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Influence of iron species on integrated microbial fuel cell and electro-Fenton process treating landfill leachate

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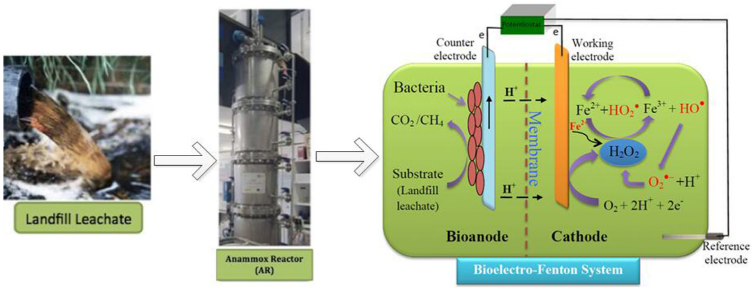
HIGHLIGHTS

- MFC-driven electro-Fenton process was evaluated to treat landfill leachate.
- A maximum current density of 1.7 A m^{-2} was obtained.
- Iron (II) catalyst showed slightly better efficiency than iron (III).
- 300 mg L^{-1} iron dosage was proved to be optimum.

GRAPHICAL ABSTRACT



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ABSTRACT

MFC-based bioelectro-Fenton (BEF) system was examined in duplicate to deal with recalcitrant organics of mature landfill leachate pre-treated with partial nitritation-anammox process. The system performance was evaluated at various iron species (iron (II) sulfate and iron (III) chloride) and iron dosages (150, 300 and 500 mg L^{-1}) as Fenton catalyst. A simultaneous anolyte and catholyte COD removal efficiency of 71–76% and 77–81% occurred respectively, having glucose substrate (anolyte) and leachate (catholyte). Upon switching the system to 80% and then 100% real leachate as anolyte substrate affected the COD removal efficiency and CE, but no significant effect was noticed in terms of current density. A maximum current density of 1.7 A m^{-2} was obtained throughout the experiment. Iron concentration of 300 mg L^{-1} proved to be optimum dose; whereas, iron (II) catalyst showed slightly better efficiency than iron (III). The results demonstrated the potential of an MFC based BEF oxidation as sustainable and efficient route for simultaneous anodic and cathodic pollutant removal coupled with power production.

Glossary

- BES (Bioelectrochemical system)

The system which converts the chemical energy stored in wastewater to electrical energy

- MFC (Microbial fuel cell)

The BES that produces electricity from microbial decomposition of organic waste stream

- BEF (Bioelectro-Fenton)

MFC-driven electro-Fenton oxidation that synthesizes H_2O_2 *in situ* in the cathode chamber followed by hydroxyl radical production in the presence of iron catalyst

- CE (Coulombic efficiency)

Ratio of electrons evacuated from the anode relative to the total electrons available from substrate consumption

- AOPs (Advanced oxidation processes)

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Chemical treatment procedures designed to degrade organic and sometimes inorganic contaminants through reactions with strong oxidants

1. Introduction

Sanitary landfill leachate especially old leachate is quite hard to treat by conventional techniques owing to presence of a wide variety of biorecalcitrant compounds with high chemical stability and/or low biodegradability [1,2]. Biological processes are effective to remove carbon and nitrogen content but limited to young landfill leachate. Anaerobic ammonium oxidation (anammox) process is a viable option to eliminate nitrogen that does not need external carbon source [3], and it can effectively treat mature landfill leachate but not meant to remove the organic matter [4].

Over the last two decades, electrochemical advanced oxidation processes (EAOPs) have received significant attention for the remediation of wastewaters having biorefractory organics; among them Electro-Fenton (EF) process is one of the most applied EAOPs for wastewater treatment [5–7]. Recently many studies integrated the EF process with certain biological processes to efficiently remove pollutants found in wastewaters. For example, in a study [8] aged refuse bioreactor and photochemical technique were successfully combined as pre and post treatment of old landfill leachate, respectively. In another experiment, Trellu et al. [9] coupled anodic oxidation– an EAOP and aerobic biological treatment for proper handling of a synthetic solid waste solution containing phenanthrene, Tween 80 and humic acids. Similarly, Olvera-Vargas et al. [10] used this terminology (bioelctro-Fenton) for a hybrid process coupling electro-Fenton (EF) process and aerobic biological treatment for effective mineralization of beta-blocker metoprolol aqueous solutions.

Bioelectrochemical system (BES) is an emerging technology that takes advantage of microbial interaction with solid electron acceptors/donors. Among various BES that have been developed, microbial fuel cells (MFCs) draw wide interest because of its capacity in terms of electricity generation from waste. They can transform chemical energy stored in waste into electrical energy with the benefit of removing the intrinsic organics in wastewater [11]. MFCs are regarded as environment friendly technologies with no pollutants generation during their operation, however, like other biological-based processes, they are inefficient alone for wastewaters like old landfill leachate containing biorecalcitrant organics [12]. Hence, recently MFCs (biological processes) have been integrated with EAOPs such as Fenton process known as MFC-mediated electro-Fenton or simply bioelectro-Fenton (BEF) for simultaneous abatement of anodic and cathodic pollutants [13–16].

As shown in Fig. 1, during bioelectro-Fenton process, the oxidation of organic compounds by anodic microbes release electrons that are transferred to the cathode via external wire. In the cathode they are consumed to reduce an electron acceptor, commonly oxygen. It results in *in-situ* synthesis of hydrogen peroxide (H_2O_2) by a two-electron transfer according to Eq. (1).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

The electrochemically generated H_2O_2 reacts with externally added iron source (Fe^{2+} (Fenton reaction) and Fe^{3+} (Fenton-like reaction)) in the cathode chamber fed with O_2 or air to produce hydroxyl ($^{\bullet}OH$) and hydroperoxyl ($HO_2^{\bullet}$) or superoxide ($O_2^{\bullet-}$) radicals (Eqs. (2)–(4)), which can remove recalcitrant organic pollutants (RP) (Eq. (5)). Some of Fe^{3+} produced can be reduced to Fe^{2+} through Eq. (3), although the rate is several orders of magnitude slower than that of Fe^{2+} to Fe^{3+} conversion through Eq. (2) [6,17].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + HO^- \tag{2}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \tag{3}$$

$$HO_2^{\bullet} \rightarrow H^+ + O_2^{\bullet-} \tag{4}$$

$$RP + {}^{\bullet}OH \rightarrow \text{Oxidation products} \tag{5}$$

Landfill leachate has been used as anodic substrate in BES but low current density, coulombic efficiency (CE) and coulombic recovery was achieved [18–20] probably owing to huge portion of highly recalcitrant organic matter. BEF has been furnished for the removal of organic substrates simultaneously from anode and cathode chambers coupled with electricity generation [13,16], but no study employed landfill leachate as feedstock simultaneously in the anode and cathode. In this study, we used for the first time the effluent of mature landfill leachate pretreated with partial nitritation-anammox process (mainly employed to remove nitrogenous pollutants) [21] as feed in both anode and cathode chambers of MFC simultaneously, having biorefractory organic matter ($BOD_5 < 166.9 \pm 29.2$ mg L^{-1}).

Few investigations have been carried out to compare the Fenton and Fenton-like processes for leachate treatment, and the reported results are controversial. Rivas et al. [22] reported that Fenton and Fenton-like reactions had similar organics removal efficiencies. However, another study revealed that Fenton process attained a higher COD removal and improved the biodegradability than Fenton-like reaction [23]. To the best of our knowledge no investigation has been carried out comparing various iron species and doses in MFC-based bioelectro-Fenton oxidation.

This work compares two iron species i.e. iron (II) sulfate heptahydrate and iron (III) hexahydrate, and doses of the later for the removal of recalcitrant organics present in the landfill leachate (effluent of anammox reactor treating landfill leachate). Moreover, the feasibility of anodic bio-oxidation of landfill leachate as substrate was also evaluated coupled with current density and columbic efficiency.

2. Experimental

2.1. Landfill leachate origin and sampling

Sanitary landfill leachate was collected from the Oris urban landfill site (Osona, Catalonia, Spain) and stored in 1000 L tanks placed at the University of Girona. The raw leachate was highly rich with nitrogen content and recalcitrant organic pollutants having a BOD_5/COD ratio <0.1. The leachate was firstly treated in a partial nitritation/anammox system installed at LEQUiA (University of Girona, Spain) laboratory, which was mostly employed for nitrogen content removal from urban landfill leachate. The mechanism, operation and efficiency has been evaluated previously [21].

2.2. Leachate characterization

Table 1 presents the mean values (± standard deviation) of the major physico-chemical characteristics of effluent of the anammox reactor treating landfill leachate. The leachate showed a dark brown colour and high values of UV_{254} (24.05 ± 8.42), attributed to the presence of dissolved organic matter, specifically those that contain aromatic rings or unsaturated bonds (double and triple) in their molecular structures (e.g. humic and fulvic acids) [24]. The leachate contained a mean COD concentration of 2152 ± 624 mg L^{-1} and low BOD_5/COD ratio of <0.1 depicting less biodegradability of the organic matter. A low concentration of ammonium (76.25 ± 54.87 mg L^{-1}) was noticed in the pre-treated leachate because it was overwhelmingly degraded by anammox process [21]. The pH of leachate sample was 7.6 ± 1.8 due to the pH control required