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Catalytic and filterable polyester-filter membrane electrode with a high performance Carbon foam-Fe-Co catalyst improved electricity generation and waste-water treatment in MBR-MFC

Tingting Yu^a, Lifen Liu^{ab*}, Qiao Yang^b, Jing Song^a, Fenglin Yang^a
Abstract

Using the flat module membrane electrodes based on polyester filter modified with Polyaniline (PANI)-phytic acid (PA), a new type of membrane bio-reactor (MBR) system is developed for both bio-electrochemical electricity generation and effluent filtration. A specifically prepared Carbon foam-Fe-Co catalyst was coated on the conductive, filterable cathode membrane which makes it catalytic for enhancing cathodic oxygen reduction reaction and electricity generation. The cell voltage (with Carbon foam-Fe-Co, 0.5~0.4 V) is superior to control test 1 (without any catalyst, 0.2 V), moreover, it is even better than control test 2 (with Pt-C catalyst, 0.5~0.3 V). The corresponding maximum power density of Carbon foam-Fe-Co is 38.5 and 2.4 times higher than control test 1 and 2, respectively. More importantly, the base electrode materials and catalyst were both lowcost. The overall removal efficiency of COD and NH₄⁺-N are satisfactory, at 95% ±2.5% and 85% ±2.5%, respectively. This integrated system is easy to scale up for practical application in waste-water treatment and offers a better option in operating and coupling MBR with bio-electricity generation.

1. Introduction

Our world is facing triple crisis in over-consumption and depletion of resources (such as clean water and fossil fuel) and climate change. The shortage of fresh water supply is aggravating over the years, because of the increase in population and in utilization. This

makes the recycle and reuse of waste-water crucially. Considering the large scale energy consumption in the water sector, it is necessary to overcome the disadvantages of traditional waste-water treatment technologies such as extra energy input, not enough recovery and values gains from the energy & substances inside waste-water. Researchers pour their attention into renovating waste-water treatment techniques, which are more efficient, low-cost and energy-saving.

Though hampered by membrane fouling¹ and high-energy consumption², MBR can provide better effluent by combining activated sludge process with membrane separation³. Microbial fuel cell (MFC) can extract electric energy from waste-water, and the generated power (still limited) can be used for membrane fouling reduction or generating H₂O₂ in situ. For MFC, the effluent quality usually is not good enough and the treatment efficiency is low⁴. For overcoming these constraints, MBR and MFC are combined in waste-water treatment and electricity generation^{5, 6}. There were also a few reports about coupling MBR with MFC into a reactor system. The use of inexpensive electrode/catalyst materials is required and filtration performance of the electrode can be improved^{7, 8}. The integration of MBR with MFC can use the generated electric field in fouling reduction and improve the removal of pollutants potentially more efficient via the bioelectrochemical pathways^{9, 10}.

In MFC or MBR-MFC system, carbon fiber cloth, carbon paper and carbon felt were often used as electrode materials. Though the conductive performance is good, rarely its filtration performance was impressive. Conductive PANI formed by polymerization of aniline in acidic aqueous solution can be used for modifying electrodes. PA can be used as dopant for conductive polymer, and significantly improve the electrical conductivity of PANI. Study of PA/PANI was suggested for high electrochemical activity hydrogel¹¹. Previous study of modifying filter cloth with PANI had been devoted to function as a conductive cathode, and the electricity generation in MFC was small¹². While, there is almost no report on using the modified polyester filter as both anode and cathode, moreover, cathode can be made functioning as catalyst for oxygen reduction reaction (ORR), while conducting electrons and filtration simultaneously in a new reactor.

One great hindrance or constraint encountered in MFC or MBR-MFC application is the prohibitive cost of cathode catalyst, for catalyzing the ORR. Previously, many kinds of non-metal^{13, 14, 15} or metal-doped¹⁶ catalyst had been developed for ORR. Pt replacement candidates had been synthesized by heating precursors comprised of nitrogen, carbon, and transition metals^{17, 18, 19}. Also, Carbon foam²⁰, prepared from a melamine sponge, has excellent characteristics such as elasticity, lightweight (5 mg cm⁻³) and extremely high porosity (over 99.6%), as well as a high specific surface area and tailored electrical conductivity. It is a source of carbon and nitrogen as an active cathode catalyst. Therefore, in this study, we prepared a new catalyst by heating a suspension containing grounded carbon foam (prepared from melamine) 20, polymer and transition metals in nitrogen atmosphere²¹ and used it as the cathode catalyst in MBR-MFC. This new catalyst is effective and at a low price. Thus, a new flat-module MBR-MFC reactor, using costeffective membrane electrode materials and high-efficiency catalyst could operate well for both waste-water treatment and electricity generation. As far as we know, this membrane electrode with this new catalytic for ORR has not been reported before.

2. Experimental

2.1 Carbon foam-Fe-Co catalyst--synthesis and characterization

The catalyst was characterized using X-ray diffraction (XRD, Rigaku DMAX IIIVC), scanning electron microscope (SEM, NOVA NANOSEM 450, USA) and high-resolution transmission electron microscopy (HR-TEM) with energy-dispersive X-ray spectrometer (EDS). HR-TEM was conducted on a FEI TecnaiG2 F30microscope equipped with an EDS at 300 kV. The XRD pattern was recorded using Cu-Ka (0.1542 nm) radiation, scanning from 5 ° to 90 ° (2 θ) at the rate of 6 ° min⁻¹.

2.2 Preparation of the membrane electrodes

The Membrane anode: Quintessentially, 2.86 g ammonium persulfate was dissolved in 10 mL DI water. Then, 9.21 mL phytic acids and 4.58 mL aniline were mixed in another 10 mL DI water. Both solutions were cooled to 4 °C and subsequently brush-coated on the polyester filter cloth (No. 747, Suita Filter-Cloth Factory, China), respectively. To remove excess acid and by-products from polymerization, the filter cloth with PANI was purified by immersion in DI water for 24 h, after that dried at 60 °C under vacuum.

Working Membrane cathode: As in Fig 1B, 0.2 g Carbon foam-Fe-Co, 0.2 g grounded carbon foam and 1.8 g graphite were added in N-N-dimethylacetamide (DMAC) solvent. Nafion (5 wt%, SIGMA-ALORICH, USA, 220 μ L) and 0.2 g polyvinylidene fluoride (PVDF) were added as the binder. After stirring to make the suspension uniform, it was brush-painted to the modified filter cloth, the same with the anode, on which the loaded PANI/PA was 0.27 mg cm⁻².

Control Membrane cathode:In control 1, the cathode has no catalyst. In control 2, the cathode is painted with Pt-C catalyst. The preparation method is same as in preparing the working cathode, (0.2 g Pt-C, 1.8 g graphite, 0.2 g PVDF and 220 μ L nafion). The loading of Pt is 10 wt% on activated carbon support (Aladdin Industrial Corporation, Shanghai, China.)

2.3 Operation conditions and water quality in the MBR- MFC system

The setup of the integrated MBR-MFC system is illustrated in Fig 2A. The size of the system was 85 mm (long) * 50 mm (wide) * 250 mm (height), which is readily suitable for study practical waste-water treatment. The spacing between adjacent chambers of the three cathode chambers and two anode chambers were 10 mm. The details of the module electrode in the MBR-MFC system are demonstrated in Fig.2B.

Compositions of synthetic waste-water in this system are shown in table 1, which were fed into the anodic chamber by a peristaltic pump continuously. The influent was fed from the bottom of the anode chamber, and overflowed from the top of the anode chamber. The effluent was drawn out by a pump after filtration through the cathode membrane (modified polyester filter with Carbon foam-Fe-Co). The anode was inoculated with electricigens: *Shewanellaoneidensis* MR-1 (ATCC: 700550 T). Cation exchange membrane

(DF-120, Shandong Tian Wei membrane technology co., LTD. China) was fixed outside of the anode. The air flow in the cathode chamber was controlled by a gas flow meter and the aeration rate was kept at 0.03~0.05 m³ h⁻¹. The sludge retention time (SRT) was kept for 60 days. The trans-membrane pressure (TMP) was monitored using a vacuum meter. The electrostatic repulsion delayed fouling which had been reported⁹, and the TMP is less than 0.03 MPa before 30 days in this MBR-MFC. A simple physical cleaning was conducted after the TMP reaching 0.03 MPa. The membrane modules were washed and back-flushed with tap water for 5 min. Carbon-fiber bundle was used to connect the cathode membrane and the anodes to an external resistance. A timer switch was used to control the operation cycle of the pump for effluent permeation in 5 min "on" and 1 min "off" mode.

The COD, NH₄⁺-N, MLSS concentrations and turbidity (NTU) of the influent and the effluent were measured using Standard Methods²². In continuous operation tests, hydraulic retention time (HRT) for the system is calculated by HRT (h) = $V.Q^{-1}$, V is the effective volume of the reactor and Q is the effluent flow rate.

2.4 Electrochemical measures

The cell voltages and anode potentials were recorded using a data collection system (PISO-813, Taiwan). A saturated calomel electrode (type of 232, 0.2415 V vs SHE) was set near the anode as the reference electrode for measurement of the anode potential. When the cell voltage of the MFC was relatively stable, the polarization curves of MFC were obtained by varying the external resistance from 9999 Ω to 100 Ω , and the voltage reading was obtained from a multimeter. Before testing, the MBR-MFC system was maintained at open circuit for 3 h until the potential became stable. The current densities and power densities were calculated by U/RA and IU/A, where U is the voltage, I is current and A is electrode area (0.012 m²). The polarization curve and power density curve were drawn using current density and power density. The coulombic efficiency efficiency (CE) was calculated as follows:

$$CE = \frac{\sum I(A)t(s)}{96485 \times b \times v \times \Delta COD / M}$$

Where I is electric current and t is time; v is the liquid volume; b is the number of mol of electrons per mol of substrate (4); \triangle COD (g L⁻¹) is the substrate concentration change over the cycle; M is the molecular weight of the substrate (32 for oxygen). The operation conditions are given in Table 2.

The cyclic voltammograms tests were conducted on a CHI 832B electrochemical station (Shanghai Chenhua Co., China) in a standard three-electrode system with a platinum plate and a saturated calomel electrode (SCE) as the counter and the reference electrode. The working electrodes are glassy carbon electrode (GCE, 3mm in diameter, Shanghai Chenhua Co., China) with PANI, Carbon foam-Fe-Co and Pt-C, respectively. The loading of the glassy carbon electrode with different catalysts is as follows. Typically, $10~\mu L$ (1mg mL⁻¹) well-dispersed catalyst suspensions with Nafion as the binder in ethanol solution were coated on the electrode surface. The working electrodes of the modified polyester filter are as described in 2.2. The electrolyte was $0.1~M~Na_2SO_4$ or H_2SO_4 solution which was purged with O_2 for 30 min prior to the electrochemical test.

3. Results and discussion

3.1. Characterization of the Carbon foam-Fe-Co catalyst

To compare the performance of the catalysts, the cyclic voltammograms (CV) of PA-NI, Carbon foam-Fe-Co and Pt-C in 0.1 M Na₂SO₄ electrolyte with O₂ were demonstrat-

ed in Fig 3. Accordingly, the Carbon foam-Fe-Co had better electrochemical activity than the PANI and Pt-C. Due to the loading of Pt is 10 wt% on activated carbon support, and the electrocatalytic activity of Pt-C is not as high as the catalyst with a high Pt content. Although the performance of Pt-C with greater content may be superior to the Carbon foam-Fe-Co, the limiting factor of the Pt loading is its cost, unlike the low-cost catalyst in this work. According to Fig.3, the reduction peak of Carbon foam-Fe-Co is much closer to the potential of the cathode in the MBR-MFC. Thus, the synthesized Carbon foam-Fe-Co catalyst was successfully effective for ORR in this system. The CV curve of PANI has two reduction peaks. However, the electricity generation in control test 1 is poor. This is caused by the poor electron transfer ability derived from the nonconductive nature of polyester filter cloth.

The XRD pattern is revealed in Fig.4, and the peaks were identified and assigned. The point at 29.88 ° was mostly C and graphitic carbon nitride materials (g-C₃N₄). The g-C₃N₄ can be formed and decomposed into various carbon nitride species with increasing temperature²³. Due to the direct involvement of carbon nitride species in the synthesis reaction, the metals in the catalyst existed in various forms. These highly active species can firstly reduce metal oxide into elemental metal during preparation $(4C_3N_4+3Fe_3O_4 \rightarrow 9Fe+8N_2+12CO, 4C_3N_4+3Co_3O_4 \rightarrow 9Co+8N_2+12CO)$. Finally, these metal atoms may further react with carbon nitride species to form metal carbide or metal nitride $(C_3N_4+9Fe\rightarrow 3Fe_3C+2N_2)$. Most of the Fe₃C, Fe₃N $(2\theta = 82.26)$ and Co₃C are decomposed to Fe, Co and C, N at over 750°C $(Fe_3C \rightarrow 3Fe+C)^{23}$. Accordingly, Fe and Co were the main components in the catalyst. The catalyst contains a strong and narrow diffraction peak at 20 of 44.63 °(Fe, Fe₃O₄, Co). There were also trace amounts of FeCo (20 = 35.46 °, 43.17 and 64.56 °), α -Fe₂O₃ (2θ = 33. 6 °, 35.46 °) and Fe₃O₄ (2θ = 64.56 °) residual in this catalyst. Different valence states of Fe and Co in the catalyst increase the activity of the Carbon foam-Fe-Co catalyst.

In Fig.5 (HR-TEM, a-d), the present nanoparticles and nanosheets structures were manifested. The carbon foam carbonized from melamine foam has many pores and reticular structures. Fe and Co species react and grow on it. Therefore, the metallic nanoparticles were dispersed in C nanosheets (Fig. 5a). This improves the dispersion and the surface area of the catalyst. PANI in-situ polymerized and deposited onto carbon foam, forming a thin film (Fig. 5b). In Fig. 5c, the core-shell structure of the carbon-encapsulated metallic nanoparticles, i.e. α-Fe₂O₃ (0.5419 nm) and bcc-Fe (0.2869 nm) was shown. The interlattice distances of the cores can be seen in Fig 5d, consistent with that of bcc-Fe (0.2869 nm) and fcc-Co (0.2146 nm). Metal-encapsulating had grown over the carbon particles. The atomic percentages of Fe, Co and C were provided in table 3. It further proved that the main ingredients in the catalyst were carbon, iron and cobalt.

3.2. Performances of the MBR-MFC system

As a result of the low diffusion rate of protons, the pH usually increased near the cathode²⁴. This problem was effectively avoided by the design of the anode chamber, which is a long and narrow opening that allowed liquid overflow at the top of the anode chamber. A continuous over-flow from the anode chambers to the cathode chambers enabled pH neutralization and the continuous operation of the reactor, leading to high stability in electricity generation.

3.2.1 Performance comparison of the Carbon foam-Fe-Co catalyst with no catalyst and Pt-C in MBR-MFC

By employing the Carbon foam-Fe-Co catalyst as the cathode coating, cell voltage with it (0.4 V, Fig. 6Aa) is enhanced evidently than without catalyst (0.2 V, Fig. 6B). This should be attributed to the coated Carbon foam-Fe-Co catalyst. The cell voltage increased from 0.4 V to 0.5 V after replacing sucrose with CH₃COONa as revealed in Fig. 6Ab. As the conductivity with CH₃COONa was 3.19 ms cm⁻¹ and it was 1.27 ms cm⁻¹ with sucrose. The higher the solution conductivity is, and the better the performance becomes. Therefore, this MBR-MFC reactor is more suitable for processing waste-water with higher conductivity, such as waste-water from electroplating industries or high salinity fields.

It was compared in the same reactor under the same experimental conditions. The cell voltage with the same amount of Pt-C (10 wt %) (Fig 6C) was inferior to Carbon foam-Fe-Co (Fig 6Ab) during operation. This non-noble catalyst with better performance is more suitable for application of the MBR-MFC system. The fluctuation of the potential (Carbon foam-Fe-Co and Pt-C) is because we found that twitching the cathode can improve electricity generated in the process of the experiment. However, when didn't twitch the cathode, the cell voltage of Carbon foam-Fe-Co and Pt-C is stable at ~0.4 V and ~0.3 V, respectively. Thus, both the catalysts and the reactor are stable in this system.

3.2.2. Cathode surface Morphology and Power density

The SEM of the cathode coated with catalyst and one merely coated with PANI is made known in Fig.7. The electrode coated with PANI had some nanoparticles adhered to the filter cloth. On the contrary, the cathode coated with Carbon foam-Fe-Co and Nafion/PVDF binder was some nanofilms with many small nanoparticles, which is more uniformly and more firmly adhered to the polyester filter. This was because of the binder of PVDF and Nafion. In this MBR-MFC system, the cell voltage was significantly improved when the cathode was coated with the catalyst.

The CE with catalyst (~78.90%) is larger than without it (~57.22%) and also a little better than with Pt-C (~71.66%). Power density and polarization curve were measured when the cell voltage became relatively stable in all stages. As summarized in Fig.8A and Fig.8B, the cathode coated with catalyst was much improved. The power density of cathode with Carbon foam-Fe-Co was 38.5 times and 2.4 times higher than the cathode made of only PANI modified filter cloth in control 1 and with Pt-C in control 2. The power density output with Carbon foam-Fe-Co was comparable to other MBR-MFC studies^{25, 26}. The conductivity of electrodes in these systems was better than the modified filter cloth used in this study. Nevertheless, they cost more and the power density was poorer than the achieved level with our modified filter cloth loaded with Carbon foam-Fe-Co. This can illustrate the excellent redox properties of the new catalyst. Current density of Carbon foam-Fe-Co was higher than in control groups. The resistance of the electrodes was measured by a standard four-point-probe method (Keithley 2401 source meter, American) with the distance of 1 cm. The resistance of filter cloth modified with PANI and further coated with catalyst was 506 Ω cm⁻¹ and 86 Ω cm⁻¹, respectively.

3.3. Waste-water treatment efficiency and the flux test in the MBR-MFC system

Throughout the tests, HRT was controlled at 5.5 ± 0.5 h and MLSS was 6-8 g L⁻¹. Fig.9 is the removal rate (RR) of COD, NH₄⁺-N, and NTU in this integrated system. The RR of NH₄⁺-N and NTU was 85% ± 2.5 % and 82.5% ± 2.5 %, respectively. The COD concentration in the influent was maintained at around 400 mg L⁻¹ when the simulated waste-water consisted mainly of sucrose. The average COD removal efficiency reached

95% \pm 2.5% in control 1, which was ahead of other MFC^{27, 28}. Compared with other MFC, the high removal rate is caused by the filtration of the cathode membrane in this MBR-MFC. However, when the main ingredient in simulate waste-water was changed to CH₃COONa, at COD 270 mg L⁻¹, and the COD RR decreased to 88% ± 2.5 %. This will be studied in the further research.

Flux of the modified filters with PANI (1), Carbon foam-Fe-Co (2) and Pt-C (3) was measured by testing with yeast (Zeta potential-12.9mV, size-7 µm) suspension, which was to simulate the condition in the MBR-MFC (Fig.S2). The flux of (1) is higher than (2) and (3), which indicates the decrease in pore size of the membrane modified with catalyst. It's better for purifying the waste-water. According to the results, the flux didn't change much in the two cycles, which indicates a good performance in flux recovery for the modified membrane. The flux of the PANI modified the filter is similar to Liu's 10, as the same polyester filter cloth was used (pore size 22µm). In this study, the filter is coated with catalyst and Nafion binder. Therefore, the pore size of the membranes is less than 5 μ m. According to the SEM (Fig.7), it is ~1 μ m.

3.4. Economic analysis

In Table 4, the market prices of related materials were given, with some small discrepancies between different companies. We can see the costs vary from ~5 times for the cathode material and ~100 times for the anode material, ~10 times for the membrane material and 10 times in the catalyst. This means that our developed system has great advantages and its electricity generation was higher than using Pt-C catalyst (1.589 \pm 0.453 mg cm⁻²) such as in reference²⁹.

Conclusions

An integrated MBR-MFC system was developed, which demonstrated favorable features in low-cost, with power generation and efficient waste-water treatment. Both anodes and cathodes are the PANI modified polyester filter membrane. After coating of Carbon foam-Fe-Co catalyst on the membrane cathode, the maximum power density increased 38.5 times. In addition, the studied membrane materials and catalysts were cost-effective, displaying high economic feasibility and practicability. Further, it is expected that the performance of MBR-MFC may be improved by enhancing the electrical conductivity of the electrode membrane.

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Notes and References

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Figures

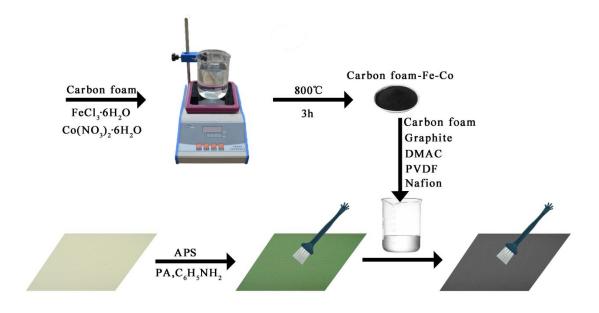


Fig.1 Preparation process of Carbon foam-Fe-Co catalyst and membrane electrode (Anode and control 1 without catalyst. Control 2: Carbon foam-Fe-Co instead of Pt-C).

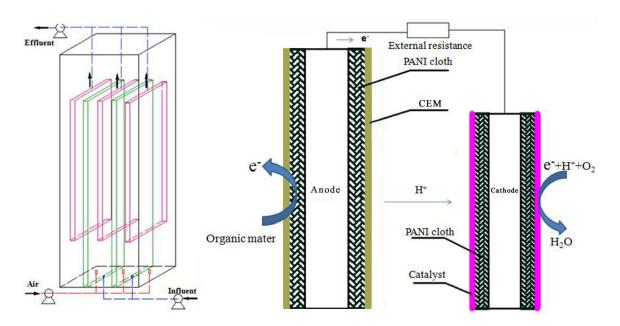


Fig.2A Schematic of the MBR-MFC integrated system. B. Mechanism and module electrode details in the MBR-MFC system.

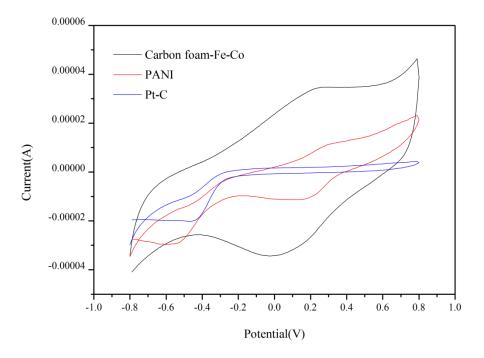


Fig.3 The Cyclic Voltammogram of different catalysts in 0.1 M Na₂SO₄ with O₂.

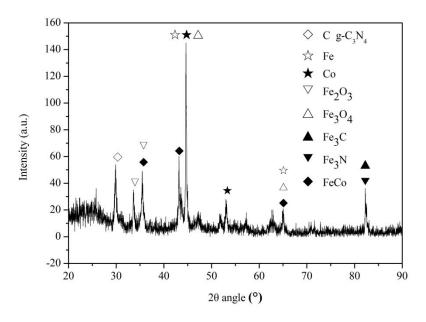


Fig.4 XRD pattern of Carbon foam-Fe-Co catalyst.

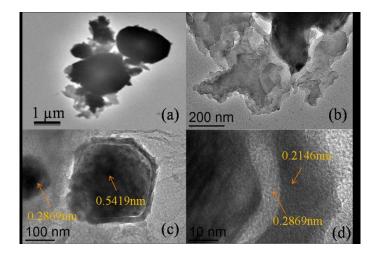


Fig.5 HRTEM images of Carbon foam-Fe-Co catalyst. (a. This sample is composed of nanoparticles and nanosheets. b. Nanoparticles are dispersed in the C nanosheets. c. Carbon-encapsulated metallic nanoparticle is core-shell structure, α -Fe₂O₃ (0.5419nm), bcc-Fe (0.2869 nm). d. The inter-lattice distance of the cores is consistent with that of bcc-Fe (0.2869 nm) and fcc-Co (0.2146 nm)).

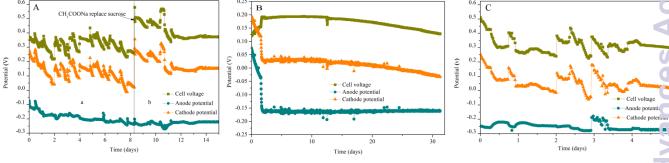


Fig.6 Cell voltage and electrode potentials

A (Cathode coated with Carbon foam-Fe-Co catalyst. a. Waste-water with sucrose and without CH₃COONa. b. Using CH₃COONa replaced sucrose.), B (Control 1, Cathode is PANI modified polyester filter), C (Control 2, Catalyst is Pt-C).

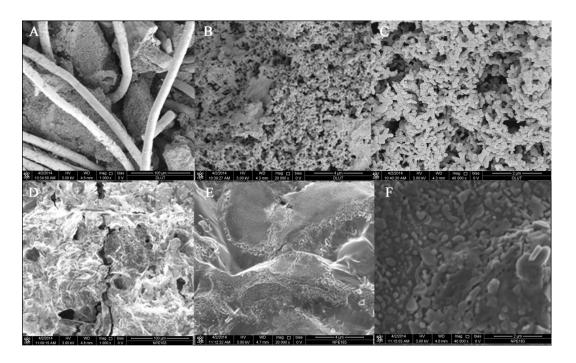


Fig.7 Comparison of the cathode coated with one merely covered with PANI (A, B, C) and Carbon foam-Fe-Co (D, E, F). (SEM)

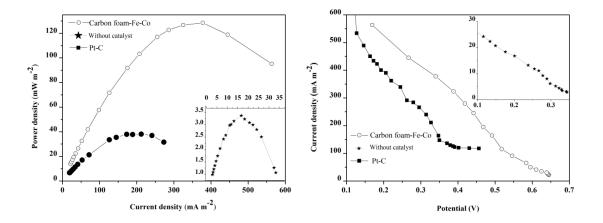


Fig.8 The contrast of power densities (A) and polarization curves (B).

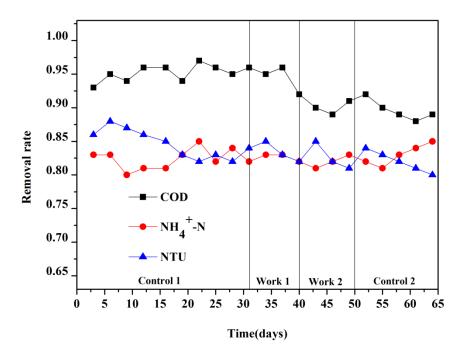


Fig.9 The removal efficiencies of COD, NH_4^+ -N and NTU in this integrated system.

Tables

Table 1 Compositions of simulated waste-water in each phase.

Stages	Sucrose	CH ₃ COONa	NH ₄ Cl	CaCl ₂	MgSO ₄	K_2HPO_4 (g L^{-1})	
Work (1)	0.4		0.06	0.005	0.01	0.015	
Work (2)		0.4	0.06	0.005	0.01	0.015	
Control 1	0.4		0.06	0.005	0.01	0.015	
Control 2		0.4	0.06	0.00	0.01	0.015	

Table 2 Different operational conditions in this system.

Stage	Work 1,2	Control 1	Control 2
Anode material	PANI Filter ^a	PANI Filter ^a	PANI Filter ^a
Cathode material	PANI Filter ^a	PANI Filter ^a	PANI Filter ^a
Catalyst	C -Fe-Co ^b without	Pt-C	
Ion exchange membrane	with	with	with
External resistance (Ω)	1000	1000	1000
Maximum power density (mW	·m ⁻²) 135	3.5	55.8

Note: ^a Polyaniline modified filter cloth ^bCarbon foam-Fe-Co

Table 3 EDS analysis of the Carbon foam-Fe-Co catalyst.

Element	Weight %	Atomic %	Uncertain %	Correction	k-Factor
С	30.48	67.42	0.97	0.28	3.685
N	0.00	0.00	100.00	0.28	3.536
Fe	49.48	23.53	0.68	0.99	1.357
Co	20.03	9.03	0.44	0.99	1.441

Table 4 Cost comparisons in conventional MBR-MFC and in this study.

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Component	other MBR/MFC	this system
Anode	Carbon cloth (E-Tek, 620 US \$ m ⁻²)	PANI Filter ^a (6 US\$ m ⁻²)
Cathode	Carbon fiber (30 US \$ m ⁻²)	PANI Filter ^a (6 US\$ m ⁻²)
Catalyst	Pt-C (10%, 36.16 US \$ g ⁻¹)	C foam-Fe-Co (3.5 US\$ g ⁻¹)
Ion exchange membrane	Nafion membranes (2500 US\$ m ⁻²)	CEM ^b (96.78 US\$ m ⁻²)
Filter membrane	MF or UF ^c (66 US \$ m ⁻²)	PANI Filter ^a (6 US \$ m ⁻²)

Note: ^a Polyaniline modified filter cloth bCation exchange membrane

^c Microfiltration or ultrafiltration membrane