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Bio-refractory pollutant removal using microbial electrochemical technologies: A short review

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Microbial electrochemical technologies (MET) is an interdisciplinary approach where microbes are used as bio-catalyst for the treatment of wastewater and generation of value-added products like electricity, biofuels etc. This technology is very robust and thus can also be used for the removal of bio-refractory substances from industrial wastewater. This short review presents gist of research demonstrating the use of this technology for the removal of recalcitrant pollutants from wastewater.

Keywords: Bio-refractory pollutants, microbial desalination, microbial electrochemical technologies, microbial fuel cell, microbial electrolysis.

Introduction

Removal of refractory compounds from wastewater has been a major concern for wastewater treatment facilities globally. Advanced wastewater treatment options are often costly such as advanced oxidation processes and electrochemical oxidation. Elimination of refractory organics from various industrial wastewaters is presently practiced by adsorption using activated charcoal or other adsorbents. However, this again levitates the problem of disposal of the contaminated adsorbents, and proper treatment and containment of such hazardous waste add on to the cost of the system. Application of microbial electrochemical technologies (MET) for the removal of the refractory organics is a sustainable proposition as it gives a scope of simultaneous treatment of wastewater and generates direct one-step bioelectricity¹. Basic MET technologies like microbial fuel cell (MFC) consist of a biotic anodic and an abiotic cathodic chamber separated by a proton exchange membrane. Protons generated in anodic chamber migrate to the cathode through proton exchange membrane and electrons are reducing anode and flows toward the cathode through an external circuit and generates bioelectricity. Electrons and protons are combined on the cathode to produce water (H₂O) or hydrogen peroxide (H₂O₂) by following four or two electron oxygen reduction reaction (ORR) pathway, respectively.

In the case of MFC, bio-refractory pollutants can be

anaerobically oxidized in the anodic chamber², and auto-generated H₂O₂ in the cathodic chamber can also be utilized for efficient removal of biorefractory pollutants and simultaneous electricity generation. MET setups have been configured for simultaneously utilizing the anaerobic degradation in the anodic chamber and the cathodic reduction of the refractory organics, thus giving a two-fold removal effect³. Anodic biodegradation of refractory organics occurs through microbial metabolism coupled with the synergistic effect of the anodic oxidation. Bacterial strains such as *Stenotrophomonas*⁴, *Chryseobacterium*⁵, *Advenella*⁶, *Azoarcus*⁷ and *Corynebacterium*⁸ have been identified as few of predominant microbial consortia, which thrives on the anodic surface. However, the breakdown of such refractory organics often has to be assisted by co-substrates metabolism, which renders the microorganisms the energy for the hydrolysis of these refractory compounds. The detailed degradation pathway varies for each refractory organics and further research is required in this area. Cathodic removal of xenobiotics occurs primarily by coupling the Fenton process with MET⁹ or by the production of H₂O₂¹⁰, which becomes a source of hydroxyl free radical or by hybrid photo catalysis-MET¹¹.

Production of H₂O₂ can be enhanced by applying high partial pressure of O₂ to the active reaction sites and 7% by wt. H₂O₂ could be produced continuously at a rate of 8.3 L h⁻¹ m⁻² cathode surface area in the cathodic chamber of

MFC¹². Few ORR catalysts like Pd, Ni-Pd nanocatalyst, have high selectivity for H₂O₂ production and may be suitable for application in MFC, but further investigations are necessary for this regards¹³. Instead of bioelectricity generation, application of external potential can enhance the yield of H₂O₂ in a microbial electrolysis cell (MEC). Application of 0.5 V (vs standard hydrogen electrode) external voltage was capable of producing 1.9±0.2 kg H₂O₂ m⁻³ day⁻¹ from acetate with an acetate conversion efficiency of 83.1±4.8%¹⁴.

Anodic oxidation of bio-refractory compounds

The MET was observed as a prominent technology compared to anaerobic digestion and several refractory compounds removal was demonstrated during anaerobic oxidation of organics. Based on a study by Jeffrey M. Morris, MFC was found to be an excellent technology for degradation of petrochemical hydrocarbon¹⁵ and diesel¹⁶. Approximately, 82% of hydrocarbons removal efficiency was reported within 21 days of retention time, which was roughly 2.5 times higher compared with the anaerobically incubated control cell (31%) and simultaneously 31 mW m⁻² of power was generated by MFC. Another study performed by Thi Hiep Han resulted in 98% methylene blue degradation within five hours using gold nanoparticle cathode catalyst and hydrogen peroxide as catholyte¹⁷. Bioelectrochemical degradation of highly concentrated pyridine (500 mg L⁻¹) up to the efficiency of 95% was observed within 24 h in MFC¹⁸. Significant success was observed during polycyclic aromatic hydrocarbons removal using bioelectrochemical technology in sediment microbial fuel cell (SMFC)¹⁹. Microcystins, a toxin produced by Blue-green algae (cyanobacteria), was also proved to be an excellent substrate and can be bioelectrochemically degraded in the anodic chamber of MFC²⁰. MET has a potential to be an excellent technology for biological degradation of toluene, which can be used as sole carbon source for bioelectrochemical anodic oxidation of the same. Almost 70 mg L⁻¹ toluene was completely degraded within 60 h with simultaneous power production of 2 mW m⁻² with respect to the electrode surface area²¹.

Hybrid MET system for cathodic degradation of refractory compounds

Efficient refractory compound degradation can also be achieved in the cathodic chamber of MFC by hybridization of advanced oxidation process with MFCs and a lot of studies

have been performed in this hybrid system. Combining the Fenton process with MFC technology, commonly known as bioelectro-Fenton (BEF), has also been applied for the removal of refractory compounds by various researchers²². Refractory pollutants removal efficiency using BEF and other MFC-Advanced oxidation process are listed in Table 1.

Table 1. Cathodic removal of refractory pollutants

Pollutant	HRT (h)	Removal (%)	Reference
Rhodamine B	12	95	22
Orange II	14	100	23
Bisphenol A	24	73	24
Estrone	24	100	24
Sulfamethazine	24	100	24
Triclocarban	24	99	24
Sulfanilamide	96	90	25
Phenol	6	95	26
Triphenyltin chloride (TPTC)	80	78	27
Amaranth	1	76	28
Metoprolol	97	100	9
Carbamazepine	24	90	29
Paracetamol	9	70	30
Methylene blue	360	83	31
Aniline	144	97	32
LG, CV, IC RB5	0.25 each	98, 96, 97, 88	33

LG – Lissamine green B, CV – Crystal violet, IC – Indigo Carmine, RB5 – Reactive Black 5.

Removal of refractory compounds in MEC and microbial desalination cell

Both, MEC and microbial desalination cell (MDC) have been commendably applied for the elimination of bio-refractory substances from wastewater. The use of these microbial electrochemical technologies has an added advantage of recovery of bioelectricity and other valuables in the process. Also, the use of biocatalysts reduces the fabrication cost of the setup in comparison with the expensive metal-based catalysts. Generally in MEC, an external potential is imposed on the cathode to accelerate the degradation of these toxic compounds. On the other hand for MDC, heavy metals are concomitantly removed with salinity by the passage of cations through cation exchange membrane separating the saline chamber and desalination chamber.

The use of biocathode for ca. 94% removal of azo dye using an applied potential of -0.2 to -0.8 V vs Ag/AgCl was

reported by Yang *et al.*³⁴. It was also found that the increase in DO concentration in the catholyte negatively affected dye removal. Also, the biofilm formed on the cathode negatively affected azo dye removal. Alizarin Yellow R is another azo dye, which was also successfully removed by more than 97% with the application of up-flow bioelectro-catalyzed electrolysis reactor³⁵. In the same study, it was also found that decolorization efficiency was directly related to the size of the cathode, which would be a major factor dictating the field-scale applicability of the technology. However on the other hand, increase in the size of cathode did not proportionately increase the current due overpotential losses. Heavy metals like copper, zinc and lead have also been removed from fly ash leachate using bioelectrochemical system³⁶. Metals like Cu were spontaneously recovered in the cathodic chamber leading to power production, but Zn and Pb required the application of imposed potential for reduction in the electrolysis reactors.

Various heavy metals like Cr, Pb etc. have been reported to be removed successfully using MDCs³⁷. In this study, ozone was used as an electron acceptor for the removal of heavy metals and its efficacy was compared to that of oxygen as an electron acceptor. The use of ozone demonstrated both higher removal efficiency of Cr and Pb and power density in MDCs, when compared to oxygen as electron acceptor. Also, stable current profiles were obtained when ozone was used as an electron acceptor, thus emphasizing the fact that ozone can be successfully used as the electron acceptor for improved power generation and heavy metals removal in MDCs. Simultaneous removal of salt, sulphate and organic matter in the form of acetate was effectively removed by employing MDC, thus elucidating the multifaceted decontaminability potential of this novel technology³⁸. COD removal and sulphate removal efficiencies of 88% and 72%, respectively, were obtained in the MDCs and also demonstrated stable current generation in the process. Bioelectro-Fenton process was used to produce H_2O_2 following two electron pathway in MDCs, which concomitantly degraded methylene blue³⁹. Also, the maximum power density of 566 mW m^{-3} was obtained, when anolyte was recirculated to the cathodic chamber to counter pH imbalance in comparison to the power density of 267 mW m^{-3} for MDC without recirculation. Biological removal of phenol in MDC using the pure culture of *Pseudomonas aeruginosa* and mixed anaerobic consortia, and concurrent 75% desalination of industrial wastewater in

72 h of reaction time was demonstrated by Pradhan *et al.*⁴⁰. Thus from the above studies, it can be said that MDC and MEC can be proficiently used for the removal of refractory substances from industrial wastewater.

Removal of metals

Removal and recovery of metals from industrial effluents have been targeted using different pathways such as anodic removal⁴¹, electrochemical reduction at cathode and uptake of metals by microbes present on biocathode. Cathodic reduction of Cr^{6+} (100 mg L^{-1}), which is found in high concentrations in effluent from electroplating and leather industries, using MET was achieved in 150 h with a maximum power density of 150 mW m^{-2} ⁴². The study was conducted with real field electroplating wastewater and 99.5% removal of hexavalent chromium was achieved. Use of MFC for the removal of V^{5+} (500 mg L^{-1}) at the cathode yielded a removal efficiency of 25.3%⁴³. The system had a HRT of 72 h. Removal of Cu (1000 mg L^{-1}) in the cathodic chamber of MFC was achieved in eight days, and the power density was observed to decrease once the copper concentration depleted⁴⁴. The MFC was operated by maintaining anaerobic conditions in cathodic chamber by flushing N_2 in the first stage of operation. Copper recovery in terms of charge utilized for the quantity of Cu^{2+} reduced, normalized in terms of the current generated, was reported as 84% in this anaerobic stage. In the second stage, the removal of Cu^{2+} was evaluated with the same cathode configuration however exposed to oxygen, resulting in a dissolved oxygen concentration of 6.5 mg L^{-1} . In this aerobic stage, the presence of oxygen as a competitive cathodic electron acceptor reduced the Cu^{2+} reduction efficiency. The Cu recovery efficiency was reported to be 43% in this aerobic stage with respect to the current generated.

Concomitant H_2 evolution and Co^{2+} recovery in the form of pure cobalt was reported at cathode at an applied voltage of 0.3–0.5 V in a MEC. The yield was reported to be $0.81\text{ mol Co mol}^{-1}\text{ COD}$ and $1.21\text{--}1.49\text{ mol H}_2\text{ per mol COD}$ with this applied voltage⁴⁵. Recovery of Ni^{2+} from the system was reported to be 99 to 33% efficient for a concentration range of 50 to 1000 mg L^{-1} . The removal of Ni was affected by the mass transport limitations at the higher concentrations. Effect of increasing the potential was pronounced on the recovery of Ni^{2+} , and the removal efficiency was found to increase from 51 to 67% while increasing the voltage from 0.5

to 1.1 V⁴⁶. Recovery of Cd²⁺ from the system was augmented by the supply of power from another MFC reducing Cr⁶⁺ at the cathode. It was observed that the composite Cr-MFC and Cd-MEC system was able to remove 93.4, 93.3 and 89.7% of Cd while using a feed concentrations of 50, 100 and 200 mg L⁻¹ during 60 h of detention time⁴⁷.

Conclusion

Removal of refractory organics and emerging contaminants from industrial effluents using the MET is a sustainable proposition as discussed in this review paper. Concomitant removal of refractory organics, possibility of recovery of metals with electricity production, which can be used onsite, make MET a prime choice for treatment of industrial effluents.

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References

- B. E. Logan, B. Hamelers, R. Rozendal, U. Schröder, J. Keller, S. Freguia, P. Aelterman, W. Verstraete and K. Rabaey, *Environ. Sci. Technol.*, 2006, **40(17)**, 5181.
- X. Xu, J. Shao, M. Li, K. Gao, J. Jin and L. Zhu, *Bioresour. Technol.*, 2016, **218**, 1037.
- H. Zhao and C. H. Kong, *Bioresour. Technol.*, 2018, **258**, 227.
- R. P. Ryan, S. Monchy, M. Cardinale, S. Taghavi, L. Crossman, M. B. Avison, G. Berg, D. Van Der Lelie and J. M. Dow, *Nat. Rev. Microbiol.*, 2009, **7(7)**, 514.
- T. Nishioka, M. M. Elsharkawy, H. Suga, K. Kageyama, M. Hyakumachi and M. Shimizu, *Microbes. Environment.*, 2016, **31(2)**, 104.
- E. Xenofontos, A. M. Tanase, I. Stoica and I. Vyrides, *New. Biotechnol.*, 2016, **33(2)**, 305.
- Z. Martín-Moldes, B. Blázquez, C. Baraquet, C. S. Harwood, M. T. Zamarro and E. Díaz, *P. Natl. Acad. Sci. USA*, 2016, **113(46)**, 13174.
- R. Gurav, H. Lyu, J. Ma, J. Tang, Q. Liu and H. Zhang, *Environ. Sci. Pollut. R.*, 2017, **24(12)**, 11392.
- H. Olvera-Vargas, T. Cocerva, N. Oturan, D. Buisson and M. A. Oturan, *J. Hazard. Mater.*, 2016, **319**, 13.
- R. A. Rozendal, E. Leone, J. Keller and K. Rabaey, *Electrochem. Commun.*, 2009, **11(9)**, 1752.
- Y. Hou, R. Zhang, Z. Yu, L. Huang, Y. Liu and Z. Zhou, *Bioresour. Technol.*, 2017, **224**, 63.
- I. Yamanaka, T. Onizawa, S. Takenaka and K. Otsuka, *Angew. Chem-Ger. Edit.*, 2003, **115(31)**, 3781.
- S. Maity and M. Eswaramoorthy, *J. Mater. Chem. A*, 2016, **4(9)**, 3233.
- R. A. Rozendal, E. Leone, J. Keller and K. Rabaey, *Electrochem. Commun.*, 2009, **11(9)**, 1752.
- J. M. Morris and S. Jin, *J. Environ. Sci. Heal. A*, 2007, **43(1)**, 18.
- J. M. Morris, S. Jin, B. Crimi and A. Pruden, *Chem. Eng. J.*, 2009, **146(2)**, 161.
- T. H. Han, M. M. Khan, S. Kalathil, J. Lee and M. H. Cho, *Ind. Eng. Chem. Res.*, 2013, **52(24)**, 8174.
- C. Zhang, M. Li, G. Liu, H. Luo and R. Zhang, *J. Hazard. Mater.*, 2009, **172(1)**, 465.
- Z. Yan, N. Song, H. Cai, J. H. Tay and H. Jiang, *J. Hazard. Mater.*, 2012, **199**, 217.
- Y. Yuan, Q. Chen, S. Zhou, L. Zhuang and P. Hu, *J. Hazard. Mater.*, 2011, **187(1-3)**, 591.
- C. W. Lin, C. H. Wu, Y. H. Chiu and S. L. Tsai, *Fuel*, 2014, **125**, 30.
- L. Zhuang, S. Zhou, Y. Yuan, M. Liu and Y. Wang, *Chem. Eng. J.*, 2010, **163(1-2)**, 160.
- C. H. Feng, F. B. Li, H. J. Mai and X. Z. Li, *Environ. Sci. Technol.*, 2010, **44(5)**, 1875.
- Y. Wang, C. Feng, Y. Li, J. Gao and C. P. Yu, *Chem. Eng. J.*, 2017, **307**, 679.
- W. Guo, H. Song, L. Zhou and J. Sun, *Desalin. Water Treat.*, 2016, **57(52)**, 24982.
- X. Zhu and B. E. Logan, *J. Hazard. Mater.*, 2013, **252**, 198.
- X. Y. Yong, D. Y. Gu, Y. D. Wu, Z. Y. Yan, J. Zhou, X. Y. Wu, P. Wei, H. H. Jia, T. Zheng and Y. C. Yong, *J. Hazard. Mater.*, 2017, **324**, 178.
- L. Fu, S. J. You, G. Q. Zhang, F. L. Yang and X. H. Fang, *Chem. Eng. J.*, 2010, **160(1)**, 164.
- W. Wang, Y. Lu, H. Luo, G. Liu, R. Zhang and S. Jin, *Water Res.*, 2018, **139**, 58.
- L. Zhang, X. Yin and S. F. Y. Li, *Chem. Eng. J.*, 2015, **276**, 185.
- G. Huang, H. Wang, H. Zhao, P. Wu and Q. Yan, *J. Power Sources*, 2018, **400**, 350.
- X. Li, X. Jin, N. Zhao, I. Angelidaki and Y. Zhang, *Water Res.*, 2017, **119**, 67.
- M. F. de Dios, O. Iglesias, E. Bocos, M. Pazos and M. A. Sanromán, *J. Ind. Eng. Chem.*, 2014, **20(5)**, 3754.
- H. Y. Yang, C. S. He, L. Li, J. Zhang, J. Y. Shen, Y. Mu and H. Q. Yu, *Sci. Rep.*, 2016, **6**, 27243.
- D. Cui, Y. Q. Guo, H. S. Lee, H. Y. Cheng, B. Liang, F. Y. Kong, Y. Z. Wang, L. P. Huang, M. Y. Xu and A. J. Wang, *Chem. Eng. J.*, 2014, **243**, 355.
- H. C. Tao, T. Lei, G. Shi, X. N. Sun, X. Y. Wei, L. J. Zhang and W. M. Wu, *J. Hazard. Mater.*, 2014, **264**, 1.

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37. A. Gholizadeh, M. H. Salmani, A. A. Ebrahimi, S. S. Hosseini, M. H. Ehrampoush, M. Miri, A. Nikoonahad and H. Pasalari, *Environ. Chem. Lett.*, 2018, **16(4)**, 1477.
38. T. Jafary, W. R. W. Daud, S. A. Aljilil, A. F. Ismail, A. Al-Mamun, M. S. Baawain and M. Ghasemi, *Desalination*, 2018, **445**, 204.
39. G. Huang, H. Wang, H. Zhao, P. Wu and Q. Yan, *J. Power Sources*, 2018, **400**, 350.
40. H. Pradhan, S. C. Jain and M. M. Ghangrekar, *Appl. Biochem. Biotech.*, 2015, **177(8)**, 1638.
41. O. Modin, X. Wang, X. Wu, S. Rauch and K. K. Fedje, *J. Hazard. Mater.*, 2012, **235**, 291.
42. G. Wang, L. Huang and Y. Zhang, *Biotechnol. Lett.*, 2008, **30(11)**, 1959.
43. B. Zhang, H. Zhao, C. Shi, S. Zhou and J. Ni, *J. Chem. Technol. Biot.*, 2009, **84(12)**, 1780.
44. A. T. Heijne, F. Liu, R. V. D. Weijden, J. Weijma, C. J. Buisman and H. V. Hamelers, *Environ. Sci. Technol.*, 2010, **44(11)**, 4376.
45. L. Jiang, L. Huang and Y. Sun, *Int. J. Hydrog. Energy*, 2014, **39(2)**, 654.
46. B. Qin, H. Luo, G. Liu, R. Zhang, S. Chen, Y. Hou and Y. Luo, *Bioresource. Technol.*, 2012, **121**, 458.
47. C. Choi, N. Hu and B. Lim, *Bioresource. Technol.*, 2014, **170**, 361.