



Practical demonstration of applicability and efficiency of platinum group metal-free based catalysts in microbial fuel cells for wastewater treatment

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HIGHLIGHTS

- The work presents a study of large area PGM-free catalyst cathode.
- Power output increased with the addition of PGM-free catalyst.
- Reactor performance fluctuated over time due to environmental conditions.
- PGM-free cathode catalysts showed high and stable performance in 2 months operations.

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ABSTRACT

In this work, PGM-free catalysts were incorporated into large scale cathodes ($2 \times 367 \text{ cm}^2$) and tested in BETT® reactors treating swine wastewater in real conditions. COD removal, cathode performance and overall reactors output was monitored along the experiments. The addition of Fe-AAPyr derived catalyst improved importantly the cathode activity and in turn the overall MFC power output. The cathode electrocatalytic activity remained comparable within the two months operation demonstrating the catalyst stability, durability and reliability in real environmental conditions. The overall power generated by the MFC system was variable and measured between 67 mW m^{-2} (day 63) and 120 mW m^{-2} (day 35). The variation in the power output along the experiment is a result of the fluctuating environmental conditions existing in natural environments.

1. Introduction

Wastewater treatment is an energy intensive and slow process. Conventional activated sludge (aerobic biological treatment) requires 2.0–6.0 kWh to remove 1 kg of biological oxygen demand (BOD) [1] and can represent up to 60% of the energy demand in a small-scale treatment facility (<1 million gallons per day). Anaerobic digestion (AD), on the other side, is the only widely accepted approach for recovering energy (as methane gas) during wastewater treatment. However, biogas recovery from AD is highly dependent on the composition and concentration of the wastewater feed, mixing, residence time, pH, and temperature [2]. Variations in any of these parameters may significantly

impact biogas production. Additionally, all AD systems operate over a multi-day batch period. Even high-rate AD will require 3–5 days, which limits biogas availability and overall footprint requirements are very large for onsite treatment [3]. Additionally, the Net Energy Recovery (NER) from AD combined with cogeneration suffers from many inefficiencies and is capital intensive.

Direct energy recovery from wastewater treatment using microbial fuel cell (MFC) systems has been a primary research and development goal for decades. The opportunity to generate clean power from waste has been shown in many lab-scale MFC studies [4,5], which all represent key innovations in waste-to-energy applications. MFCs use natural microbial communities to convert the chemical energy stored in organic

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compounds into electrical energy as direct DC current by exploiting microbial extracellular respiration mechanisms in engineered electrochemical systems. However, commercial deployment of MFCs has been hindered to a big extent by the sluggish cathodic reaction.

In MFCs, organics are oxidized by bacteria at the anode while on the cathode, oxygen is reduced. The oxygen reduction reaction (ORR) occurring at the cathode is often the rate limiting step of the system. In fact, firstly, the neutral pH required in MFCs required by bacteria, limit significantly the electrochemical cathodic performance due to the several orders of magnitude lower concentration of H^+ compared to acid proton exchange membrane fuel cells (PEMFCs). Secondly, high cathodic activation overpotential occurs in close to neutral pHs. Thirdly, in order to reduce the operational cost, passive diffusion of oxygen naturally present in the atmosphere is used, which limits the oxygen concentration to not more than 8.6 mM in saturated water solutions [6].

The only solution of the above-mentioned problem is the utilization of catalysts for ORR, which possess high activity in neutral environment. Biotic and abiotic catalysts have been explored to enhance ORR [7]. Biotic catalysts based on enzymes or bacteria have been successfully used. Enzymatic catalysts have shown high activity towards ORR in close to neutral environment [8], but high cost and low durability hinder their application [9,10]. Bacterial catalysts still show high cathodic activation overpotential and their pre-selection and cultivation is time-consuming, and their long-term reliability still have to be proven [11]. Abiotic, specifically inorganic, ORR catalysts are much more reliable and scalable. Platinum or platinum containing materials were initially used as cathode catalyst but later abandoned due to their extremely high cost and decreased activity due to adsorption of anions present in the wastewater, which irreversibly reduce platinum catalytic activity. Consequently, high surface area conductive carbonaceous materials have been widely adopted as ORR catalysts. It is worth mentioning that nowadays, activated carbon (AC) is the most widely used cathode catalyst in MFCs [12]. AC has large surface area and it is commercially available at low cost [13]. It was shown that AC is active towards ORR and durable in close to neutral media [14,15].

The utilization of carbonaceous materials has been even further expanded in the last 10–15 years after discovering that the addition of Fe, Mn, Co and Ni over nitrogen containing carbonaceous backbone significantly enhances the electrocatalytic performance towards ORR. Particularly, transition metal coordinated with pyridinic nitrogen resembling porphyrins or phthalocyanines seem to be the most efficient active site for ORR [6]. This category of catalysts is named as M-N-C where M refers to a transition metal such as Fe, Mn, Co and Ni. M-N-C catalysts are mainly synthesized through: i) impregnation of commercially available metal- N_4 chelate macrocycles over a carbon support [16–20] or ii) high temperature processes (pyrolysis) in controlled inert/reducing atmosphere involving nitrogen rich organic precursors and iron salt [21,22]. Several advancements were achieved in the last few years [23]. These include but are not limited to: i) demonstrating the superiority of Fe compared to the other transition metals [24,25]; ii) using bimetallic catalysts (M1-M2-N-C) [26,27]; iii) adding graphene within the cathode structure [28,29]; ii) correlating surface chemistry with catalytic performance [30,31]; v) understanding the effect of the catalyst loading on ORR [32], etc. Most importantly, M-N-C catalysts are: i) more cost effective compared to Pt; ii) more durable and less prone to poisoning and deactivation than Pt; iii) have higher activity compared to AC [33].

In this work, Fe-N-C material was used as a cathode catalyst in BioElectrochemical Treatment Technology (BETT®) reactor or BETT® reactor developed and commercialized by Aquacycl LLC (<https://www.aquacycl.com>) for onsite wastewater treatment. BETT® reactor design and operation are based on the principle of MFCs, where a plurality of anode units is electrically connected in series operating as single anode and two gas-diffusion electrodes are electrically connected as cathode. The study was conducted for approximately 80 days treating swine wastewater in a pilot scale setup. The work presented considers MFC

reactor with large area (367 cm^2) full-scale cathodes containing PGM-free catalyst operating in a real field environment. The performance of BETT reactor with Fe-N-C cathode (NPGM-BETT) was evaluated and compared to BETT reactor with AC cathode catalyst (AC-BETT).

2. Materials and methods

Two BETT® reactors were assembled, inoculated and tested simultaneously. Both reactors had identical design with the only difference being the cathode catalysts used. In fact, activated carbon (AC) was used as catalysts for the first reactor and PGM-free material as a cathodic catalyst was used for the second reactor. The two reactors will be referred as AC-BETT (activated carbon catalyst) and NPGM-BETT (with the addition of PGM-free catalyst) reactors. The catalyst loading in terms of mass was kept the same for both reactors.

2.1. Fe-N-C catalyst (Fe-AAPyr)

Fe-N-C catalyst was synthesized through Sacrificial Support Method (SSM) as previously reported [34,35]. Particularly, iron nitrate as metal salt, aminoantipyrine (AAPyr) as nitrogen rich organic precursor and fumed silica (Cab-O-Sil M5; surface area: $\sim 250 \text{ m}^2 \text{ g}^{-1}$) as templating agent were mixed through wet impregnation. The formed mixture was then dried overnight then was ground to fine powder using a ball milling. The powder was then subject to heat treatment (950 °C for 30 min) after the temperature was increased with a ramp of 25 K min^{-1} . Pyrolysis processes occurred under controlled atmosphere of UHP (Ultra High Purity) nitrogen (flow rate 100 mL min^{-1}). After pyrolysis, the silica template was removed using 20 wt% HF. The obtained catalyst was then washed with deionized water till was reached neutral pH and then dried overnight.

2.2. BETT® reactor design

BETT® reactor is a single chamber MFC having a rectangular shape with internal dimensions: 31 cm \times 17 cm \times 15 cm and an empty volume of 7.9 L (Fig. 1 a–c). The anode was composed of twenty graphite fiber brushes [36], each with a 10 cm height and 2.5 cm diameter. All carbon brushes were electrically connected in series to form one anode. Before used, all carbon brushes were soaked with acetone for 1 h to remove organic contaminants and then washed thoroughly with DI water. Two gas-diffusion cathodes (13.5 cm \times 27.2 cm, geometric surface area 367 cm^2) were placed on both sides of the reactor and connected in series. The cathode composition and manufacturing are Aquacycl LLC trade secret and further details cannot be revealed. The inner side of the cathode was in direct contact with the solution without utilization of membrane or a separator and from the outer side was directly exposed to the atmosphere. Regarding NPGM-BETT reactor, Fe-AAPyr catalyst was used instead of AC. Flow guides were built into each reactor to direct flow of the solution inside the reactors. Details on the BETT® reactor design are reported in Ref. [37].

2.3. Pilot design

The two BETT reactors were installed on a pilot system originally composed of twelve MFC reactors hydraulically connected in series with a consecutive flow of the wastewater from Reactor 1 to Reactor 12 as reported in Fig. 1 d. The pilot site was located at the Agriculture Center at San Pasqual High School (Escondido, CA, USA), a part of the Escondido Union High School District. The pilot was installed outside with only a shade structure to provide cover. Thus, the reactors were exposed to the naturally occurring environmental variables in terms of temperature, humidity, wind and dust throughout the entire operations. The overall volume of the system was 110 L and was treating 570 L per day of swine wastewater at a 380 mL min^{-1} flow rate (for 12 reactors). The waste stream was gravity-fed into the reactors through the utilization of

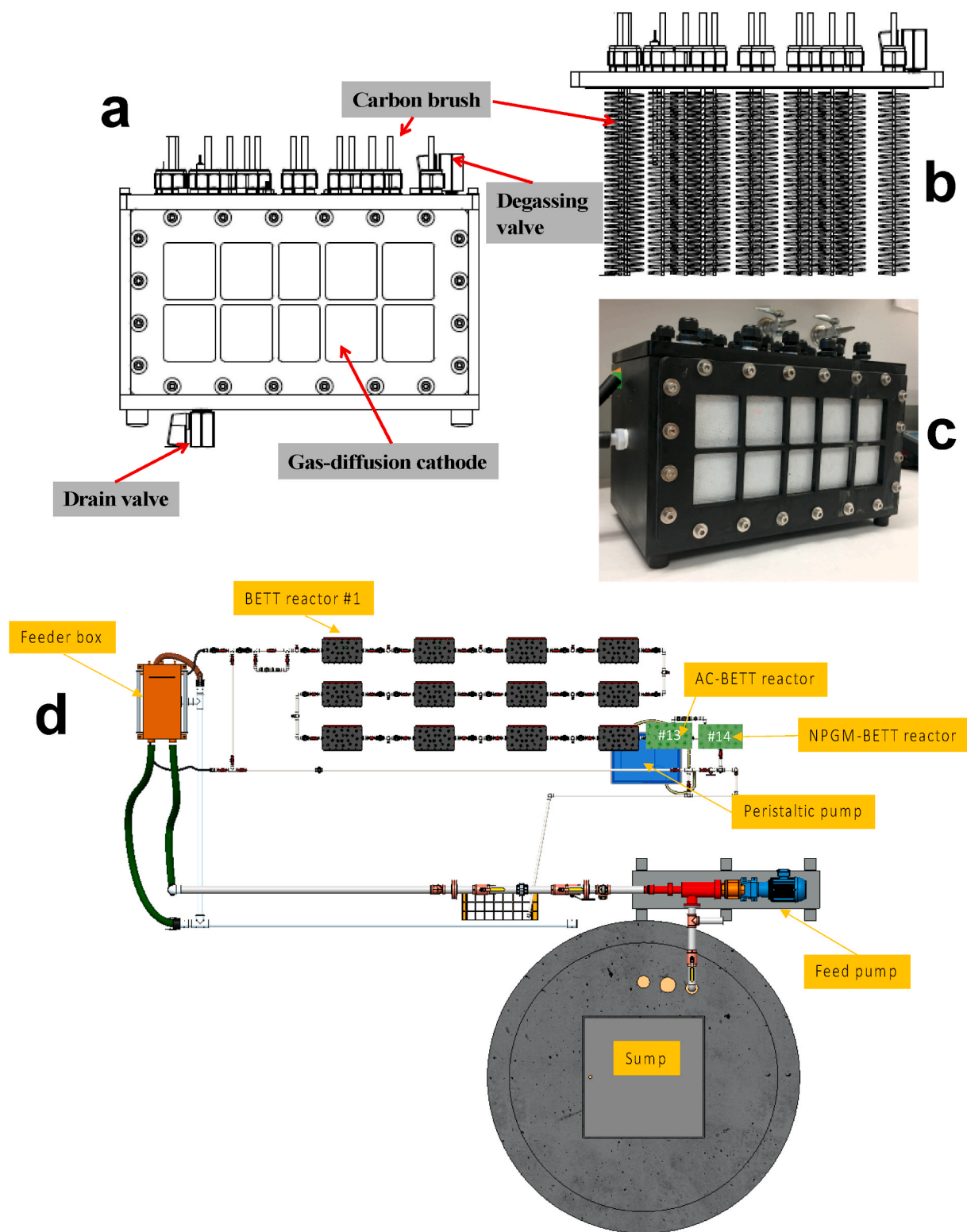


Fig. 1. (a) Schematic of the lateral view of BETT reactor. (b) Schematic of the anode set up using twenty carbon brushes. (c) Picture of BETT reactor. (d) Schematic representation of BETT pilot installation after the addition of AC-BETT and NPGM-BETT reactors. The pilot is located at San Pasqual High School (Escondido, CA, USA).

an elevated feeder box, and a peristaltic pump was used to control the outflow rate. During continuous mode operation, the waste solution was prepared and stored in an underground sump and transferred into the feeder box with a cavitation pump. Treated effluents from the BETT system was discharged to sanitary sewer. The overall pilot operation is

described in detail in Ref. [37]. The two additional reactors described above (AC-BETT and NPGM-BETT) were installed on day 105 of pilot inoculation and operation. AC-BETT and NPGM-BETT reactor were placed after reactor 12 of the pilot i.e. the AC-BETT reactor was reactor #13 and NPGM-BETT was the last reactor in the hydraulic line i.e.

reactor #14.

2.4. Reactor inoculation and operation

Since AC-BETT and NPGM-BETT reactors were installed more than 3 months after the pilot inoculation, the reactors were inoculated separately and run under batch mode for two weeks to establish robust anodic biofilm. The AC-BETT and NPGM-BETT reactors were inoculated with the effluent of the pilot installation. No additional bacterial source was introduced into the inoculum besides the bacteria already present in the wastewater and preselected during the operation of BETT pilot. The two reactors were connected in hydraulic series with AC-BETT reactor being before NPGM-BETT reactor. Importantly, the two reactors shared the same inoculation wastewater. The flow rate through the reactors was 380 mL min^{-1} .

The inoculum composition for AC-BETT and NPGM-BETT reactors was as follows: COD (T) = 621 mg L^{-1} , COD (S) = 103 mg L^{-1} , pH = 8.24, DO = 0.06 mg L^{-1} . The reactors were connected to $47,000 \Omega$ after inoculation. The resistor was subsequently changed to $4,700 \Omega$ on day 7, from $4,700 \Omega$ – 630Ω on day 12 and from 630Ω to 330Ω on day 51.

On day 12 after inoculation, AC-BETT and NPGM-BETT reactors were installed at the end of the hydraulic treatment train of the pilot after reactor 12 as shown in Fig. 1. At that time the pilot was operating under continuous mode with a flow rate of 380 mL min^{-1} and the hydraulic retention time (HRT) of the wastewater through a single reactor was 20 min.

The AC-BETT reactor was continuously treating the effluent of the BETT reactor #12 of the pilot and NPGM-BETT was treating the effluent from AC-BETT reactor.

2.5. Electrochemical characterization

The reactor voltage (V) across the external resistor was recorded in 10 min intervals using a data logger (GraphTech GL820). The reactors were periodically disconnected to measure open circuit potential (OCP) of the electrodes and perform polarization curves measurements.

Polarization measurements were carried out periodically by varying the external resistor from open circuit to 3Ω in 5 min intervals. The voltage of the reactor as well as the electrodes potentials were measured with each resistor applied. Current (I) was calculated using Ohm's law, $I=V/R$. Power (P) was calculated using the following formula: $P=VxI$. The potentials of the anode and the cathode were measured against an Ag/AgCl reference electrode. The current and power densities of each individual reactor were calculated as the current of the reactor normalized to the cathodes geometric surface area (0.0734 m^2).

Potentiostatic polarization measurements of the cathodes were performed using a Potentiostat/Galvanostat Gamry 600. Chronoamperometry measurements from 0.2 to $-0.6 \text{ V vs. Ag/AgCl}$ (step 0.1 V) were carried out remaining at each potential value for 300 s. The anode was used as counter electrode and the corresponding cathode was used as a working electrode. Ag/AgCl was the reference electrode for these measurements.

In the case of measurements in pristine and "clean" conditions, the reactors were filled only with 33 mM carbonate buffer at pH 7.

2.6. Chemical analyses

Chemical oxygen demand (COD) of the wastewater was periodically analyzed during the reactor's inoculation using Hach DR850 vials and DR900 instruments following the associated method. After the reactors were installed on the pilot, influent and effluent samples (before and after AC-BETT and NPGM-BETT reactors) were taken and analyzed periodically for total COD (COD (T)).

3. Results and discussion

3.1. COD removal

Both AC-BETT and NPGM-BETT reactors were operated under batch mode for two weeks during the inoculation phase. As expected for batch mode of operation, the majority of the COD was removed during the first 24 h and the COD concentration did not notably change after as reported in Fig. 2 a. This could be due to the low COD values and the accumulation of final products, which were shown to have a negative effect on the bioelectrochemical treatment process [37]. Both AC-BETT and NPGM-BETT reactors were then connected into the pilot installation with HRT of 20 min through a single reactor. The pilot was equipped with sampling ports in between each reactor, which allowed the estimation of COD removal rates for each reactor separately. The COD removal rate in percentage is reported in Fig. 2 b. Inlet and outlet COD concentrations for AC-BETT and NPGM-BETT reactors are reported in Fig. 2c and 2 d respectively. The COD concentrations were measured at day 16, 23, 28, 42, 49, 56, 63, 70 and 77.

Theoretically the COD removal rate is a function of the applied resistance, the lower the resistance – the higher the COD removal rate. That usually holds true when the COD concentration is the rate limiting factor for MFCs operation. In reality, this is not the case because the cathode ability to fully utilize the released during the oxidation process electrons is the rate limiting step in most MFCs. Therefore, at high resistances (low current) a sluggish cathodic reaction will not significantly impact the COD removal rates because the number of electrons released at the anode is small. At low resistances (high current), though, the number of electrons is much higher, and the sluggish ORR cannot utilize them all, thus reducing the COD removal rate.

The COD removal rate at higher resistances ($47,000 \Omega$, $4,700 \Omega$ and 630Ω) was slightly higher for AC-BETT reactor in comparison to NPGM-BETT. This was not the case for lower resistance (330Ω) where NPGM-BETT reactor demonstrated higher COD removal rates (days 56–77). The reason for this phenomenon is the limiting cathodic performance at lower resistances (higher current) more pronounced for AC-BETT reactor than NPGM-BETT reactor due to the superior cathodic performance of NPGM-BETT.

3.2. Electrochemical performance

3.2.1. Cathode evaluation

Potentiostatic polarization measurements of the cathodes in pristine conditions using 33 mM carbonate buffer (pH 7) as electrolyte were done before the reactors were inoculated (Fig. 3a). Potentiostatic polarization characterization of the cathodes was also performed before the reactors were decommissioned (Fig. 3b). In this case, the measurements were done in swine wastewater as electrolyte.

Initial OCP for both cathodes (left and right side) regardless of the catalyst was measured to be around $+200 \text{ mV vs. Ag/AgCl}$ (3 M KCl) (Fig. 3a). As predicted by previous studies [6], the incorporation of Fe–N–C catalyst improved significantly the electrocatalytic activity towards ORR (Fig. 3a). The performance of both, AC and Fe–N–C based cathodes was dictated by ohmic losses, which were lower when PGM-free catalyst was present.

The tests done before decommissioning the reactors still showed superior performance of Fe–N–C catalyst over AC. The slightly lowered performance might be due to biofilm accumulation at the cathode and/or different composition of the electrolyte. It is worth noting that 33 mM carbonate buffer and swine wastewater had similar solution conductivity of roughly 2.5 mS cm^{-1} , therefore the decrease in performance was imputed to the biofouling as previously shown by Santini et al. [38, 39].

3.2.2. Open circuit potential and current produced over time

The OCP of the separate electrodes was also measured periodically

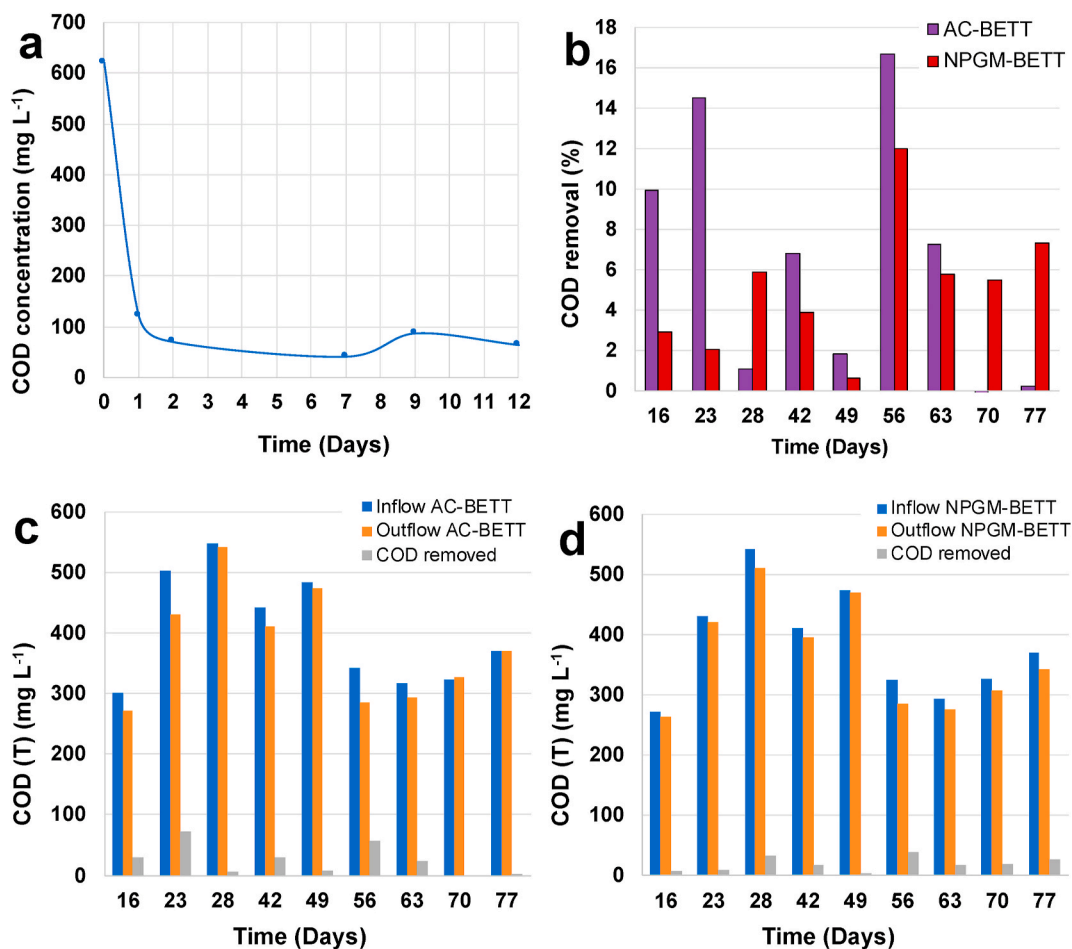


Fig. 2. (a) Changes in COD concentration of AC-BETT and NPGM-BETT reactors during inoculation. (b) COD removal in percentage for both AC-BETT and NPGM-BETT reactors. COD concentrations for influent and effluent (c) in AC-BETT and (d) NPGM-BETT reactors in mg L⁻¹.

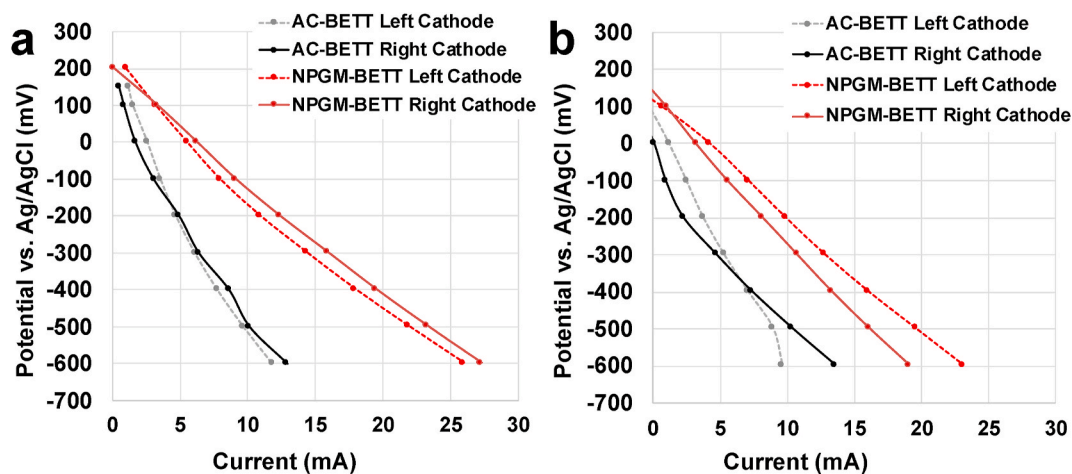


Fig. 3. Cathode polarizations at the beginning of the experiments in pristine conditions (a) and before decommissioning in wastewater (b).

against Ag/AgCl reference electrode (Fig. 4a). The reactors were disconnected and left under open circuit for an hour before the OCP measurement. It is worth noting the increase in the anode potential at days 7, 14, 35 and 72. This was due to decreased liquid level in the reactors leaving the top 2–3 cm of the anode brushes exposed to air. The latter led to a very fast and significant response from the anode. The aerobic conditions increased the OCP of the anode confirming the importance of anaerobic conditions for proper anodic performance. The

cathodes of the AC-BETT reactor showed unstable potential over time with fluctuations in the cathodic OCP from +150 mV to -450 mV vs. Ag/AgCl. It has been established in other pilot installations and wastewater types that the potential of the AC based BETT cathode is highly dependent on the wastewater composition, and in particular the concentration of sulfide and sulfate anions and protein. The latter releases sulfate and sulfide ions during degradation (data not shown). Given the more stable potential of Fe–N–C cathodes, it can be speculated that the

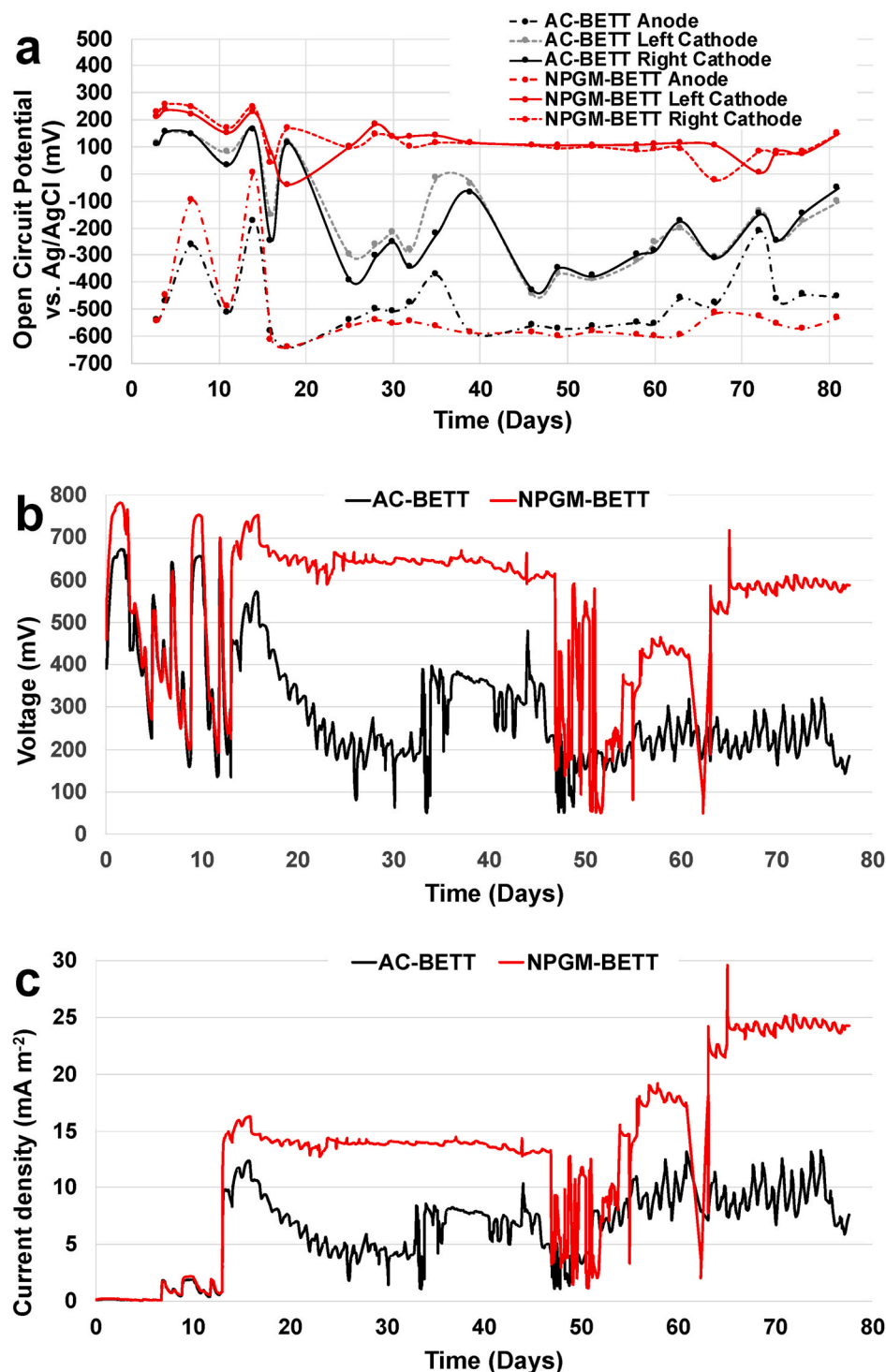


Fig. 4. Anode and Cathode OCP (a); voltage (b) and current density (c) recorded over the 77 days study.

PGM-free catalyst was less prone to sulfide poisoning and deactivation. The OCPs of the PGM-free cathodes were significantly more stable and remained positive throughout the study.

The voltage over an external resistor was recorded every 10 min (Fig. 4b). The external resistor was 47,000 Ω from day 0 to day 7. It was then changed at day 7 from 47,000 Ω to 4,700 Ω , at day 12 from 4,700 Ω –630 Ω and from 630 Ω to 330 Ω on day 51. The corresponding current density (mA m⁻²) over time is reported in Fig. 4 c. The noisy current recorded from day 47–63 for NPGM-BETT reactor was due to poor electrical connection and reached its normal values after the connection

was fixed.

As it can be seen, the current density generated by NPGM-BETT was much higher compared to AC-BETT underlining the beneficial positive contribution given by the use of Fe–N–C catalyst at the cathode (Fig. 4c). The “oscillations” in the current were the day and night fluctuations in the voltage induced by the temperature changes.

Knowing the current produced by the reactor and the COD removed during the operations, the Net Energy Recovery (NER) and the Coulombic Efficiency (CE) were calculated [40,41]. Particularly, NER for the two reactors at 630 Ω was 164 Wh kg-COD⁻¹ and 46 Wh

kg-COD⁻¹ for NPGM-BETT and AC-BETT, respectively. The corresponding CE was 53% for NPGM-BETT and 28% for AC-BETT reactors. Therefore, the use of PGM-free catalyst not only led to more stable cathodic performance but also to higher voltage produced and higher energy recovered from the oxidation of organic contaminants in the wastewater. Parasitic reactions were more pronounced for AC-BETT than NPGM-BETT as a result of the non-sufficient cathode operation.

3.2.3. Reactor polarization curves and power performance

Polarization curves of the two reactors were taken periodically to evaluate electrodes performance and overall reactors current and power generation. Particularly, the electrochemical performance of the two reactors at day 22 and day 77 was compared as shown in Fig. 5.

At day 22, AC-BETT reactor generated power of 12 mW m⁻² (Fig. 5a), which was eight times lower than the power recorded for NPGM-BETT reactor (95 mW m⁻²). It is obvious from Fig. 5 b that the lower power generated by AC-BETT reactor was mainly a result of the poor cathode operation. The anodic potential for both reactors was typical for organics oxidation under anaerobic conditions (Fig. 5b) indicating well developed anodic biofilm. On the contrary, the cathodic potential was very different for the two reactors with around 150 mV vs. Ag/AgCl for NPGM-BETT cathodes and close to -300 mV vs. Ag/AgCl for AC-BETT cathodes (Fig. 5b).

Obviously, the Fe-N-C material notably improved the cathodic reaction and in turn the overall MFC electrical output. It was shown previously that the addition of Fe-containing PGM-free catalyst into the cathode improve the cathode potential, which remains stable in long-term operations [33,34].

At day 77, the NPGM-BETT reactor continued to show high current and power output (Fig. 5a). The cathode activity slightly decreased after 77 days but still retained between 74 and 99% of the initial cathodic performance depending on the potential applied (Fig. 5b). The anode polarization showed identical behavior with no important changes in the output.

The decreased cathodic activity was the main reason for the significantly lower power density of AC-BETT reactor, which decreased from 12 mW m⁻² to 5 mW m⁻² (Fig. 5a).

Power curves were also periodically recorded through the entire experimentation. The maximum power density for AC-BETT and NPGM-BETT reactors are reported in Fig. 6 a. The internal resistance (R_{int}) of the reactors was calculated from the slope of the polarization curves (Fig. 6b). Generally, the power density for both reactors was variable over time because of the variance in the wastewater composition and environmental conditions. While operations in laboratory scale are well controlled and therefore a certain repeatability in the output is expected,

operations in real environments can be subject to several natural fluctuation in temperature, humidity, solution conductivity, solution composition and other parameters. Despite these variations, the power density generated by the NPGM-BETT reactor was 2–16 time higher compared to AC-BETT due to the presence of Fe-N-C catalyst. NPGM-BETT reactor generated power density between 67 mW m⁻² (day 63) and 120 mW m⁻² (day 35). In parallel, AC-BETT reactor had a power density that varied between 3 mW m⁻² (day 63) and 43 mW m⁻² (day 35).

Although the R_{int} of AC-BETT reactor was higher than R_{int} of NPGM-BETT, the difference cannot explain the significantly lower performance of AC-BETT reactor, which is obviously a result of the poorer catalytic activity of AC.

4. Outlook

4.1. Utilization of PGM-free catalysts

Fe-based PGM-free catalysts have captured the attention of the scientific community in the past 10–15 years due to the superior electrocatalytic activity compared to solely carbonaceous catalysts and to the improved durability and lower cost compared to platinum-based catalysts [6]. Despite the multiple experiments done in laboratory setting, to the best of our knowledge, only one big-scale field trial using PGM-free transition metal-containing catalysts was presented [42]. Particularly, in that study, Co_{0.5}-Zn_{0.5}-Fe₂O₄ and Sn₅-Cu₈₄ catalysts were used during the experimentation [42]. It must be mentioned that AC/PTFE/Fe-N-C air breathing cathode of roughly 39 cm² was also fabricated attempting to scale up the manufacturing process and was tested in laboratory set up [43].

Only few studies with Fe-N-C catalyst have been conducted over a period of time longer than a month. Particularly, Zhang et al., operated MFCs containing Fe-based catalysts in batch mode, showing a decrease in performance of 40% after 12 months of operation [44]. Fe-N-C catalyst was also utilized by Rossi et al. in MFCs operating in batch mode and the power output decreased by 26% over 2 months period [45]. Gajda et al. showed that Fe-N-C catalyst had similar current generation over several months without significant decrease in the electrochemical output [46]. Fe-streptomycin derived catalysts showed stable power output over time in ceramic MFC fed with hydrolyzed human urine [47]. Fe-N-C cathode catalysts synthesized through SSM (e.g. Fe-Ribocendazole and Fe-Niclosamide derived catalyst) showed a decrease in activity of roughly 20% after one month of operation once used in a single chamber membrane-less MFC [33]. Higher power density losses up to 50% in the first month of operation were recorded by

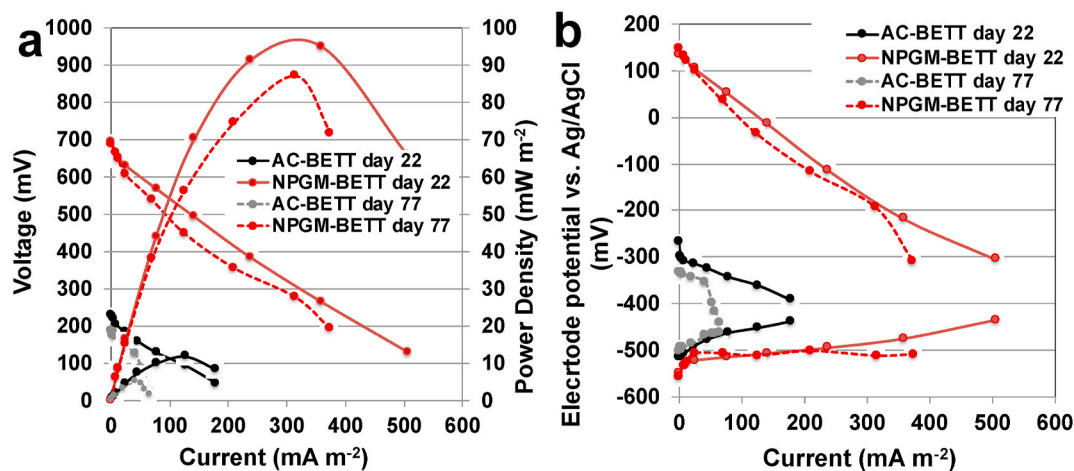


Fig. 5. AC-BETT and NPGM-BETT polarization measurements obtained at day 22 and 77. Overall polarization curves and power curves (a). Cathode and anode polarization curves (b).

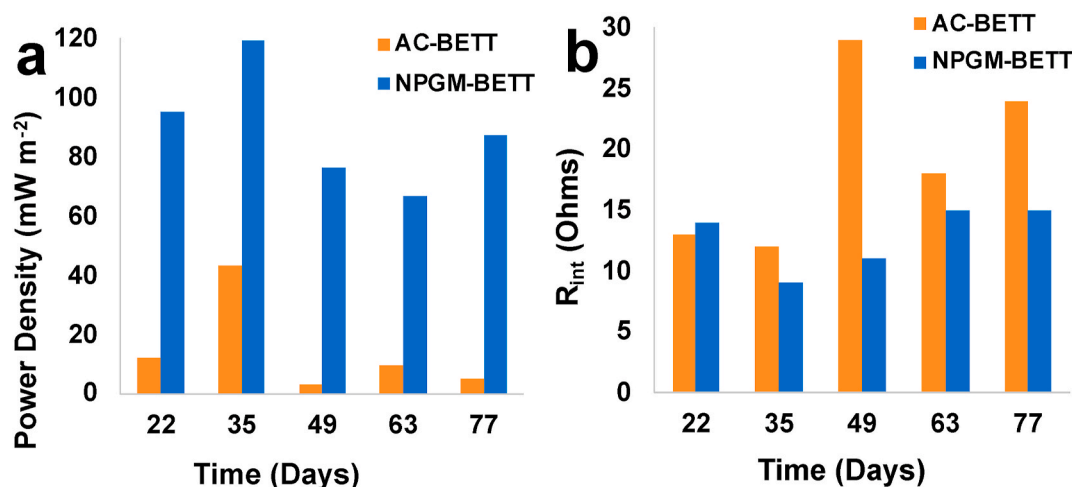


Fig. 6. Maximum power density for AC-BETT and NPGM-BETT over time (a). Internal resistance calculated from the polarization curves for AC-BETT and NPGM-BETT reactors (b).

Mecheri et al. while using Fe-derived catalysts with Benzimidazole and Aminobenzimidazole as nitrogen rich organic precursors [48].

In this work, iron-aminoantipyrine derived Fe–N–C catalyst was tested in a BETT reactor operating in real environmental conditions with continuous feed of swine wastewater for over 2 months. The addition of Fe–N–C material within the cathode architecture boosted importantly the energy harvesting capabilities of the reactor. The results obtained indicate a pathway for improving electrochemical performance of MFCs. In addition, despite operating in real conditions, the cathode performance did not seem to decrease during the 2.6 months of operation indicating a good stability and durability of the catalyst. Therefore, this work underlines the importance of utilizing PGM-free catalysts at the cathode of MFCs towards developing energy-neutral technology for wastewater treatment and/or use wastewater as a source of renewable energy. More effort has to be devoted to decreasing the cost of the catalyst by pursuing novel synthesis routes or utilizing waste biomass as nitrogen rich organic precursors.

4.2. MFC pilot scale studies

Scaling up MFC in the next logical step bringing bioelectrochemical technology from the laboratory to a real-world application. There two main approaches taken to scale up MFCs: i) increase the size of MFCs to treat higher volumes of wastewater [49–51], and ii) connect multiple MFCs in hydraulic series [37,52,53]. The first approach faces challenges related to scaling up the electrodes and still maintain performance, prevent redox gradient within the large reactor, provide proper proton transport, etc. The second approach overcomes these challenges but becomes cost prohibitive if MFCs reactors don't reduce price.

Table 1
Pilot Scale MFCs for treatment of different types of wastewaters and power generation.

MFC Reactor Type	Reactor Volume L	Organic Feeding	Cathode geometric area	Cathode	Max Power Density		Ref.
					mW m ⁻²	W m ⁻³	
Single Chamber	255	civil WW	85 x 85 cm	AC-based	78	0.317	[54]
Single Chamber	85	civil WW	6200 cm ²	AC-based	83	0.605	[55]
Flat floating	–	civil WW	50 x 50 cm	Carbon felt	12	–	[56]
Flat floating	–	civil WW	20 x 15 cm	Carbon cloth	15.5	–	[57]
Flat floating	–	civil WW	30 x 20 cm	Carbon cloth	13	–	[57]
Flat floating	–	civil WW	40 x 30 cm	Carbon cloth	7.35	–	[57]
Single Chamber	120 x 6	sewage	2430 cm ²	Co–Zn–Fe-based	6.62	0.013	[42]
Single Chamber	120 x 6	sewage	2430 cm ²	Sn–Cu-based	7.29	0.015	[42]
Tubular	96 x 2	primary clarifier	–	N-AC-based	–	0.58	[58]
Single Chamber	7.9	swine WW	2x 13.5 x 27.2 cm	AC-based	67	0.623	This work
Single Chamber	7.9	swine WW	2x 13.5 x 27.2 cm	Fe-AAPyr-based	120	1.116	This work

The work presented herein adopted the second approach, where the size of the reactor was scaled only to 7.9 L with multiple anode units connected in electric series and two gas-diffusion cathodes working as one. To achieve effluent quality, multiple BETT reactors are operating in hydraulic series to create a treatment train; and to increase treated volumes, multiple treatment trains are considered to run in parallel.

Table 1 summarize the electrochemical performance and the operating conditions of few pilot scales recently presented in literature [42, 54–58]. The performance achieved in this study is higher or comparable to the other reported in Table 1. However, a direct comparison among these studies is very difficult to be done due to the different: i) electrode materials and surface area, ii) reactor type and design, iii) membranes and separator, iv) wastewater type, 5) operating conditions (temperature, pH, flow rate, etc.). This work demonstrates that the utilization of Fe–N–C cathode catalyst can improve substantially the power produced and the removal of organic pollutants.

5. Conclusions

In this work, we report a large area, full-scale cathode containing PGM-free Fe–N–C catalysts and operating into a pilot trial treating real swine wastewater. PGM-free Fe-based catalyst was integrated in the cathode and tested in BETT pilot system treating swine wastewater. Fe–N–C catalyst showed superior electrocatalytic activity towards ORR and boosted the cathodic activity while preserving and even improving the COD removal rates at higher currents. The overall power generated by NPGM-BETT reactor treating real wastewater varied between 67 mW m⁻² (day 63) and 120 mW m⁻² (day 35), which was 2–16 time higher than its AC-based counterpart. BETT containing PGM-free catalyst

showed durability over two months of operation.

CRediT authorship contribution statement

Sofia Babanova: Conceptualization, Methodology, Investigation, Data curation, Visualization, Writing - original draft. **Carlo Santoro:** Conceptualization, Methodology, Data curation, Visualization, Writing - original draft. **Jason Jones:** Conceptualization, Methodology, Investigation. **Tony Phan:** Conceptualization, Methodology, Investigation. **Alexey Serov:** Conceptualization, Investigation, Writing - original draft. **Plamen Atanassov:** Conceptualization, Methodology, Supervision, Writing - review & editing. **Orianna Bretschger:** Conceptualization, Methodology, Supervision, Writing - review & editing, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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