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Life cycle, techno-economic and dynamic simulation assessment of bioelectrochemical systems: A case of formic acid synthesis

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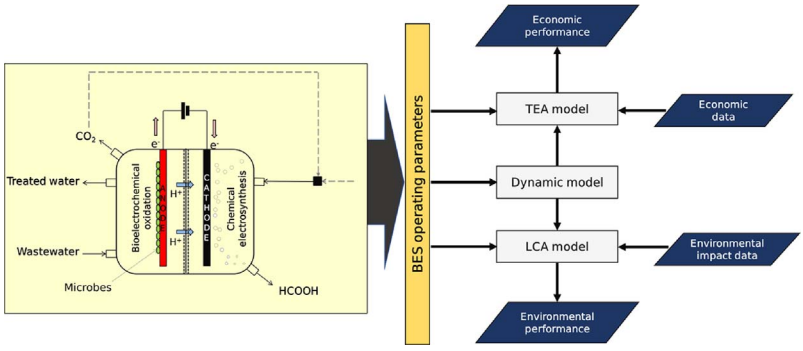
GRAPHICAL ABSTRACT



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ABSTRACT

A novel framework, integrating dynamic simulation (DS), life cycle assessment (LCA) and techno-economic assessment (TEA) of a bioelectrochemical system (BES), has been developed to study for the first time wastewater treatment by removal of chemical oxygen demand (COD) by oxidation in anode and thereby harvesting electron and proton for carbon dioxide reduction reaction or reuse to produce products in cathode. Increases in initial COD and applied potential increase COD removal and production (in this case formic acid) rates. DS correlations are used in LCA and TEA for holistic performance analyses. The cost of production of HCOOH is €0.015–0.005 g^{-1} for its production rate of 0.094–0.26 kg yr^{-1} and a COD removal rate of 0.038–0.106 kg yr^{-1}. The life cycle (LC) benefits by avoiding fossil-based formic acid production (93%) and electricity for wastewater treatment (12%) outweigh LC costs of operation and assemblage of BES (−5%), giving a net 61MJkg^{-1} HCOOH saving.

1. Introduction

Research interest in renewable fuels has intensified over the last two decades due to the finiteness of fossil fuels and concern about their environmental issues (IPCC, 2014). Lately, there has been a particular focus on the production of renewable fuels and chemicals from waste, as it does not only enable the reuse of an otherwise insignificant stream to maximise utility but also capacitates the realisation of a circular

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Nomenclature

q	COD Consumption rate in the biofilm (kgCOD kgVS^{-1} day^{-1}), VS = Volatile solids as a measure of biomass
S_D	COD (substrate) concentration (kgCOD cm^{-3})
ϕ_a,ϕ_i	volumetric fraction of active and inactive biomass (dimensionless)
R,F	universal gas constant and Faraday constant
v	advective velocity (cm^{-2} day^{-1})
r_{res}	specific rate of endogenous respiration (day^{-1})
$D_{ED,f}$	diffusion coefficient of substrate in the biofilm (cm^2 day^{-1})
ρ_a,ρ_i	density of active and inactive biomass (kgVS cm^{-3})
j	current density (mA cm^{-2})
k_{bio}	biofilm conductivity (Sm^{-1})
γ_1	electron equivalence of substrate
τ	time conversion factor (s day^{-1})
V_1,V_2	constants of the linear applied potential-related function
r_{dec}	rate of active biomass inactivation (day^{-1})
R_{HCOOH}	rate of formic acid production (mg L^{-1} hr^{-1})
FE_{HCOOH}	Faradic efficiency for formic acid production (%)
n	number of electrons transferred per mole of formic acid
J_{SD}	molar flux of substrate passing through the biofilm (kgCOD cm^{-2} day^{-1})
C_i	total initial capital investment
β	cost avoided from an activated sludge plant for equivalent COD removal
O_n	annual operating cost
T_n	annual income tax
$q_{\max}$	maximum consumption rate in the biofilm (kgCOD kgVS^{-1} day^{-1})
K_{SD}	half maximum rate concentration (KgCOD cm^{-3})
η	local electric potential of the biofilm (V)
T	temperature (298.15 K)
E_{KA}	half maximum rate potential (V)
b_{res}	endogenous decay coefficient of active biomass (day^{-1})
$D_{ED,l}$	diffusion coefficient of substrate in the bulk liquid (cm^2 day^{-1})
L,L_f	thickness of diffusion layer and biofilm (cm)
Q_s	general source term (mA cm^{-3})
f_0^e	fraction of energy generating electrons (dimensionless)
γ_2	electron equivalence of biomass
Y	true yield (kgVS kgCOD^{-1})
V_{app}	applied cell potential (V)
b_{dec}	first-order inactivation rate coefficient (day^{-1})
A_{an},A_{cat}	Anode and Cathode surface area (cm^2)
V_{an},V_{cat}	Anode and Cathode compartment volume (cm^3)
M_w	molecular weight of acetate (g mol^{-1})
z	Spatial longitudinal coordinate from the anode surface (cm)
θ	HCOOH selling price
t	number of operational years
r	required rate of return
$(\hat{\theta})$	HCOOH selling minimum price

economy. At the same time, environmental pollution and waste generation in the industrial, municipal and agricultural sectors continue to grow (Pant et al., 2011). For example, the pollution of aquatic ecosystems by industrial and municipal wastewaters, containing metallic and organic contaminants, is a growing environmental concern. The accumulation of these contaminants in aquatic ecosystems poses a toxicological hazard to public health and communities of dependent living organisms. Moreover, traditional wastewater treatment methods significantly contribute to greenhouse gas (GHG) emissions globally (IPCC, 2014). Global GHG emissions from conventional wastewater treatment plants could, in fact, reach about 12.1 ktd^{-1} by 2025 (Rosso and Stenstrom, 2008). Thus, innovative wastewater treatment technologies with synergetic resource recovery and transformation capabilities are currently being developed (Puyol et al., 2017).

One of such technologies, bioelectrochemical systems (BESs), present a promising opportunity for wastewater treatment and simultaneous *in-situ* electricity, fuel and chemical production (Sadhukhan et al., 2016) as well as metal recovery (Ng et al., 2016). BESs are electrochemical devices that are aided by pure cultures, bacteria communities or isolated enzymes for catalysing redox reactions (Rabaey et al., 2009). In a typical BES setup, wastewater is fed to the anodic chamber, where its organic contaminants are oxidised to produce CO_2, protons and electrons. Depending on the mode of operation, the electrons travel through a circuit to either solely generate electricity or combine with CO_2 or other substrates and protons (which diffuse through a membrane) to produce fuels or chemicals in the cathodic chamber. Various operational modes of BESs, including microbial fuel cells (MFCs), microbial electrolysis cells (MECs), microbial electrosynthesis systems and other variants have been trialled with promising results (Rozendal et al., 2008). These BESs are targeted towards various applications, notably remote electricity generation and wastewater treatment, resource recovery, sensor applications, desalination and electrochemical reduction of CO_2 into high-value chemical compounds (Bajracharya et al., 2016). Among these applications, the synthesis of chemical compounds *via* CO_2 reduction offers multifunctional benefits towards the implementation of several the United Nations' Sustainable Development Goals (SDGs), such as SDG 6: clean water and sanitation; SDG 7: affordable and clean energy, and SDG 13: climate action (Sadhukhan et al., 2018). These benefits include wastewater treatment through the removal of chemical oxygen demand (COD), renewable energy production from electrons liberated from the wastewater and temporary storage and utilisation of CO_2 (a potent GHG) to synthesise chemical products otherwise produced from fossil fuels (Shemfe et al., 2018).

Several valuable chemical compounds, including methane, formic acid, acetic acid, propanol, butanol and ethanol, can be produced from BESs *via* CO_2 reduction at different reduction potentials (Sadhukhan et al., 2016). Formic acid (HCOOH) stands out from other feasible chemical products due to its versatility. It is used as a chemical feedstock in the textile, pharmaceutical and food preservative industries, a liquid carrier for safe hydrogen storage and transportation, and fuel for fuel cells (IHS Markit, 2017; Kim et al., 2009; Rice et al., 2002). The global production of HCOOH has reached 620 kt in 2012, and it is projected to exceed 760 kt by 2019 at an average annual growth rate of 3.8% (Pérez-Fortes et al., 2016). Despite the versatility of HCOOH, it is primarily produced industrially from resource-intensive and environmentally damaging fossil-based methods, decarboxlative cyclization of adipic acid, oxidation of butane and hydrolysis of methyl formate (Ecoinvent, 2013). Thus, a BES-based production route, considering its plausible relative environmental benignity, could potentially replace current fossil-based production methods (Sadhukhan, 2017). To this end, only one technical and sustainability analysis study exists. Sadhukhan (2017) has investigated sustainable development of BES, encompassing technical modelling by analytically solving partial differential equations and triple-bottom-line life cycle sustainability assessment, applied to wastewater treatment in anode and formic acid synthesis in cathhode.

In a typical BES setup, at pH = 7 Normal Hydrogen Electrode, the open circuit potential for COD oxidation (acetate) at bioanode is ~ −0.3 V (Call and Logan, 2008). However, CO_2 reduction to HCOOH requires a potential of at least −0.41 V (Rabaey and Rozendal, 2010). As the resulting cell potential (−0.41 − (−0.3) = −0.11 V) is