetten M. S. M., 2003 CANON and ANAMMOX in a gas lift reactor. FEMS Microbiol Lett 218:339-344.
Szpyrkowicz L., Kaul S. N., Neti R. N., Satyanarayan S., 2005 Influence of anode material on electrochemical oxidation for the treatment of tannery wastewater. Water Research 39:1601-1613.
Van Dongen U., Jetten M. S. M., MVan Loosdrecht C. M., 2001 The SHARON ANAMMOX process for treatment of ammonium rich wastewater. Water Science and Technology 44:153-160.
Zhang H., Zhang D., Zhou J., 2006 Removal of COD from landfill leachate by electro-Fenton method. Journal of Hazardous Materials 135(1-3):106-111.
Zhao X., Qu J., Liu H., Wang C., Xiao S., Liu R., Liu P., Lan H., Hu C., 2010 Photoelectrochemical treatment of landfill leachate in a continuous flow reactor. Bioresource Technology 101(3):865-869.

Received: 07 June 2014. Accepted: 28 June 2014. Published online: 30 June 2014.
Authors:
Irina Aura Istrate, University “Politehnica” of Bucharest, Faculty of Biotechnical Systems Engineering, Splaiul Independentei, 313, 060042 Bucharest, Romania, e-mail: ia_istrate@yahoo.com
Tiberiu Apostol, University “Politehnica” of Bucharest, Department of Producing and Using Energy, Splaiul Independentei, 313, 060042 Bucharest, Romania
Adrian Badea, University “Politehnica” of Bucharest, Department of Producing and Using Energy, Splaiul Independentei, 313, 060042 Bucharest, Romania

How to cite this article:
Istrate I. A., Apostol T., Badea A., 2014 An alternative to the treatment of leachate contaminated soil. Ecoterra 11(2):78-84.