Supplementary Information (SI) for Journal of Materials Chemistry A.

Catalysing Holistic Wastewater Treatment, Electricity Generation, and Emerging Contaminant Removal in a Pre-pilot Fenton-microbial Fuel Cell

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Supplementary Materials

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Text S1. Instrumental Characterisation

The electrochemical characterisations, including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and linear sweep voltammetry (LSV), were performed using a Metrohm, Autolab: PGSTAT 204 workstation with a three-electrode setup. The as-obtained rGO-Co_3O_4 was coated over a 2 cm × 2 cm carbon felt, acting as a working electrode with a catalyst loading of 2 mg/cm^2. The Pt plate acted as the counter electrode, whereas the Ag/AgCl (0.198 V *vs* standard hydrogen electrode (SHE)) served as a reference electrode. The CV and LSV analysis were carried out by varying the potential range from −1 V to +1 V at a scan rate of 25 mV/s. The EIS was performed by fluctuating the frequency from 100 mHz to 1 MHz. The CV, LSV, and EIS measurements were performed in a 50 mM Na_2SO_4 electrolyte and O_2-saturated environment. The rotating ring disk electrode (RRDE) experiment was performed at varying scan rates (400 – 2400 rpm) in a potential range of 0 to 1.2 V (*vs* RHE) in 0.1 M KOH electrolyte to calculate the number of electrons (*n*) transferred during the ORR. The precise value of *n* and H_2O_2 selectivity of the catalyst was estimated using Eq. 1 and Eq. 2.

$$n = 4 \times \frac{I_d}{I_d + \frac{I_r}{N}} \qquad (1)$$

$$H_2O_2\,selectivity\,(\%) = 200 \times \frac{\frac{I_r}{N}}{I_d + \frac{I_r}{N}} \tag{2}$$

Where, I_d represents disk current, I_r denotes ring current and N is the current collection efficiency of the Pt ring on the RRDE electrode.

The physicochemical features of the synthesised catalyst were examined *via* X-ray diffraction (XRD, Panalytical X'pert Pro), field emission-scanning electron microscope (FE-SEM), surface area and porosity analysis, Fourier transform infrared (FTIR) spectroscopy (Spectrum Rx, PerkinElmer, Inc., USA), and X-ray photoelectron spectroscopy (XPS) using XRD Panalytical X'pert pro, Spectrum Rx (PerkinElmer, Inc., USA), ZEISS EVO 60 Carl ZEISS SMT Germany, BELSORP-mini ll Japan, and, VG ESCA 220i-XL (Thermo VG Scientific Ltd., UK) instruments, respectively. Reactive oxygen species production in the cathodic chamber was confirmed using room-temperature pulsed electron paramagnetic resonance (EPR) spectroscopy (Bruker, ELEXSYS 580, USA). The remnants produced from the breakdown of Congo red were examined using matrix-assisted laser desorption ionisation time-of-flight mass spectrometry (MALDI-TOF-MS) technology from Applied Biosystems Inc., based in CA, USA.

Text S2 Environmental footprint assessment

Text S2.1 Methodology

Text S2.1.1 Goal and scope

The primary objective of the life cycle analysis (LCA) was to estimate the gate-to-gate environmental impact of contaminant removal from water and chemical oxygen demand (COD) removal from synthetic wastewater employing the reactor fabricated and operated in IIT Kharagpur (West Bengal, India). The methodology was based on recommendations provided in ISO 14040 and ISO 14044 [1, 2]. The geographical scope of the study is limited to

India and the temporal scope of 2023 to 2024. The system boundary includes both the construction and operational phases, considering two different scenarios, namely, Congo red (CR) removal from 20 ppm aqueous solution (P1) and wastewater treatment by first anodic degradation followed by cathodic degradation (P2). Accordingly, a functional unit of one gram of CR removal and one gram of COD removal was adopted for assessing and comparing P1 and P2, respectively. ReCiPe 2016 (H) was adopted as a life cycle impact assessment methodology for estimating the footprint in SimaPro v9.4.0.2, with midpoint and endpoint normalization performed based on World (2010) H and World (2010) H/H approach.

Text S2.1.2 Life Cycle Inventory

The life cycle inventory (LCI) consisted of the material required for reactor fabrication, along with the energy and chemicals consumed during the electrode synthesis and operation phase (Table S1 and Table S2). The primary data of the LCI was compiled from the lab-scale study, and the background data was adopted from the EcoInvent v3.8 database. Some of the major assumptions considered while compiling the LCI are as follows:

1. The life of all the construction materials (i.e., ceramic membrane, stainless steel, carbon felt, steel wire, and glass hollow tube) has been considered as two years.
2. The electricity consumption during aeration was 0.20 kWh/m^3 [3].
3. Due to the absence of $CoCl_2$ in the EcoInvent v3 database, stoichiometrically equivalent amounts of $Co(OH)_2$ and HCl were considered to account environmental impact of $CoCl_2$.
4. The wastewater treated in the anodic chamber in case P1 was treated as avoided wastewater treatment, considering the process proxy of "Wastewater, from residue {RoW} treatment of, capacity 1.1E10l/year | Cut-off, U" and considering an equivalent volume of wastewater treated. Specifically, the wastewater dataset in the Ecoinvent database has an influent COD

concentration of 155.6 ppm. The equivalent volume of wastewater treated was calculated by converting the influent wastewater with a COD concentration of 3000 ppm.

Table S1 LCI of material synthesis and construction components of the reactor.

Phase	**Inputs**			**Outputs**		
	Field	**Unit**	**Value**	**Field**	**Unit**	**Value**
GO preparation	Graphite powder	g	2.00	GO	g	3
	$KMnO_4$	g	8.00			
	H_2SO_4	g	92.00			
	H_2O_2	g	2.18			
	DI water	kg	19.50			
	Electricity (centrifugation)	kWh	0.90			
	Electricity (magnetic stirrer)	kWh	0.03			
	Electricity (Oven drying)	kWh	1.80			
$rGO-Co_3O_4$ preparation	GO	g	0.08	$rGO-Co_3O_4$ composite	g	0.35
	$CoCl_2$.6H2O	g	0.43			
	$NaHCO_3$	g	0.30			
	H_2O_2	g	2.18			
	DI water	kg	0.09			
	Electricity (magnetic stirrer)	Wh	0.85			
	CO_2 sparging	g	594.00			
	N_2H_4	mg	102.00			
	Electricity (magnetic stirrer)	kWh	0.96			
	Hydrothermal treatment	kWh	2.40			
	Electricity (Oven drying)	kWh	1.80			
Cathode	Carbon felt	g	9.60			
	Ceramic membrane	kg	1.35			
	Stainless steel mesh	g	95.16			
	Steel wire	g	0.60			
Anode	Carbon felt	g	32.64			
	Steel wire	g	2.20			
Central support	Glass hollow tube	g	15.00			

Table S2 LCI of the chemicals and energy requirement during the operational phase of the wastewater treatment.

Phase	**Inputs**			**Outputs**		
	Field	**Unit**	**Value**	**Field**	**Unit**	**Value**
Operation phase (P1)	Influent Congo Red (P1)	g	210.24	Effluent Congo Red	g	0.54
	$FeSO_4.7H_2O$	g	981.12	Electricity generation	Wh	33.67
	H_2SO_4	kg	1.26			
	Electricity (aeration) for 72 h	Wh	74.66			
	rGO-Co_3O_4	g	224.64			
	Carbon black	g	56.16			
	PDMS	kg	1.45			
Operation phase (P2)	Influent COD	g	730.00	Effluent COD	g	39.42
	$FeSO_4.7H_2O$	g	62.22	Electricity generation	Wh	135.29
	H_2SO_4	g	43.80			
	Electricity (aeration) for 72 h	Wh	74.66			
	rGO-Co_3O_4	g	7.79			
	Carbon black	g	1.95			
	PDMS	g	50.29			

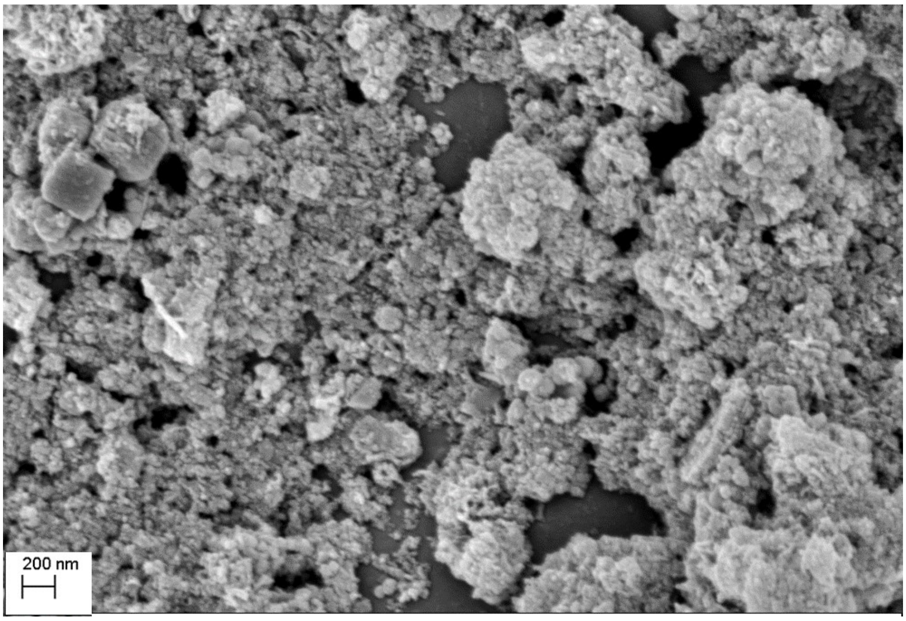


Fig. S1 Field emission scanning electron microscope image of synthesised Co_3O_4 catalyst

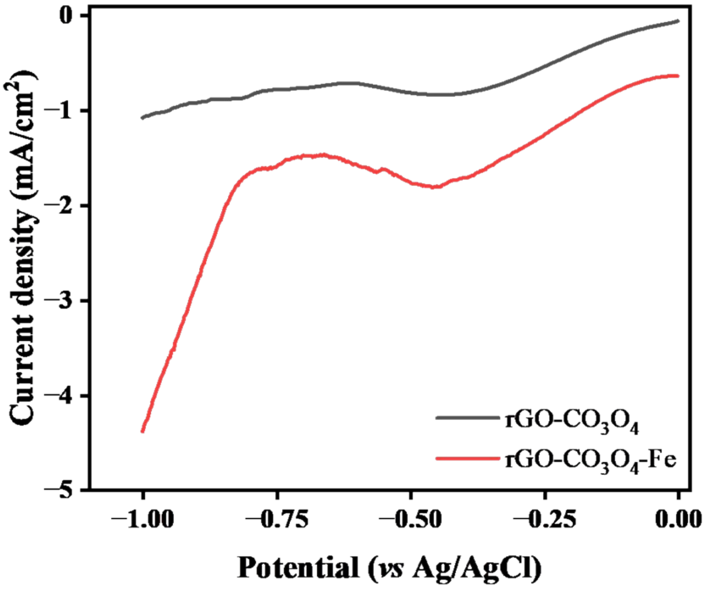


Fig S2 Linear sweep voltammetry plot for rGO-Co_3O_4 catalyst.

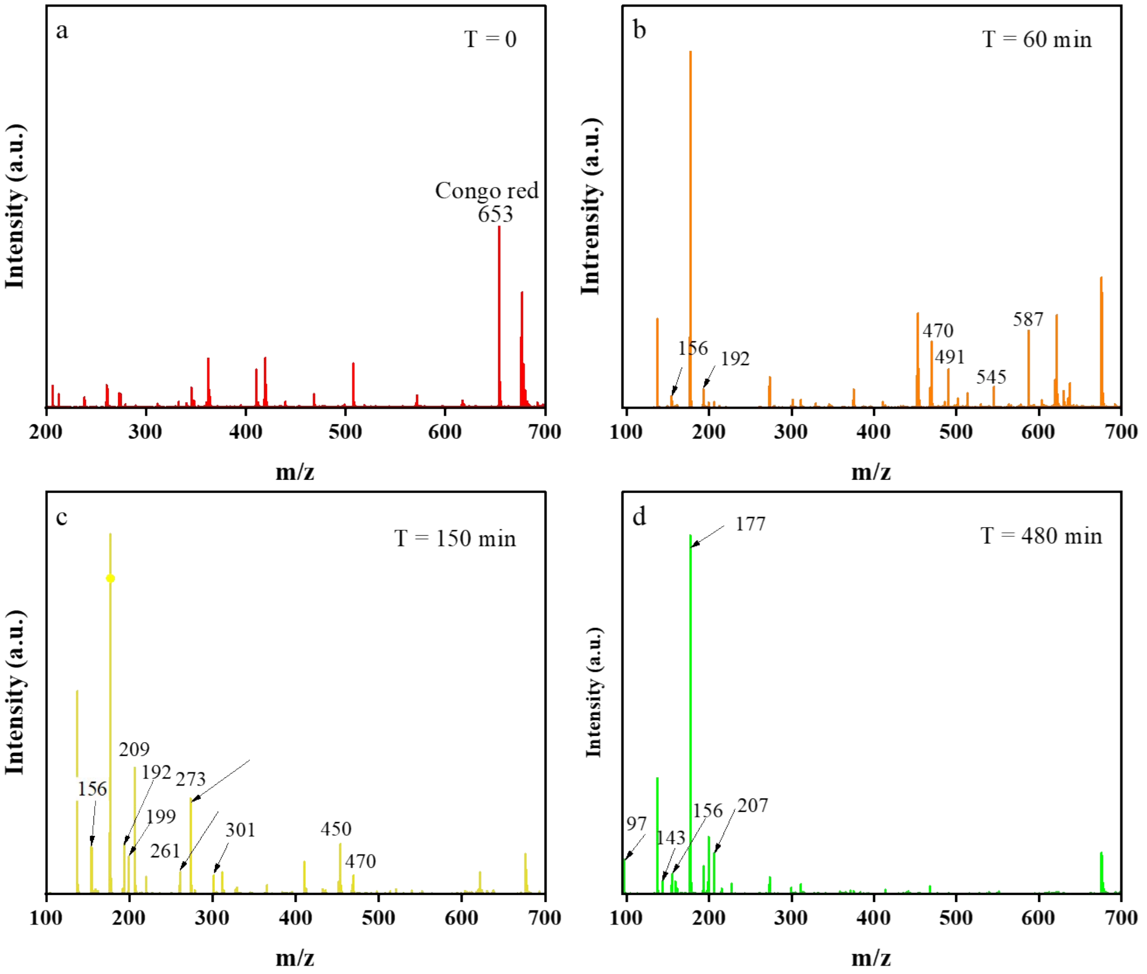


Fig. S3 Mass spectra chromatograms of the catholyte sample at different time intervals

Table S3 Identified degradation by-products using MALDI-TOF analysis

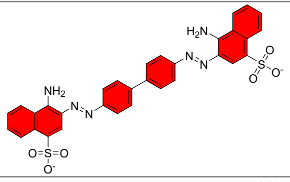
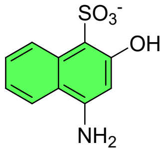
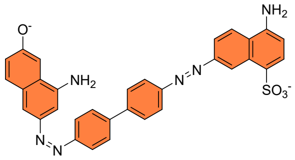
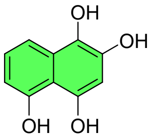
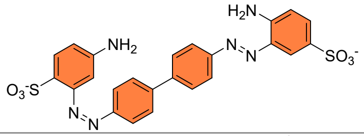
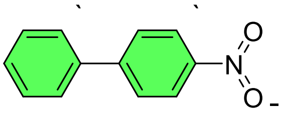
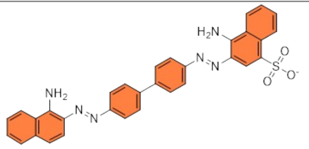
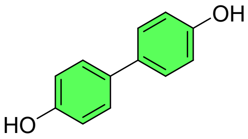
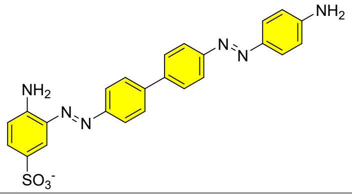
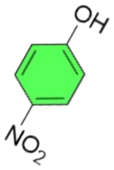
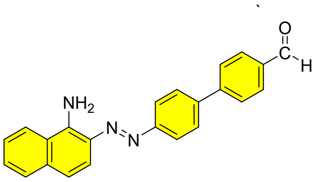
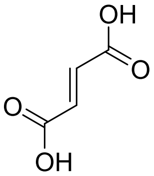
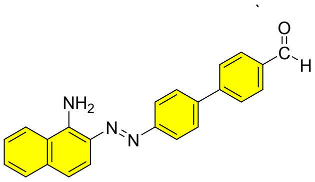
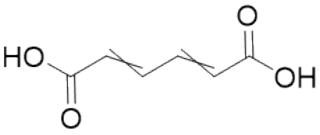
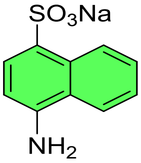
DB	m/z	Chemical str.	DB	m/z	Chemical str.
0			**8**	261	
1	587		**9**	209	
2	545		**10**	199	
3	491		**11**	192	
4	470		**12**	177	
5	450		**13**	156	
6	301		**14**	97/99	
7	273				

Table S4 Results of uncertainty analysis for 10000 simulations and a confidence interval of 95%

Impact category	**Unit**	**Scenario P1**				**Scenario P2**			
		Mean	**Median**	**SD**	**CV (%)**	**Mean**	**Median**	**SD**	**CV (%)**
Fine particulate matter formation	kg PM2.5 eq	7.36E-02	7.10E-02	1.92E-02	26.12	6.88E-04	6.64E-04	1.76E-04	25.61
Fossil resource scarcity	kg oil eq	7.67E+00	7.40E+00	2.04E+00	26.56	7.17E-02	6.92E-02	1.88E-02	26.23
Freshwater eutrophication	kg P eq	1.41E-02	1.11E-02	1.09E-02	77.36	1.33E-04	1.04E-04	1.04E-04	78.26
Global warming	kg CO_2 eq	3.06E+01	2.95E+01	7.54E+00	24.67	2.86E-01	2.77E-01	6.90E-02	24.12
Human carcinogenic toxicity	kg 1,4-DCB	1.10E+00	6.09E-01	2.85E+00	260.12	1.08E-02	5.66E-03	2.66E-02	247.64
Ozone formation, Human health	kg NOx eq	6.11E-02	5.90E-02	1.56E-02	25.5	5.72E-04	5.53E-04	1.44E-04	25.18
Ozone formation, Terrestrial ecosystems	kg NO_x eq	6.15E-02	5.94E-02	1.57E-02	25.5	5.75E-04	5.57E-04	1.45E-04	25.18
Terrestrial acidification	kg SO_2 eq	9.22E-02	8.76E-02	2.79E-02	30.26	8.62E-04	8.21E-04	2.53E-04	29.36
Terrestrial ecotoxicity	kg 1,4-DCB	1.74E+01	1.67E+01	4.91E+00	28.27	1.64E-01	1.56E-01	4.61E-02	28.16

Table S5 Composition of synthetic wastewater used as anolyte

Compounds	Weight (g) per litre
Sucrose	2.7
$NaHCO_3$	4.5
NH_4Cl	0.95
K_2HPO_4	0.08
KH_2PO_4	0.03
$MgSO_4.7H_2O$	0.19
$FeSO_4.7H_2O$	0.06
$CaCl_2.2H_2O$	0.75
Trace Metal solution	1.50 mL

References

1. I. Standard, *Environmental management-Life cycle assessment-Requirements and guidelines*, ISO, 2006.
2. E. Iso, *Environmental management—Life cycle assessment—Requirements and guidelines*, 2006, 1-46.
3. Y. Yang, X. Li, X. Yang and Z. He, *RSC Advances*, 2016, **6**, 49787-49791.