

1 Bioelectrochemical recovery of silver from wastewater with sustainable power
2 generation and its reuse for biofouling mitigation

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20 **Abstract**

21 Precious metals recovery and wastewater treatment using the microbial fuel cell (MFC) is an
22 attractive approach for a sustainable environment. Silver recovery from wastewater and its
23 valorization in the form of silver nanoflakes (AgNFs) brings back waste material to production
24 stream and helps in transition from linear to circular economy. In the present study,
25 bioelectrochemical performance of MFC fed with silver laden artificial wastewater (MFC-Ag)

26 was compared with MFC fed with potassium ferricyanide (MFC-FC) and MFC fed
27 with phosphate buffer as catholyte (MFC-blank). High silver removal ($83 \pm 0.7\%$)
28 and recovery ($67.8 \pm 1\%$) efficiencies were achieved from MFC-Ag after 72 h operation. The
29 maximum power density (3006 mW/m^3) and current density (34100 mA/m^3) of MFC-Ag were
30 found to be significantly higher than the MFC-FC and MFC-blank. High chemical oxygen
31 demand (COD) removal efficiency of MFC-Ag ($82.7 \pm 1.5\%$) compared with MFC-FC ($76 \pm$
32 2) highlighted the suitability of silver laden wastewater as a cost effective catholyte. The high
33 coulombic efficiency ($8.73 \pm 0.9 \%$) and low solution resistance (24.38Ω) for MFC-Ag also
34 indicate the potential of silver laden wastewater for large scale applications. Analytical
35 characterizations of electrochemically recovered silver revealed the pure (99%) and crystalline
36 AgNFs with a mean diameter of $18 \pm 1.2 \text{ nm}$ on the cathode surface. Furthermore, a significant
37 anti-biofouling activity of recovered AgNFs indicate the valorization of waste by current study
38 with potential applications in several industrial and environmental processes. Our method has
39 diverse potential to scale up the MFC technology for industrial waste management as a closed
40 loop process with minimum facilities and higher sustainability.

41 Keywords: Microbial fuel cell; Resource recovery; Sustainable; Anti-biofouling; Silver;
42 wastewater

43 **1. Introduction**

44 Silver has widely been used in various industries such as jewellery, photography,
45 medical/pharmaceutical applications, personal care products (PCP) and electronic industries
46 (Dutta, 2019; Ho et al., 2018). Silver discharge from different industries can accumulate in the
47 environment can cause serious clinical implications owing to its potential toxicity (Lei et al.,
48 2018). The United States Environmental Protection Agency (US-EPA) has recommended 0.1
49 and 0.01 mg Ag per litre of water as permissible limits for human beings and aquatic

50 invertebrates respectively (Greulich et al., 2012; Kahlon et al., 2018). Also, European Union
51 has listed the silver as a priority pollutant for the aquatic environment (Directive 2006/11/EC)
52 due to increased demand of silver-based products in Europe, North America, and Asia
53 (Deycard et al., 2017). Presence of silver ions and silver nanoparticles (AgNPs) can lower the
54 efficiency of biological wastewater treatment plants (Ward et al., 2019). Recently, a four
55 percent increase in the global industrial demand and a two percent fall in mining supply of
56 silver has been reported (Deycard et al., 2017; Dutta, 2019). A gap of 6000 tons between
57 production and usage of silver is continuously growing annually during the last decade
58 (Grandell and Thorenz, 2014). Hence, silver recovery from wastewater and secondary sources
59 would not only be an eco-friendly process but would also be helpful in fulfilling the global
60 demand of the expensive metal. Currently, numerous technologies are being used for the
61 extraction and recovery of silver from the waste and wastewater, which include bio-sorption,
62 bio-hydrometallurgical, leaching, ion exchange adsorption, reverse osmosis, ultrafiltration,
63 cementation and electrochemical deposition (Choi and Cui, 2012; Syed, 2016).

64 Sorption and desorption decrease the bioavailability of silver in aqueous solutions (Staroń et
65 al., 2017). Hybrid cyanidation and high-pressure membrane processes have been employed to
66 recover silver from mining wastewater (Koseoglu and Kitis, 2009; Lei et al., 2018). Besides,
67 industries have adapted various hydrometallurgical processes integrated with pyrolysis to
68 recover precious metals from the waste printed circuit boards (Niu et al., 2017; Rigoldi et al.,
69 2018). Unfortunately, hydrometallurgical processes are based on dissolving noble metals by
70 acids and caustic leachates, which is not a cost effective process. Several other technologies,
71 like cementation, may involve the use of toxic thiocyanate and subsequent production of
72 secondary pollutants may limit their applications on a larger scale (Rigoldi et al., 2018). Thus,
73 more efficient and eco-friendly strategies must be developed for sustainable silver recovery
74 from the wastewater. Microbial fuel cell (MFC) technology has emerged as a promising way

75 to recover precious metals, harvest electrical energy and wastewater treatment through
76 microbial metabolism (Ali et al., 2018; Liu et al., 2005).

77 Despite the significant improvements in its performance and design, MFC technology is
78 still far from practical applications due to relatively higher costs, slow reaction kinetics, low
79 power density and high internal resistance. Terminal electron acceptor (TEA) in the cathodic
80 chamber plays a crucial role in modulating the performance of MFC. Molecular oxygen,
81 ferricyanide, and permanganate are among the most commonly used TEAs due to high redox
82 potential and low overpotential. However, slow reaction kinetics for oxygen reduction reaction
83 (ORR) and frequent replacement of precious catholytes are practically unsustainable (Liu et
84 al., 2005). Metal ions with high redox potential such as Cr^{6+} , Cu^{2+} , Ag^+ , Hg^{2+} can be reduced
85 to stable metal nanostructures on the cathode, which exemplify the ability of MFC to generate
86 electricity with metal recovery from wastewater (Nancharaiah et al., 2016). Majority of studies
87 have reported the reduction of hexavalent chromium in MFC, which might be due to its high
88 redox potential. Cathodic reduction of copper (Cu) in dual chamber MFC was done from
89 CuSO_4 solution in 288 h (Heijne et al., 2010). Retrieval of three precious metals (Au, Cu, Ag)
90 with electricity generation by coupled redox reactor was also studied (Zhang, H.-M. et al.,
91 2017). A three dimensional MFC recovered the cobalt from stripping solution of the spent
92 lithium-ion batteries with low power production (Huang, T. et al., 2019).

93 Silver has high standard redox potential [Ag^+/Ag^0 , $E^0 = 0.799 \text{ V (vs. SHE)}$], and it can
94 serve as a potential TEA which will lead to silver recovery coupled with wastewater treatment
95 and electricity production. Choi and Cui (2012) provided the earliest demonstration of the
96 silver recovery with a power density of 4.25 W/m^2 in an MFC used for jewellery wastewater
97 treatment. Similarly, ammonia chelated silver alkaline wastewater was used to recover 1.6 g of
98 silver and 3.2 J of energy in BES (Wang et al., 2013). Effect of various operational parameters
99 on silver recovery and performance of BES were evaluated (Ho, N. et al., 2017; Ho, N.A.D. et

100 al., 2017). A bioelectrochemical system (BES) recovered the silver from wastewater containing
101 diamine complex while power production was enhanced with the addition of 10 mM NaNO_3
102 as a supporting catholyte (Ho et al., 2018). However, aforementioned studies have some
103 drawbacks such as the very high concentration of the silver, i.e., 1000-3000 mg/L was used.
104 Though real wastewater may not contain such a high concentration of silver, thus negating the
105 MFC applications for silver recovery from real wastewater. Also, addition of supporting
106 catholytes to enhance power density is not a sustainable approach (Ho et al., 2018). High
107 internal resistance due to anion exchange membranes, substrate loss from the anode and Ag^+
108 ions toxicity for biofilm also contributed for low efficiency (Ho, N. et al., 2017). Moreover,
109 the valorization of silver waste through MFCs needs to be explored, which can help in moving
110 towards the circular economy. For example, AgNPs are already known for their anti-biofouling
111 properties (Yang et al., 2018). So, silver recovered from wastewater could serve as a cheap
112 antibiofouling materials along with catalytic properties. Pure cultures are considered more
113 suitable to explore the microbe-electrode interactions, required to scale up the
114 bioelectrochemical recovery of precious metals (Nimje et al., 2012).

115 In fact, silver recovery from the wastewater using MFC is still in its infancy, hence
116 detailed understanding about the silver recovery from wastewater using MFC and re-utilization
117 of recovered metals is highly needed to apply this lucrative technology for real wastewater.
118 Thus, the aim of the current study was to present an alternative approach for silver recovery
119 from wastewater with bioenergy generation using MFC from low concentrated wastewater and
120 valorization of silver waste for anti-biofouling applications. Compared with other studies our
121 method has provided a one-step resource recovery and its valorization for environmental
122 applications along with bioenergy production as a closed loop, and it has diverse potential to
123 scale up the MFC technology for industrial wastewater with minimum facilities and high
124 sustainability.

125 2. Materials and methods

126 2.1. Anodic inoculum, electrolytes preparation

127 The pure culture of *Pseudomonas aeruginosa* (MK 163529) was obtained from the key
128 laboratory of environmental nanotechnology and health effects, RCEES, Beijing, China. It was
129 then suspended in LB broth to propagate it further. *Pseudomonas aeruginosa* culture was
130 serially diluted in phosphate buffer to get $1-5 \times 10^7$ cells/mL. Furthermore, anolyte was
131 prepared by dissolving the (g/L) 1.0 $C_2H_3NaO_2$, 4.4 KH_2PO_4 , 3.4 K_2HPO_4 , 1.0 KNO_3 , 0.5
132 $NaCl$, 0.2 $MgSO_4$, $CaCl_2$ 0.014 and 1 mL of trace elements solution [dissolving the (mg/L)
133 0.39 $Na_2MoO_4 \cdot 2H_2O$, 0.22 $ZnSO_4 \cdot 7H_2O$, 1.81 $MnCl_2 \cdot 4H_2O$, 0.08 $CuSO_4 \cdot 5H_2O$ and 2.86
134 H_3BO_3 in distal water]. Three different catholytes were prepared containing 500 mg/L of
135 $AgNO_3$ in distal water, and 500 mg/L of $K_3[Fe(CN)_6]$ in 100 mM phosphate buffer and only
136 100 mM phosphate buffer.

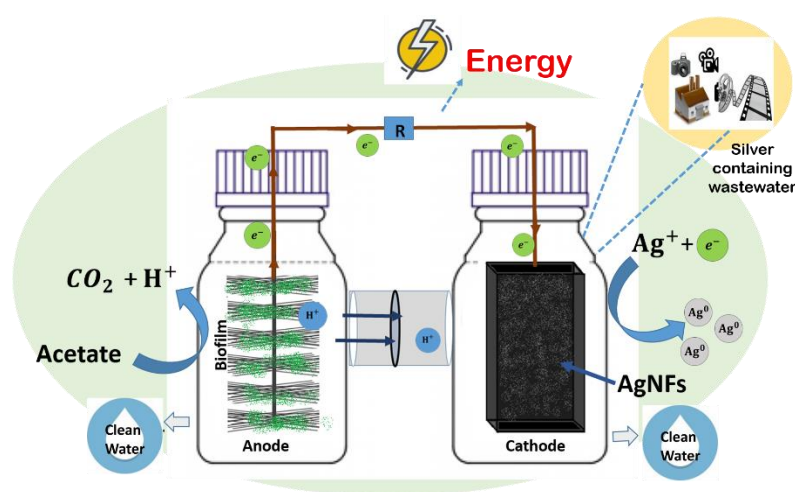
137 2.2. MFC construction and operation

138 Three identical dual chamber microbial fuel cells [classification based on catholytes: MFC-
139 Ag ($AgNO_3$), MFC-FC (Potassium ferricyanide) and MFC-blank (buffer)] made of Plexiglass
140 were used to study the simultaneous silver recovery and electricity generation with wastewater
141 treatment. MFC-Ag was the experimental cell, and MFC-FC & MFC-blank worked as control
142 cells to compare the electrochemical performance. Each chamber had an active working
143 volume of 160 mL. Graphite fibre brush (3.5 cm long and 2.5 cm in diameter) and graphite felt
144 (4×2.5 cm) purchased from Shanghai Hesun Electrical Co., Ltd. was used as anode and
145 cathode of MFCs respectively. Pre-treatment of electrodes was done by overnight incubation
146 in acetone solution followed by heating in a muffle furnace at 450 °C about 30 min as described
147 by Cheng et al. (2006). Proton exchange membrane (PEM, Nafion™ 117, Dupont Co.) with an
148 active surface area 12.56 cm² was used as a separator between anode and cathode chambers.
149 However, pre-treatment of PEM was done by boiling in H_2O_2 (30% v/v), deionized water,

150 H₂SO₄ (0.5 M), and then stored in deionized water, each for one hr as described in the literature
151 (Sravan et al., 2017).

152 The distance between two electrodes was 4 cm, and titanium wire was used to connect the
153 electrodes and external resistance (Fig. 1). After successful installation of MFCs, each anode
154 chamber was fed with same anolyte and *Pseudomonas aeruginosa* to develop a biofilm. While
155 the catholyte was different in each MFC as described in section 2.1. Nitrogen purging was
156 performed to remove the dissolved oxygen (DO) from each chamber. Initially, MFCs was
157 allowed to run in open circuit mode at room temperature. When a stable open circuit potential
158 (OCP) was achieved, the MFCs were ready for electrochemical analysis. A 1 KΩ resistance
159 was connected externally to measure the voltage generation (Fig. 1). Anolyte and catholyte
160 were replaced from time to time when OCP was below the 0.25 mV.

161



162

163 Fig. 1. Schematic illustration of MFC describing the working principal and components

164 2.3. Analytical methods and calculations

165 2.3.1. Electrochemical characterization of MFC

166 All MFCs were operated with different catholytes to compare the electrochemical
167 performance of MFC-Ag coupled with recovery of silver nanoflakes (AgNFs). Cell voltage
168 was continuously recorded for every 20 min using a multimeter data acquisition system (model

169 2700 Keithley Instruments, Cleveland, USA). Polarization curves were drawn by linear sweep
170 voltammetry (LSV) performed in two electrode mode, where anode was working electrode and
171 cathode served as a counter as well as a reference electrode. The potential was scanned from
172 open circuit potential (OCP, vs. cathode) to 0 V at the scan rate of 1 mVs⁻¹ in the reverse
173 direction. Current (I) and Power (P) were calculated using voltage data and the ohms law as (V
174 = IR_{ext}) or Power ($P_{\text{max}} = V \times I$). The power density was computed by normalizing the power
175 with anodic working volume. Electrochemical impedance spectroscopy (EIS) measurement
176 was done over a frequency range from 100 kHz to 10 mHz with an AC signal of 10 mV
177 amplitude at OCP using the potentiostat CHI660A system (CH Instruments, Inc.) in two
178 electrode mode.

179 Electrochemical performance of MFCs was also investigated by Tafel analysis using the
180 potentiostat CHI660A system (CH Instruments, Inc.) in three electrode mode. Anode and
181 cathode served as working and counter electrode respectively with Ag/AgCl as a reference
182 electrode. This technique is useful to study the electrochemical reaction kinetics and
183 mechanism of electrode reactions involved in biofilms. Tafel equation describes the
184 relationship between the electrode overpotential and the current density in the high
185 overpotential region and can be expressed as equation (3). In equation.3 η is the overpotential
186 (vs. Ag/AgCl) against which current density (i) is measured, F the Faraday constant (96, 485
187 C/mole), R the ideal gas constant (8.31 J/mol K), T the temperature (K) and β the symmetry
188 factor (a critical constant reflecting the activation energy).

189 Moreover, i_0 is exchanged current density obtained from extrapolation of the linear region
190 of the Tafel plot. However, CV analysis was carried out in a conventional three-electrode cell
191 using CHI660A system (CH Instruments, Inc.). The anode of MFCs was used as the working
192 electrode, and Ag/AgCl as a reference electrode, while the cathode served as the counter
193 electrode. The potentials were applied from - 0.8 V to + 0.8 V (vs. Ag/AgCl) at a scan rate of

194 10 mV/s with continuous monitoring of the current response. The CV was also performed after
 195 anolyte replacement in all anodes and spent removed from the anode of all MFCs to explore
 196 the main electron transfer mechanism involved in anodic biofilm (Ndayisenga et al., 2018).

$$197 \quad \ln(i|i_0) = \frac{\beta F \eta}{RT} \quad (3)$$

198 2.3.2. COD removal and columbic efficiency

199 To analyse the COD removal efficiency of anodic biofilm during the complete cycle of
 200 MFCs. Sample aliquots were taken from anolyte at frequent intervals of 12 h. Before analysis
 201 samples were filtered through syringe filter PTFE 0.45 μm (advanced Japan), COD was
 202 measured using the COD meter and high range (0-1500 mg/L) kit (Dr 2800, HACH, Loveland,
 203 CO, USA). Finally Coulombic efficiencies (CE) were calculated according to the Cheng et al.
 204 (2006), where, M is the molecular weight of oxygen, I is current, F is Faraday constant, n is
 205 the number of electrons required for reduction of 1 mole of oxygen, V is the working volume
 206 of anodic chamber ΔCOD is the difference between initial and final COD after time.

$$207 \quad CE = \frac{M \int_0^t I dt}{FnV \Delta\text{COD}} \quad (4)$$

208 2.3.3. Silver removal and Silver recovery efficiency

209 Samples from catholyte of MFC-Ag were taken after 72 h, and Ag^+ ions concentration
 210 was measured by Inductively Coupled Plasma-optical emission spectroscopy (ICP-OES
 211 Agilent 7500 series, Japan). The silver removal efficiency was calculated using equation 5.
 212 Where C_0 is the initial Ag^+ concentration in the catholyte (mg/L), C_t is the remaining Ag^+
 213 concentration in the catholyte at time t (mg/L). However, silver recovery efficiency was
 214 estimated from the mass of AgNFs deposited (M_d) on the electrode vs. removed concentration
 215 from the catholyte and equation. 6.

$$216 \quad \text{Silver removal efficiency (\%)} = E_{Rem} = \frac{C_0 - C_t}{C_0} \times 100 \quad (5)$$

217 Silver recovered efficiency (%) = $E_{Rec} = \frac{M_d}{C_0 - C_t} \times 100$ (6)

218 *2.4. Characterization of recovered silver nanoflakes*

219 After completion of 72 h successful operation of MFCs, the cathode from MFC-Ag was
220 carefully removed to characterize the deposited AgNFs on its surface. X-ray diffraction
221 analysis of the cathode was performed using X-ray diffraction machine (XRD, PANalytical
222 Empyrean, diffractometer equipped with a Cu K α 1 radiation). Surface morphology and
223 elemental composition of deposited silver nanoflakes were characterized by scanning electron
224 microscopy (SEM, S4800, HITACHI), energy dispersive X-ray spectroscopy (EDX, Horiba)
225 and X-ray fluorescence (ARL-PERFORM'X SEQUENTIAL XRF, USA). The X-ray
226 photoelectron spectroscopy (XPS, ESCALAB 250) was performed to analyse the elemental
227 composition and chemical state on the surface of graphite felt cathode and data was collected
228 at an axis ultra-ESCA system with monochromatic Al K α standard radiation source.
229 Furthermore, AgNFs were scrapped from the graphite electrode to explore the detailed
230 morphology of AgNFs by HRTEM (JEM 2100-plus transmission electron microscope, JEOL,
231 Tokyo, Japan) operated at an accelerating voltage of 200 kV.

232 *2.5. Evaluating the antifouling potential of the silver deposited electrode*

233 *2.5.1. Agar diffusion and broth dilution method*

234 The anti-biofouling activity of the electrochemically deposited AgNFs on graphite felt
235 was evaluated by the agar diffusion method. *Pseudomonas aeruginosa*, *Shewanella*
236 *putrefaciens*, and *E.coli* were selected as model strains to investigate the anti-biofouling
237 potential of in situ modified cathode. First of all, bacterial cultures were inoculated in sterilized
238 nutrient broth (pH 7.4 \pm 0.2) and incubated in shaking incubator (160 rpm.) at 37 °C for 24 h.
239 Subsequently, the bacterial suspension was diluted by 1-5 \times 10⁷ cells/mL with NB. A total of
240 20 μ L from each diluted bacterial solution was well spread on two different nutrient agar to

241 make a lawn. Silver-deposited electrode (Ag-electrode) from MFC-Ag and control (without
242 silver) were cut into circular pieces with 2.5 cm in diameter. Later on, these pieces of Ag-
243 electrode and control were placed on the freshly prepared lawns of bacteria. After overnight
244 incubation at 37 °C, the inhibition zones were measured to calculate the anti-biofouling activity.
245 A correlation between anti-biofouling activities and recovered silver was obtained by modified
246 broth dilution method. In situ modified cathode pieces (2.5 cm) from MFC-50, MFC-100,
247 MFC-150, MFC-250, and MFC-500 were dispensed in five test tubes containing 10 mL of
248 Mueller Hinton broth. An unmodified cathode was used as a control with the same treatment.
249 Then *E. coli* dilution (500 µL) prepared in the same medium and adjusted to 0.5 McFarland
250 scale was inoculated in all test tubes and incubated at 37 °C for 12 hours. And growth was
251 measured at 600 nm using a spectrophotometer.

252 2.5.2. Activated sludge immersion test

253 Furthermore, anti-biofouling potential of the Ag-electrode was also evaluated by sludge
254 immersion test. The Ag-electrode and control were immersed in activated sludge to observe
255 the biofilm formation up to 10 weeks. Biofilm formation on the electrode samples was observed
256 by SEM (S4800, HITACHI) and confocal laser scanning microscope (CLSM, Zeiss LSM 510
257 META, Carl Zeiss, Germany) equipped with a plan-apochromat. For the sample preparation
258 electrodes were cut from the centre of the intensively biofouled area, then live, and dead cells
259 were stained using the red fluorescent propidium iodide (PI) and 4',6-diamidino-2-
260 phenylindole (DAPI Sigma, Germany). Finally, images were obtained using a 63 × objective
261 lens with a 0.95 numerical aperture. A 543 nm helium/neon laser was used to excite the
262 propidium iodide-stained cells. Simulated three-dimensional images were generated by the use
263 of IMARIS software (Bitplane, Switzerland).

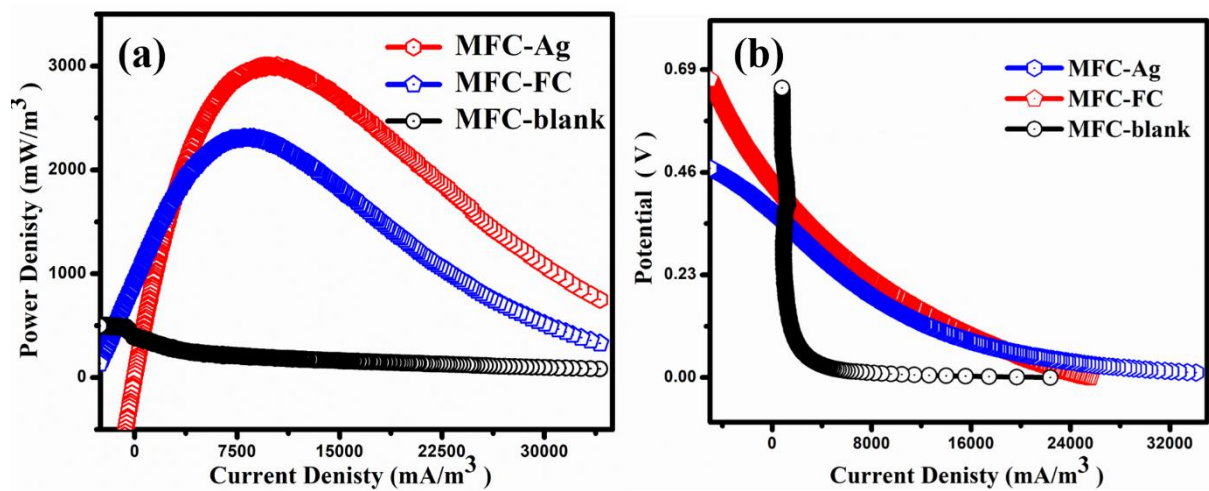
264 3. Results and Discussion

265 *3.1. Open circuit potential and polarization curves*

266 The open circuit potentials (OCP) of three MFCs (MFC-Ag, MFC-FC & MFC-blank)
267 were gradually increased and reached the stabilized OCP as 0.70 V, 0.68 V, and 0.65 V after
268 36 h, 40 h and 44 h of operation respectively. Although no remarkable difference in final OCP
269 values of all MFCs was observed, but the time to achieve this OCP was significantly lesser for
270 MFC-Ag among the others. Different upsurge rates of OCP in MFCs can be linked with the
271 availability of different TEAs (Srikanth and Mohan, 2012). Polarization curves were plotted
272 by LSV, at the stable phase of operation, to study the maximum power production using silver
273 laden wastewater compared with conventional catholytes for each MFC., Polarization profiles
274 depict that MFC-Ag has delivered the maximum current density of 34100 mA/m³ which was
275 approximately 1.3 and 1.5 times higher than the current density of MFC-FC (25600 mA/m³)
276 and MFC-blank (22375 mA/m³) respectively (Fig. 2a). The maximum power density extracted
277 from MFC-Ag (3006 mW/m³) was 1.3 times higher than MFC-FC (2310 mW/m³) and 5.6 times
278 higher than MFC-blank (528 mW/m³) (Fig. 2b). Polarization curves of MFC-Ag indicated the
279 cell design point (CDP) was ~70 Ω accounting the maximum power density. The low CDP
280 value suggests the feasibility of MFC treating the silver laden wastewater in the order of small
281 applications in LED, rotary discs and monitoring devices in waste management areas (Sravan
282 et al., 2017; Srikanth and Mohan, 2012).

283 The high current density and power density for the MFC-Ag indicate that Ag
284 contaminated wastewater has effectively served as TEA in the cathode to facilitate the
285 simultaneous silver recovery and sustainable power production from wastewater. Availability
286 and type of suitable TEA have a significant influence on the anodic oxidation and electrogenic
287 activity of MFCs (Choi and Cui, 2012; Sravan et al., 2017). The current study has demonstrated
288 a comparable power production to previous studies which have used a high concentration of
289 precious catholytes. For example, Ho, N. et al. (2017) reported the approximately similar power

290 density (3385 mW/m^3) to current study using the 2000 mg/L of catholyte. In another
 291 investigation a power density of 641.84 mW/m^3 was extracted from 1000 mg/L of silver
 292 containing catholyte, however power density in present study was 5 times higher (Ho et al.,
 293 2018). Effective utilization of industrial wastewater as a cheap catholyte will help to scale up
 294 MFC technology avoiding the frequent replacement of expensive TEAs. Our method is
 295 expected to reduce industrial waste generation and to improve the environmental sustainability
 296 by efficient resource management.



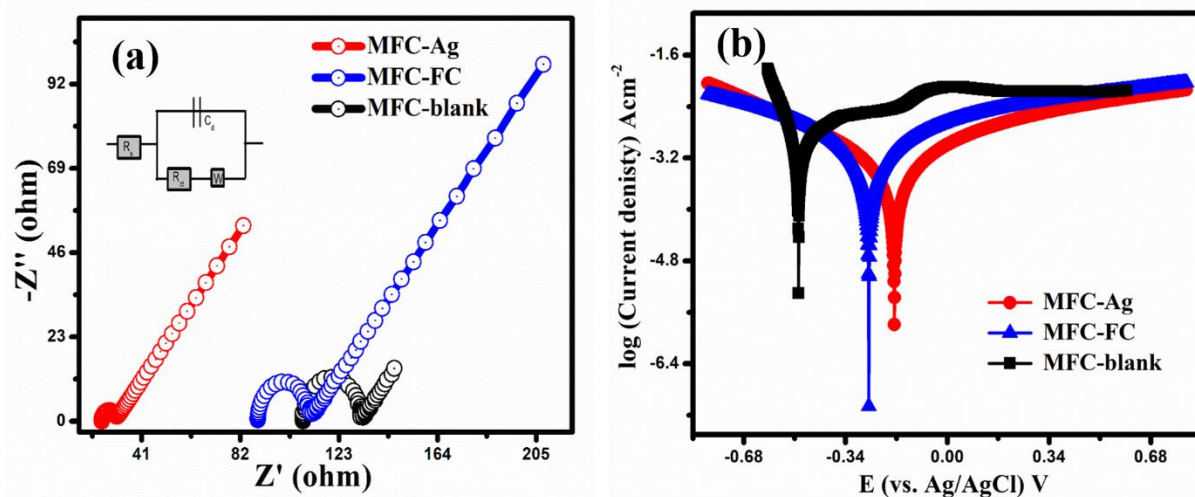
297
 298 Fig. 2. Polarization curves of MFCs drawn by LSV (a) power densities vs. current density (b)
 299 potential of MFCs vs. current density

300 3.2. Electrochemical impedance spectroscopy and Tafel analysis

301 Electrochemical impedance spectroscopy (EIS) was performed to measure the internal
 302 resistance of all MFCs offered during the electrochemical reactions. Electrolyte resistance,
 303 polarization /charge transfer resistance, and diffusion resistance were estimated by Nyquist
 304 plot. Electrochemical fitting of impedance spectra was also done to the Randles equivalent
 305 circuit using the Zview software. As there was only one semicircle for all MFCs, so one-time
 306 constant model (OTCM) was opted to determine all other parameters, where ohmic resistance
 307 (R_o) was in series with a parallel combination of capacitance of MFCs (C_{dl}) to the

308 Warburg/diffusion resistance (W) having charge transfer resistance (R_{ct}) in series. The Nyquist
309 plot of the EIS spectra was measured during the stable phase of the MFCs (Fig. 3a). Reaction
310 kinetics of electrode and electrolyte interface were investigated by fitting the impedance data
311 to the Randles equivalent circuit with the one-time constant model. Fit parameters are also
312 shown in Table 1. Ohmic resistance (R_s) usually contribute to the significant part of the internal
313 resistance of the system, including the sum of total resistance from the biofilm, electrode, and
314 electrolyte. MFC-Ag displayed the lower R_o (24.38 Ω) as compared with MFC-FC (90 Ω) and
315 MFC-blank (108 Ω). The solution resistance (R_s) has a direct influence on maximum power
316 production in MFCs (Islam et al., 2017; Logan et al., 2018). Another critical component of
317 internal resistance is charge transfer/polarization resistance (R_{ct}), which arise from charge
318 transfer barriers, either from electron transfer between capacitive material and current collector
319 or ion transfer between capacitive material and electrolyte. In this study, R_{ct} was of the order
320 of 5.413 Ω , 21.78 Ω , and 23.7 for MFC-Ag, MFC-FC, and MFC-blank, respectively. Warburg
321 element (W) specify the diffusional resistance during the mass transfer toward and away from
322 electrodes. Low polarization resistance (R_{ct} & W) direct the small activation losses,
323 concentration losses and high exchange current density in MFC-Ag as compared with control
324 MFCs as suggested by the Tafel equation (Kim and Chang, 2018; Yong et al., 2014). The
325 overall low internal resistance of MFC-Ag can be linked with significantly improved reaction
326 kinetics. Consequently, silver loaded wastewater has improved the conductivity of catholyte,
327 which will also help in enhanced AgNFs recovery and sustainable power production. The high
328 internal resistance of MFC is considered a major hurdle for the high power density and large
329 scale applications. Previously, various complicated methods have been used to load silver
330 nanomaterials at cathode to reduce internal resistance and to improve the power production in
331 MFCs (Islam et al., 2017; Zhao et al., 2019). In this study, electrodeposition of silver resulted
332 as an additional advantage with wastewater treatment, thereby presenting a facile and clean

333 method for in situ modification of electrodes. Waste minimization and renewable energy
334 generation intend to improve efficiency of sustainable industrial processes. The bio-
335 electrochemical performance and electrode kinetics of all MFCs were also evaluated through
336 Tafel analysis. This analysis helps to estimate the electrochemical activity of biofilms favoured
337 by different TEAs in MFCs. Tafel slope ($RT/\beta F$) is an indirect measure of electron transfer
338 efficiency among different MFCs fed with different catholyte (Equation .4). The exchange
339 current densities (i_0) were obtained from extrapolating the linear region of Tafel slopes. The
340 calculated exchange current densities (i_0) of MFC-Ag (0.086 Acm^{-2}), MFC-FC (0.084 Acm^{-2})
341 and MFC-blank (0.05 Acm^{-2}) corresponds to the oxidative Tafel slopes at 4.9 V/dec, 4.8 V/dec
342 and 10.8 V/dec, respectively. High exchange current densities (i_0) and lower Tafel slopes
343 indicate the higher electron transfer efficiencies in MFC-Ag (Fig. 3b). Although Tafel slope
344 for MFC-FC was approximately close to that of MFC-Ag, but higher over-potential will also
345 affect the exchange current and ultimately will hinder the reaction kinetics in the former. Tafel
346 analysis also provides a visual understanding of activation losses during the electrochemical
347 reactions such as ORR and OER (Raghavulu et al., 2012). MFC-blank showed the highest
348 activation losses due to unavailability of any effective TEA in the solution. Comparable Tafel
349 slope values of MFC-Ag and MFC-FC also suggest that silver contaminated water can serve
350 as an alternate and sustainable TEA for MFCs. Enhanced electron transfer efficiency of MFC-
351 Ag will also improve silver recovery and bioenergy generation. Overall simultaneous silver
352 recovery and bioenergy generation from wastewater will be a closed loop process for an
353 industrial economy with no harmful impacts on the environment.



354

355 Fig. 3. EIS and Tafel plots (a) electrochemical impedance spectrum of all MFCs showing the
 356 internal resistances, (b) Tafel plots describing the activation losses and Tafel slopes

357

358 Table. 1. Details of electrochemical impedance spectroscopy results and parameters

Element	MFC-Ag	MFC-FC	MFC-blank ²⁵⁹
Ohmic resistance	24.38	89.27	108.1
Charge transfer resistance	5.513	21.8	23.76
Capacitance	5.53E ⁻⁵	2.5E ⁻⁵	5.01E ⁻⁰⁶
Warburg element	0.05284	0.19	0.028
Error (%)	0.024	0.012	0.3

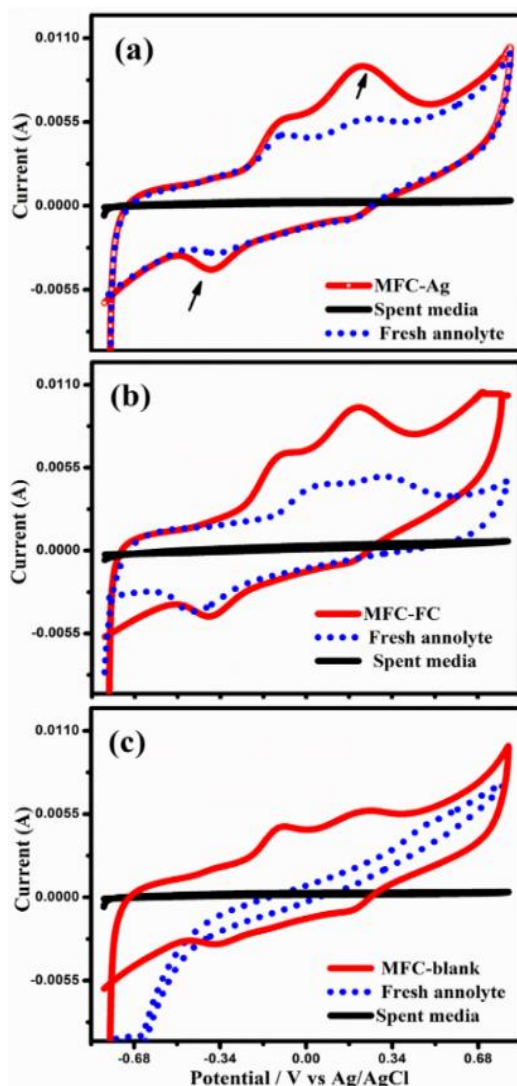
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361 3.3. Cyclic Voltammetry

362 To understand the regulatory effect of silver ions (catholyte) on the anodic biofilm, cyclic
 363 voltammetry (CV) analysis was performed during the stabilized phase of MFCs in open circuit
 364 mode at the scan rate of 10 mV/s. Cyclic voltammogram from MFC-Ag showed the oxidation
 365 and reduction peaks centred around 0.22 V and - 0.37 V (Fig. 4a). While, oxidation-reduction
 366 peaks for MFC-FC (0.30 V & 0.44V) and MFC-blank (0.24 & 0.35V) evinced the similar

367 redox-active molecules in all MFCs, which corresponds to the coenzyme NADH oxidation and
368 cytochrome redox potential of *Pseudomonas aeruginosa* (Fig. 4). These respiratory proteins
369 are essential for electron transfer during the metabolism of bacteria (Feng et al., 2010; Zhang,
370 P. et al., 2017). Numerous studies have reported the exceptional contribution of endogenous
371 mediators such pyocyanin for *Pseudomonas aeruginosa* in various MFCs (Yong et al., 2014).
372 Relatively high oxidative ($i_o = 2.151e^{-3}A$) and reductive currents ($i_r = -1.009e^{-3}A$) than the
373 MFC-FC ($i_o = 4.304e^{-4}A$ & $i_r = -8.1209e^{-4}A$) and MFC-blank ($i_o = 1.63e^{-4}A$ & $i_r = -1.509e^{-3}A$)
374 were observed (Fig. 4). The high oxidative current was ascribed to the low activation losses
375 and efficient electron transfer kinetics as a result of improved oxidation of acetate (Sravan et
376 al., 2017). The CV results are also in agreement with the outcomes of EIS and Tafel plots.

377 To explore the underlying electron transfer mechanism in all MFCs, a CV analysis was
378 carried out after anodic media replacement and spent solution. Cyclic voltammogram further
379 aided the understanding of the electron transfer kinetics and metabolic changes in terms of
380 redox mediators and substrate degradation efficiency (Grobber et al., 2018). Rapid retrieval of
381 voltage and CV analysis showed the direct electron transfer mechanism was dominant for all
382 the MFCs (Fig. 4). Moreover, extracellular mediators like phenazines were not detected in CV
383 analysis, which might be membrane-bounded redox active moieties (Saunders and Newman,
384 2018). However, the reductive currents can be correlated with the reduction of Ag ions, which
385 implies that silver containing wastewater will lower the cost of catholytes and improve the
386 overall efficiency required for large scale applications of MFC. Therefore, our method may
387 provide a sustainable approach for on-site waste management and resource recovery from
388 electronic industrial wastes.



389

390 Fig. 4. Cyclic voltammogram of MFCs (a) MFC-Ag, (b) MFC-FC and (c) MFC-blank

391

392 3.4. Simultaneous wastewater treatment, silver removal, and electricity generation

393 After the electrochemical characterization, all MFCs were connected with $1\text{k}\Omega$ resistance

394 for evaluating the electricity generation and wastewater treatment in the presence of different

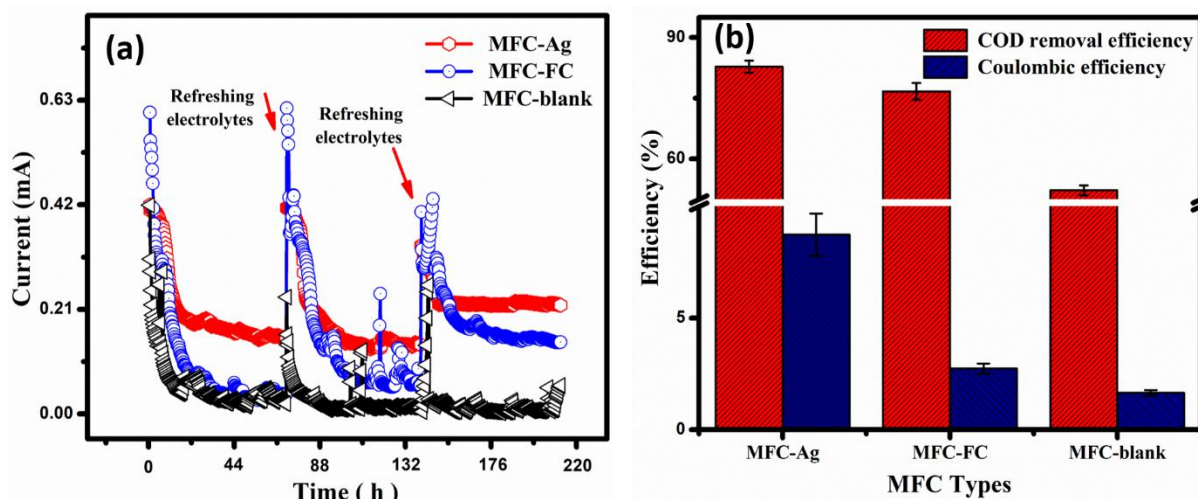
395 catholytes, where acetate served as an electron donor. Electricity generation profile indicates

396 that MFC-Ag produced a relatively stable voltage as compared with control MFCs (Fig. 5a)

397 Although initial overpotential was low in MFC-FC, the voltage was dropped sharply after 30

398 h operation, which can be ascribed with the unavailability of TEA. Periodic COD removal

399 efficiency profile indicate that TEA replacement in MFC-FC could upsurge and stabilize the
400 voltage generation, thus hampers the large scale applications of MFC. Similarly, MFC-Ag
401 showed the highest COD removal efficiency ($82.7 \pm 1.5\%$) and coulmbic efficiency ($8.73 \pm$
402 0.9%) as compared with MFC-FC (COD: $76 \pm 2.1\%$, CE: $2.73 \pm 0.2\%$) and MFC-blank (COD:
403 $52.2 \pm 1.2\%$, CE: $1.6 \pm 0.13\%$) respectively (Fig. 5b). This COD removal efficiency was higher
404 than previous studies reporting the bioelectrochemical recovery of silver (Ho et al., 2018; Wang
405 et al., 2013). The highest COD removal efficiency of MFC-Ag corroborate the availability of
406 TEA and enhanced electrogenic activities of anodic microbes (Sravan et al., 2017; Zhang et
407 al., 2015). In the past, most of the MFCs studies had majorly focused power production instead
408 of COD removal. Although coulmbic efficiency is sufficient to explain the amount of current
409 production, but COD removal efficiency is a crucial parameter to analyse the treatment
410 efficiency of wastewater treatment reactors and it must be low to meet discharge limitations
411 (Zhang et al., 2015). Therefore, high COD removal efficiency is beneficial for enhanced
412 electrogenic activity and sustainable resource recovery from indutrial wastewater (Djellabi et
413 al., 2019). Simultaneous wastewater treatment and enhnaced power production using MFC also
414 highlighted the feasibility to sacle up MFC technology. Integration of MFC with other waste
415 management processes at industries will reduce energy consumption and lower the carbon foot
416 print. Current method of silver removal is preffreable to other conventional technologies due
417 to renewable energy and lower carbon emission, which is necessary for sustianable and clean
418 environment.



419

420 Fig. 5. Wastewater treatment efficiencies and electricity generation in MFCs (a) electrogenic

421

performance and (b) treatment efficiencies of MFCs

422

423 The effect of various catholyte (silver) concentrations on electricity production, silver

424 removal, and silver recovery efficiency was also evaluated. Five different concentrations of

425 catholyte (i.e., 50, 100, 150, 250 and 500 mg/L) were used in respective MFCs, designated as

426 MFC-50, MFC-100, MFC-150, MFC-250 and MFC-500, respectively. Fig. 6a shows the silver

427 removal rate was increased with the concentration of silver in the catholyte. MFC-500

428 delivered highest silver removal ($83 \pm 0.7\%$) and recovery efficiency ($67.8 \pm 1.0\%$). Generally,

429 a decreasing trend for COD removal, silver removal, and silver recovery was observed as MFC-

430 $500 < \text{MFC-250} < \text{MFC-150} < \text{MFC-100} < \text{MFC-50}$, suggesting that high concentration of

431 silver in catholyte is favourable for treating the wastewater in MFCs. Moreover, voltage

432 generation profile was also in accordance with the trend observed for silver removal at various

433 concentrations (Fig. 6b). The low overpotential in MFC-500 as compared with other MFCs can

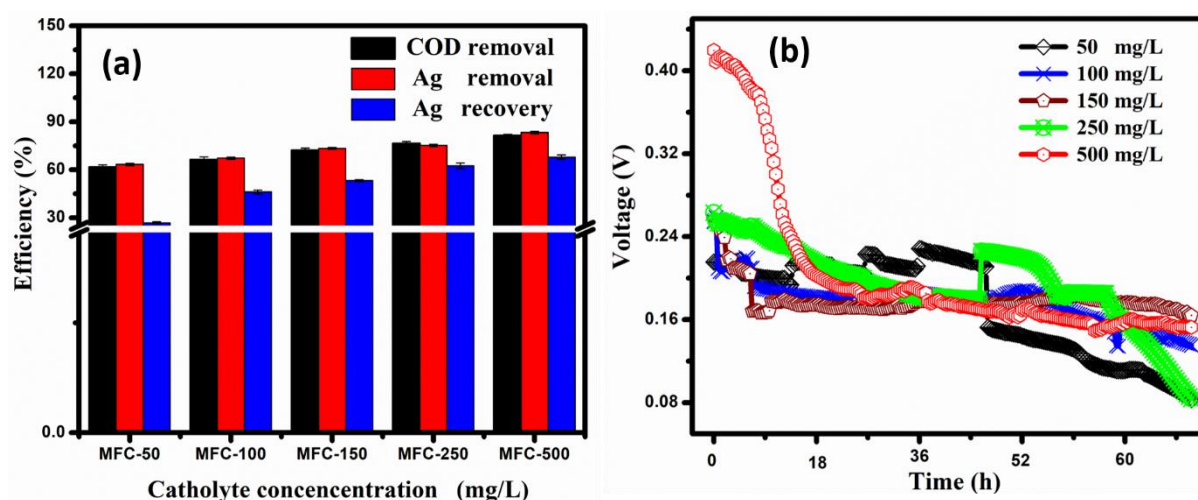
434 also be attributed to the extra deposited AgNFs at the cathode surface, which may increase the

435 conductivity and enhance the electron transfer kinetics by decreasing the charge transfer

436 resistance (Fig. 6b). In situ, modified cathodes can be further utilized for various catalytic/

437 environmental applications, such as electrodeposited silver have been employed to improve the
 438 performance of air cathode MFC via mitigating the biofouling and catalyzing the ORR
 439 (Firouzjaei et al., 2018; Linge et al., 2018). This method will also bring back material to the
 440 production stream as a resource and will help to address the economic issues of
 441 electronic/semiconductor manufacturing industries. Thus, simultaneous waste removal and
 442 valorization can be achieved using this simple process, which does not rely on special lab
 443 facilities for implementation.

444



445

446 Fig. 6. Effect of various concentrations of catholyte on MFC performance (a) silver removal
 447 and silver recovery and COD removal efficiency (b) voltage generation profile

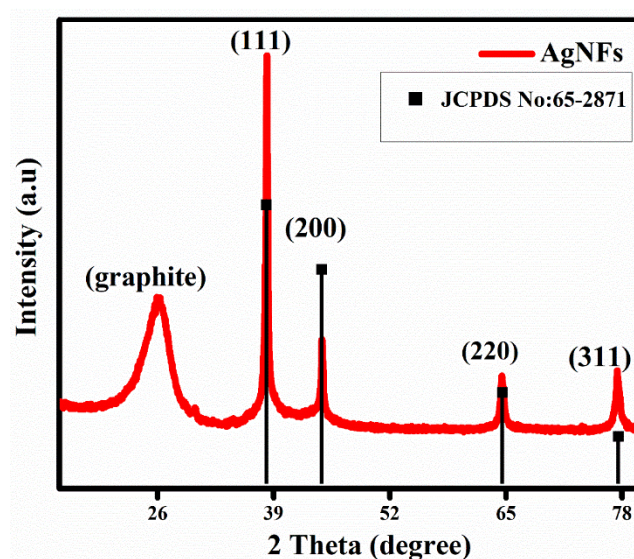
448

449 3.5. Characterization of the silver nanoflakes deposited on the cathode

450 Bioelectrochemical reduction of silver nitrate resulted in the deposition of silver nanoflakes
 451 (AgNFs) on the cathode surface. In order to investigate the morphology and nature of AgNFs
 452 several techniques such as XRD, SEM, XPS, EDX, XRF, and TEM were used. XRD pattern
 453 of the AgNFs revealed the characteristic peaks of the face-centered cubic structures of Ag at
 454 the $2\theta = 38.12, 44.30, 64.42, 74.41$ (JCPDS card No. 65-2871), which indicate the reduction

455 of the Ag⁺ ions to AgNFs by electrons produced *Pseudomonas aeruginosa* in the anode. Also,
456 a short peak representing the graphite felt also appeared at the $2\theta = 26.7$ (Fig. 7). Interestingly,
457 a high ratio of the plane (111) suggests that recovered AgNFs were dominated by (111) facets
458 which is consistent with previous findings of the silver nanomaterials (Ali et al., 2017; Ali et
459 al., 2016).

460



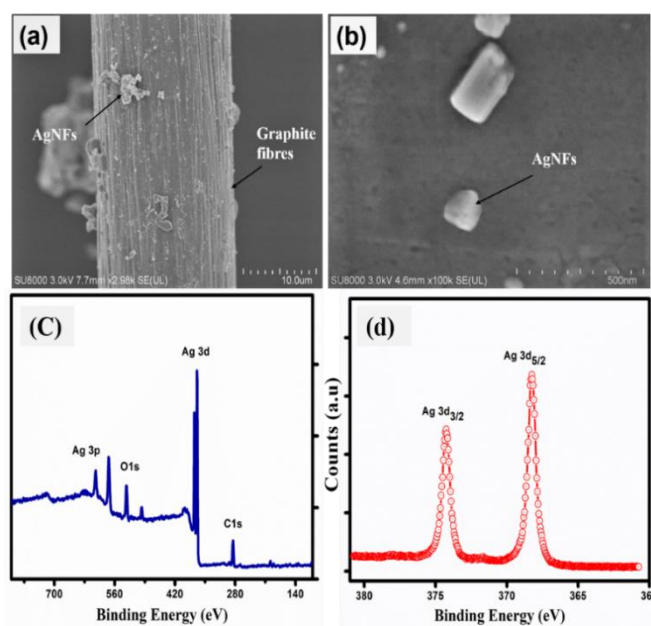
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462 Fig. 7. XRD patterns of silver nanoflakes deposited on the cathode of MFC-Ag

463

464 The overall morphology of AgNFs indicated some irregularly shaped entities at higher
465 magnification of SEM (Fig. 8 a, b). And Fig. 8 (c, d) shows the complete survey and Ag (3d)
466 XPS spectrum of AgNFs. The overall survey of AgNFs recovered in MFC-Ag display the
467 expected characteristic peaks of C1s, O1s at 285 and 574 and Ag (3d) (Fig. 8c). The Ag (3d)
468 peaks were appeared as a doublet due to spin-orbit coupling ($3d_{5/2}$ and $3d_{3/2}$) at the binding
469 energies of 368 eV and 374 eV respectively (Fig. 8d). These characteristic peaks at specific
470 binding energies confirm the synthesis of AgNFs mediated by the electrochemical pathway in
471 MFC-Ag (Ajitha et al., 2015; Yan et al., 2018). There were no oxide peaks in the XPS
472 spectrum, indicating the high stability of AgNFs. However, carbon and oxygen peaks may arise

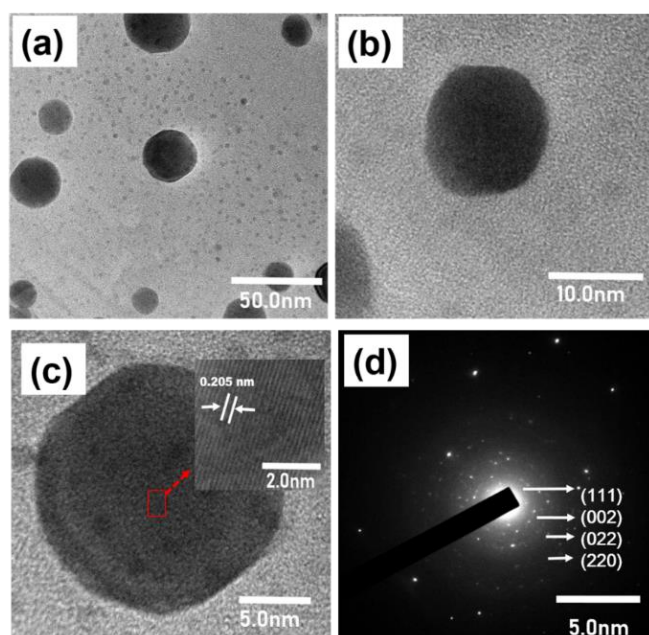
473 from the graphite felt fibres of cathode attached to AgNFs. Elemental composition analysis by
 474 Wavelength dispersive XRF of AgNFs showed recovered particles were 99 ± 0.05 % of pure
 475 silver (Fig. S2). The purity of the recovered AgNFs in this study was highest among the
 476 reported studies in literature (Choi and Cui, 2012; Ho, N. et al., 2017). All these results have
 477 highlighted the utility of the proposed method for extracting the silver from industrial
 478 wastewater even with low concentration.



479
 480 Fig. 8 SEM images of silver nanoflakes deposited on the cathode of MFC (a) AgNFs attached
 481 on graphite felt fibre, and (b) irregular shaped AgNFs at high magnification; The X-ray
 482 photoelectron spectrum (XPS) of AgNFs (c) the overall survey and (d) the spectrum of Ag
 483 (3d)

484
 485 A more detailed understanding of the morphology of AgNFs was provided by high-
 486 resolution TEM (HRTEM) images. HRTEM images at various magnifications, and selected
 487 area electron diffraction (SAED) pattern are displayed in Fig. 9. The variable size range (10-
 488 26 nm) and the period of $2d = 0.205$ nm in AgNFs lattice were evident in Fig. 9c. Also, the
 489 indexed SAED pattern with bright and circular fringes corresponding to the (111), (200), (220)

490 and (311) planes of crystalline AgNFs (Fig. 9d). Current findings are in accordance with our
491 XRD results and previous studies about AgNFs (Wei et al., 2015). These results explain the
492 successful bioelectrochemical reduction of silver ions to AgNFs and subsequent
493 electrodeposition at the cathode. The proposed underlying mechanism for the synthesis of
494 AgNFs can be two steps, (a) electron provided from the anode transform the Ag^+ to Ag^0 at the
495 cathode surface, (b) which initiate the nucleation and growth of nanoflakes (Ali et al., 2019).
496 Hence, the current method delivers in situ waste remediation approach for industrial
497 wastewater and also provide an opportunity for waste recycling (valorization). This one-step
498 conversion of waste to wealth will defiantly address challenges required for sustainable waste
499 management.



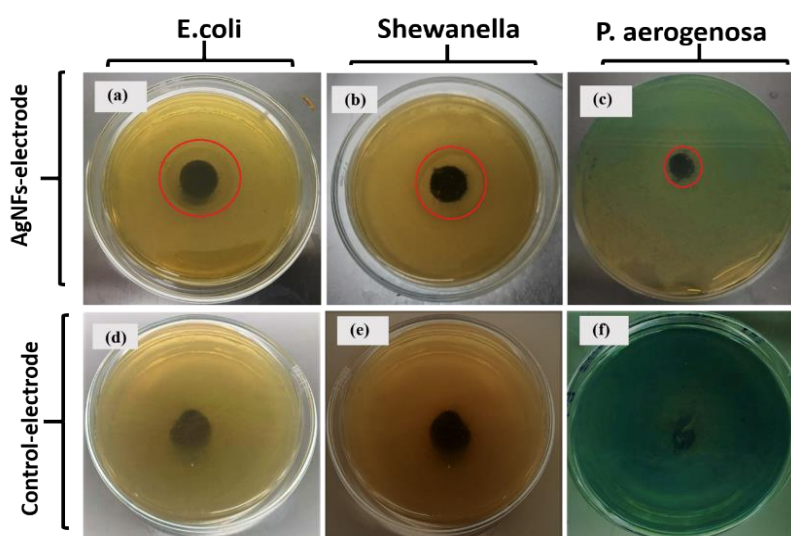
500
501 Fig. 9. TEM images of silver nanoflakes (AgNFs) under various resolutions (a) & (b)
502 displaying the spherical shaped AgNFs (c) HRTEM image of AgNFs (d) SAED pattern of
503 AgNFs

505 3.6. Anti-biofouling activity

506 3.6.1. Antibacterial sensitivity test

507 The antibacterial activity of the AgNFs against the *E.coli*, *Shewanella*, and *Pseudomonas*
508 *aeruginosa* was observed by the modified disk diffusion method (Fig. 10). The control graphite
509 felt didn't show any inhibition zone in all cases, while Ag-electrode clearly showed the
510 inhibition zones of 13.8 ± 0.12 mm, 15 ± 0.24 mm and 10.45 ± 4 mm for *E.coli*, *Shewanella*
511 and *Pseudomonas aerogenosa* respectively. A positive correlation ($R^2 = 0.93$) was observed
512 between anti-biofouling potential and concentration of recovered AgNFs (Fig. S3). These
513 results indicate the effectiveness of electrochemically deposited AgNFs as an inexpensive anti-
514 biofouling agent. Thus, recovered AgNFs could be directly applied for biofouling mitigation
515 in electrochemical reactors, where low dissolved oxygen renders the slow reaction kinetics due
516 to mass transfer losses. Our findings will advance the strategies used for biofilm inhibition and
517 improving the catalytic performance of fuel cells (Noori et al., 2016).

518



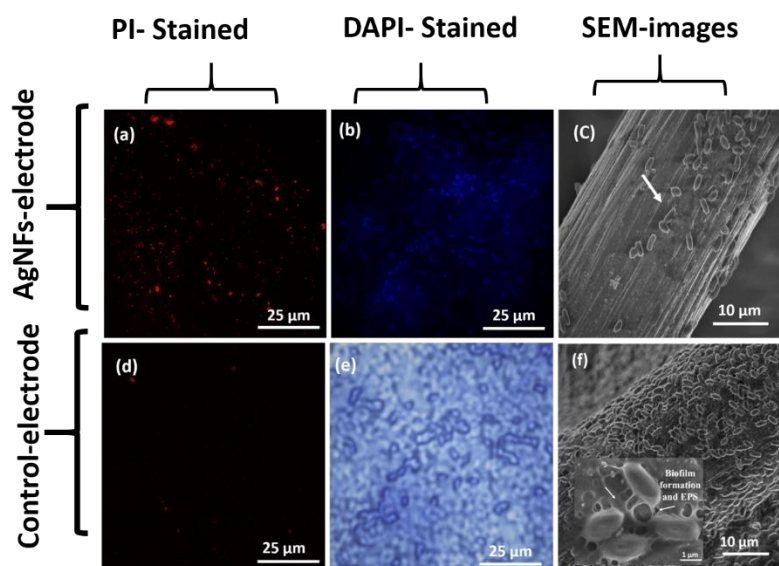
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520 Fig. 10. Antibacterial activities of electrochemically deposited AgNFs, (a, b & c) indicate the
521 inhibition zones formation with Ag-electrode by *E.coli*, *Shewanella* and *Pseudomonas*
522 *aeruginosa*, respectively, (d, e, f) represent the no growth inhibition with control electrodes

523 3.6.2. Activated sludge immersion test

524 The anti-biofouling activity of the silver deposited electrodes (Ag-electrode) is also
525 compared with control a non-silver control (graphite) after seven days incubation in activated
526 sludge. CLSM micrographs stained by PI and DAPI shows the majority of dead bacterial cells
527 which indicate the biofilm formation was inhibited on Ag-electrode (Fig. 11a, b) due to the
528 antibacterial effect of AgNFs. Whereas, biofilm formation was evident from the extensive
529 bacterial growth and presence of EPS matrix on control electrodes (Fig.11d, e). The additional
530 evidence provided by the SEM micrographs also indicated the biofilm formation and dense
531 EPS matrix on the control electrode (Fig.11c, f). However, few bacteria and absence of EPS
532 matrix on Ag-electrode reveals its anti-biofouling activity, and these findings also support the
533 CLSM results. Earlier, EPS production has been entirely attributed to adhesion and successful
534 establishment of biofouling in membrane reactors (Kim, T.-S. et al., 2019; Yi et al., 2019).
535 Moreover, EPS has been postulated to contribute most to the hydraulic resistance of biofilms.
536 Biofouling in ORR based reactors increase the mass transport losses and lower their optimal
537 performance by consuming the DO (Huang, J. et al., 2019; Kim, H.-S. et al., 2019).
538 Interestingly, Ag-based catalytic materials have been regarded as an efficient platinum free
539 electrocatalysts toward ORR for anion exchange membrane fuel cells (Erikson et al., 2019;
540 Kim, T.-S. et al., 2019).

541 Electrodes with innate anti-biofouling potential and enhanced catalytic properties are
542 required for the long-term and stable performance of fuel cells and biological reactors.
543 Therefore, it is expected Ag-electrode has potential applications for anti-biofouling and ORR
544 processes, that will not only mitigate the biofouling problem but will also enhance the catalytic
545 reduction of oxygen (Farhat et al., 2019; Noori et al., 2018). Briefly, in situ preparation of
546 antibiofouling material was achieved from wastewater, which will reduce the cost of
547 antibiofouling materials for sustainable resource recovery or waste valorization.



548

549 Fig. 11. CLSM and SEM results of activated sludge immersion test, images (a, d), (b, e) and
 550 (c, f) represent the PI-stained, DAPI stained and SEM images respectively. Images a, b, and c
 551 specified the biofilm inhibition at Ag-electrode and images e and f show the biofilm
 552 formation at the control electrode

553 4. Conclusion

554 Silver contaminated wastewater can serve as a cost-effective catholyte for MFCs. The current
 555 method can recover approximately 339 g of silver from 1.5 litre of wastewater after 30 days.
 556 Therefore, stacked MFCs with high retention volumes can efficiently treat industrial
 557 wastewater. The eco-friendly method has not only recovered unprecedented amounts of silver
 558 (67.8%) but also generated sufficient bioenergy (3006 mW/m^3) from low concentrated
 559 wastewater (500 mg/L) through MFC. The lowest solution resistance (24.38Ω) and charge
 560 transfer resistance (5.413Ω) of MFC-Ag improved the reaction kinetics to deliver a significant
 561 exchange current density (0.086 Acm^{-2}) in the reactor. Highest COD removal efficiency of
 562 MFC-Ag ($82.7 \pm 1.5\%$) compared with controls was also linked with the enhanced silver
 563 removal efficiency ($83 \pm 0.7\%$). High crystalline and pure (99 %) silver was recovered from
 564 silver containing wastewater. The high potential of recovered silver in anti-biofouling
 565 applications has showed a way forward in exploring the utility of recovered nanoflakes

566 particularly in membrane bioreactors. The one-step resource recovery and valorization of silver
567 from industrial wastewater can contribute significantly in moving towards circular economy.
568 In contrast to conventional technologies, high efficiency and effective resource management
569 indicate the high potential of this clean process for attaining environmental protection and
570 economic sustainability. It implies that, current findings will minimize the continuously
571 increasing gap between production and usage of silver. The present study was conducted on
572 pilot scale, therefore large scale applications for real wastewater must be evaluated.
573 Implications of current study may involve high capital cost and durability of electrode
574 materials for longterm industrial applications. Operational issues associated with optimum
575 recovery efficiency, types of wastewater and anodic biofilm development must also be
576 considered. In addition, stability of generated electricity by industrial wastewater and suitable
577 power management programs can be useful for attaining the sustainable goals. Futuristic
578 applications of recovered silver nanoflakes can replace the platinum based precious catalysts,
579 which is considered as a major challenge for renewable energy conversion systems.

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589

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