Chemical Engineering Journal 288 (2016) 87–98

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Landfill leachate treatment: Comparison of standalone electrochemical degradation and combined with a novel biofilter

G. Del Moro [a], L. Prieto-Rodríguez [b], M. De Sanctis [a], C. Di Iaconi [a], S. Malato [b], G. Mascolo [a,*]

[a] Istituto di Ricerca Sulle Acque, Consiglio Nazionale delle Ricerche, Viale F. De Blasio 5, 70132 Bari, Italy
[b] Plataforma Solar de Almería, CIEMAT, Carretera Senés, km 4, 04200 Tabernas, Almería, Spain

HIGHLIGHTS

- Landfill leachate treatment involving electrolysis using DSA® electrodes and a new type of biological reactor.
- With a current density of 83 mA/cm^2 for 240 min can be obtained an effluent dischargeable into sewer.
- Where ammonia is present, 82% of it is removed after 240 min of electrolysis at 200 mA/cm^2.
- At 133 and 200 mA/cm^2, the AOX concentration decrease if the electrolysis is extended over 60–70 min.
- Electrochemical treatment leads to a decrease in toxicity, regardless the applied current density.

ARTICLE INFO

Article history:
Received 8 July 2015
Received in revised form 19 November 2015
Accepted 21 November 2015
Available online 2 December 2015

Keywords:
Landfill leachate
Electro-oxidation
AOX
Toxicity evaluation
Residual chlorine

ABSTRACT

Raw leachate and a biological effluent coming from the same raw leachate that has been biologically treated in a new type of biological reactor, were electrochemically treated. A batch-type electrolytic cell using two patented DSA® electrodes was employed. Raw leachate, treated for 240 min at a current density of 200 mA/cm^2, falls within the sewer discharge limits set by Italian legislation for the COD. Instead, effluent obtained through combined biological and electro-oxidation treatment (by using 83 mA/cm^2 and 133 mA/cm^2) has a COD such that could be discharged into the sewer and, after applying a current density equal to 200 mA/cm^2 after 240 min, has a COD value such that can even discharged into receiving water bodies. The electrochemical oxidation carried out is only effective on nitrogen ammonia through indirect electro-oxidation; it is not effective on other nitrogen-containing species. In any case, where ammonia is present (i.e., in the raw leachate), 82% is removed by the end of the test (i.e., after 240 min of electrolysis) at 200 mA/cm^2. Also, for the raw leachate, chloramine formation is most marked at low current densities. Nevertheless, the toxicity does not appear to be affected; in fact, decrease regardless of the applied current density.

1. Introduction

One of the main problems related with this common practice in a landfill is the highly polluted liquid, known as leachate, generated by rainwater percolation through wastes, biochemical processes in waste cells and the inherent water content of the waste itself [1–4]. According to widely employed regulations, landfill leachate must be properly treated before it is disposed into receiving water bodies. The most common practice to avoid environmental risks is to pump and discharge leachate into conventional wastewater treatment plants [5]. Although, new technologies and new treatment combinations are required to reach the target discharge limits [6]. Among the others, electrochemical oxidation is, in principle, superior to conventional treatments, owing to its versatility, absence of sludge production and possibility of automation [7]. During recent years, electrochemical processes have been proposed as alternative treatment methods for both carbon and ammonium removal, owing to advantages concerning environmental compatibility, safety, selectivity and cost effectiveness [8–13]. There are two possible mechanisms for pollutant degradation through electro-oxidation, namely, (i) direct anodic oxidation, where pollutants are oxidised after adsorption on the anode surface, without involvement of any substances other than the electron or (ii) indirect electrolysis, in which organic pollutant oxidation is mediated by reactive electro-generated species. Each mechanism can dominate on the basis of the nature and structure

* Corresponding author. Tel.: +39 080 5820519; fax: +39 080 5313365.
E-mail address: giuseppe.mascolo@ba.irsa.cnr.it (G. Mascolo).

http://dx.doi.org/10.1016/j.cej.2015.11.069
1385-8947/

of electrode material, experimental conditions and electrolyte composition [14,15].

Chemical reaction with electro generated species from water discharge at the anode such as physisorbed hydroxyl radical (·OH) or chemisorbed such as oxygen in the lattice of a metal oxide (MO) anode can occur. During indirect oxidation, the agents produced on the anode, that are responsible for oxidation of inorganic and organic matters may be chlorine and hypochlorite, hydrogen peroxide, and ozone. Moreover, during electrolysis, two species of active oxygen can be electrochemically produced on oxide anodes (MO*x*). One is the chemisorbed "active oxygen" (oxygen in the oxide lattice, MO*x* + 1), while the other is the physisorbed "active oxygen" (adsorbed hydroxyl radicals, ·OH) [16,17]. Contaminants are, to a large extent, destroyed through indirect oxidation by oxidants (such as hypochlorite) generated from the anodic oxidation of chloride, which is abundant in the leachate [18,19]. Nevertheless, in the presence of chloride there are some reactions that can take place, leading to the formation of undesirable by-products. Chloramines, produced by the reaction between ammonia and free chlorine in the electrolysis system, are of great concern because of their negative impact on the environment through their toxicity [20,21]. Unfortunately, there is a lack of information in this field, because few detailed studies have focused on the formation of undesired inorganic by-products during the electrolysis of wastewaters containing chloride. In the present work, the effectiveness of electrochemical oxidation treatment was evaluated on both raw and biologically treated leachates. The biological reactor is a sequencing batch biofilter granular reactor whose acronym is SBBGR. This technology is based on a submerged biofilter that operates in a "fill and draw" mode. In this biofilter all the phases of the biological treatment (i.e., carbon removal, nitrogen removal, secondary sedimentation) were carried out in a single operative unit. The effectiveness of the technology stems from the fact that the biomass, growing as granules, are four-to-five times more dense than that of conventional activated sludge granules, making it possible to treat concentrated wastewater over a shorter timescale and in very small reactors. Indeed, biological treatments of landfill leachate are attractive and they are, probably, the most cheapest processes that can reduce the chemical oxygen demand (COD) and nitrogen in leachates. However, landfill leachate is very difficult to treat biologically, owing to the presence of recalcitrant compounds and a high concentration of ammonia. In fact, such biological processes are quite effective for leachate that is generated in the early stages of landfill life, which is generally characterised by a high BOD_5/COD. Conversely, they generally fail to treat leachates coming from aged landfills, which are usually characterised by a rather low BOD_5/COD ratio [22–27]. That being the case the biological process alone would hardly be effective, but combined with other treatments could help to control costs and to achieve discharge legal limits. On the other hand, advanced oxidation processes (AOPs) are able to decompose a great variety of compounds. AOPs have been demonstrated to directly produce hydroxyl radicals electrochemically in an anodic reaction from water. These hydroxyl radicals react strongly with all organic substances, usually by hydrogen abstraction [28]. In this context, oxidative electrochemical technologies, which are widely recognised as being highly efficient for recalcitrant wastewater treatment, offer an effective solution to the landfill leachate problem [29–34]. The effectiveness of the process was assessed in terms of the removal of the main gross physicochemical parameters. Assessment of the electrochemical oxidation of ammonium contained in the landfill leachate was carried out by analysing, not only the formation of nitrogen oxidation compounds, but also the formation and time evolution of total organo-chlorine derivatives. The investigation also included an estimation of the toxicity, both at the end and during the treatments. The significance of this work is to explore aspects that have not previously been highlighted during electro-oxidation studies of landfill leachates. The treatment of wastewater containing large quantities of ammonia, nitrogen and chloride species, while leading to satisfactory gross parameters in terms of removal efficiency, can generate harmful by-products, whose presence must be taken into consideration for possible landfill leachate treatments. To the best of our knowledge, there are some papers dealing with issues somehow related to this topic. Here we merely name a few of the most significant and potentially comparable with the work in question. Two of these previous works were focused on the details of ammonia electro-oxidation mechanism, one using synthetic wastewater [8] and the other using a Ru–Ir/TiO_2 anode immersed in a continuous flow reactor filled with powdered activated carbon (PAC) [32]. Another report by Pérez et al. [10] presents by-product behaviour during the electro-catalytic treatment of ammonium whilst a different study focused on GC–MS analysis of organic compounds when landfill leachate was treated by means of combined aged-refuse bioreactor and electro-oxidation processes [9]. Zhang and colleagues [18] also studied the electro-oxidation of leachate but using different electrodes materials from those described in this work. In addition, all the work of Zhang et al. is focused on the mathematical modelling of the process relative to the decay of COD and ammonia leaving out entirely the analysis of the mechanisms related to the nitrogen forms and any by-products formation as AOX. Instead, Anglada et al. [35] dealing with by-products of anodic oxidation such as chloroform and haloacetonitriles but they used only the electro-oxidation and with electrodes different from those employed in this work. It is worth noting that the experimental apparatus of the cited works were different to that used in the present one. Furthermore, different aspects of the considered treatment set-up are handled within the same research work (i.e., we study the gross parameters, fate of the nitrogen species, chlorinated by-products, halogenated organic compounds and toxicity).

2. Materials and methods

2.1. Landfill leachate

The leachate comes from a landfill located in the Foggia province, in the south of Italy. The landfill is used for the disposal of municipal solid waste from a basin of users who belong to 29 municipalities including that of Foggia. The landfill is about 10 km from the centre of the city of Foggia. The plant, was built in an old quarry. The filling of the dump is taking place in elevation. For the realisation of the containment parietal walls has been used a landfill mining technique called "Walls and reinforced embankments in waste". This technique is made to increase in height the stacking capacity of municipal solid waste landfill. As for climate aspects, it is present a continental climate with high temperature ranges, due especially to the maximum values which are especially high. The temperature annual average is 20 °C, with peaks sometimes that have touched even 50 °C. The average annual precipitation is around 700 mm, but is not uncommon the case of annual values that fall below 500 mm.

Table 1 details the compositions of the raw and biologically treated leachate stocks used during this experimentation.

2.2. Setup

2.2.1. Biological system

The lab-scale biological plant system consisted of a sequencing batch biofilter granular reactor (SBBGR). The SBBGR is an innovative biological system that combines advantages of attached biomass systems, including greater robustness and compactness,