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Nutrient removal and recovery from wastewater by microbial fuel cell-based systems – A review

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ABSTRACT

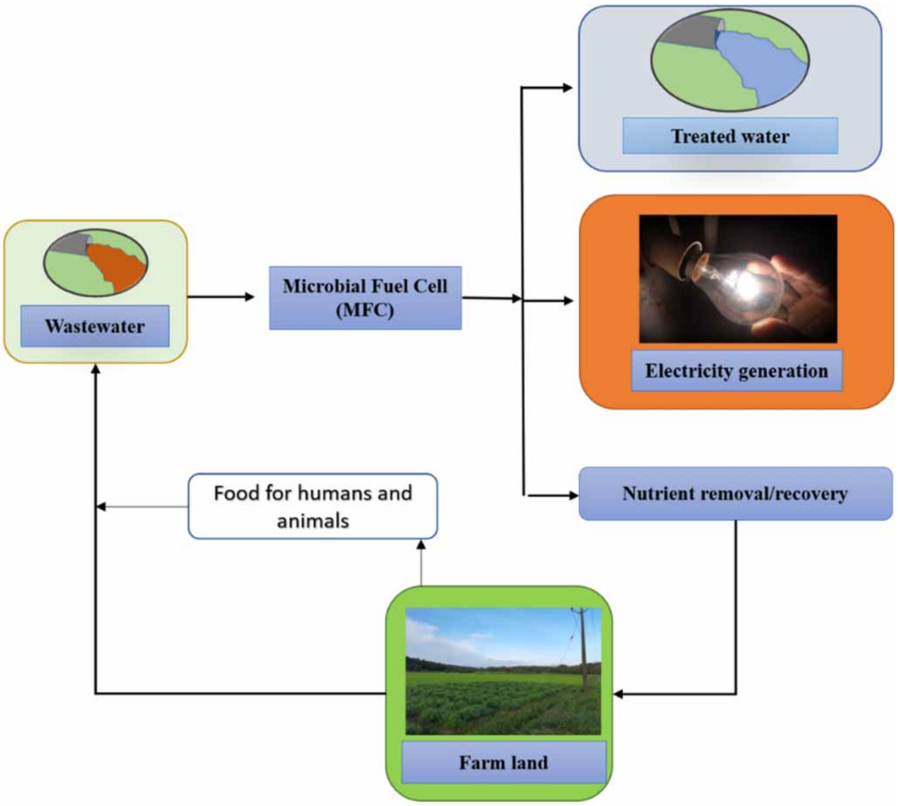
Microbial fuel cell (MFC) is a green innovative technology that can be employed for nutrient removal/recovery as well as for energy production from wastewater. This paper summarizes the recent advances in the use of MFCs for nutrient removal/recovery. Different configurations of MFCs used for nutrient removal are first described. Different types of nutrient removal/recovery mechanisms such as precipitation, biological uptake by microalgae, nitrification, denitrification and ammonia stripping occurring in MFCs are discussed. Recovery of nutrients as struvite or cattiite by precipitation, as microalgal biomass and as ammonium salts are common. This review shows that while higher nutrient removal/recovery is possible with MFCs and their modifications compared to other techniques as indicated by many laboratory studies, field-scale studies and optimization of operational parameters are needed to develop efficient MFCs for nutrient removal and recovery and electricity generation from different types of wastewaters.

Key words: biological assimilation, electricity generation, microbial fuel cell, nutrient removal/recovery, struvite

HIGHLIGHTS

- Several different configurations of MFCs are available for nutrient removal/recovery.
- In MFCs nutrients are removed by a number of different mechanisms.
- Nutrient can be recovered from a variety of wastewaters with MFCs.
- Optimization of operating parameters and more field scale studies are required.

GRAPHICAL ABSTRACT



1. INTRODUCTION

The human population is struggling hard to meet their energy, freshwater and food requirements, and the water-energy-food nexus has now become an important topic of discussion (Wicaksono *et al.* 2017). The world is facing a serious energy crisis as the supply of conventional energy sources are not adequate to meet the needs of the entire human population. The increased use of conventional energy resources results in the emission of greenhouse gases causing climatic changes. Therefore, attempts to develop renewable energy resources and to reduce carbon footprint have gained momentum in recent years (Gielen *et al.* 2019). Similarly, the water crisis is another major problem that is faced by human beings. Wastewater treatment and reuse can rejuvenate the depleting water resources. However, most of the conventional wastewater treatment plants (WWTPs) are energy-consuming facilities that employ energy-intensive techniques (Tao & Chengwen 2012; Negi & Chandel 2021). It has been reported that the consumption of electrical energy in WWTPs in developed countries is about 3–5% of total electricity demand (Ye *et al.* 2019a). Wastewater can be considered as a renewable resource of water, energy and nutrients (Huang *et al.* 2011; Do *et al.* 2018). These nutrients recovered from wastewater can be used as a source to enhance agricultural production, thus reducing wastewater treatment costs (Yetilmezsoy *et al.* 2017; Ye *et al.* 2020b). Treating wastewater and recovering resources and energy can be adopted as a sustainable model in this scenario (Mohammed & Ismail 2018).

Wastewater can be treated using a variety of biological, physiochemical and membrane processes. Even though anaerobic technologies such as up-flow anaerobic sludge blanket can generate electricity by utilizing the methane produced during the process, their conversion efficiency is very low. A microbial fuel cell (MFC) is a system that uses electrodes and an ion exchange membrane (IEM) to generate electricity by utilizing the electrons produced during the metabolic activities of microorganisms. MFCs can be implemented in WWTPs simultaneously to treat the water and to generate electricity, which can solve water crisis and reduce the consumption of energy for wastewater treatment. During the oxidation of organic matter in the anode chamber of an MFC, electrons are transferred to the anode by an extracellular electron transfer mechanism in microorganisms (Sharma *et al.* 2021). Thus, MFC can be a suitable method of treatment where there is a power supply shortage. Wastewater can be added as a substrate in the anode chamber where microbial degradation and electron generation take place. Further, use of microalgae in the cathode chamber will help in CO_2 sequestration, harvesting value-added products, and reducing the aeration cost in the cathode chamber (Wang *et al.* 2010). MFCs have been investigated for organic matter removal, removal and recovery of heavy metals and nutrients, sulphide removal and dye removal from various types of wastewaters (Yadav *et al.* 2012; Varanasi *et al.* 2015; Chen *et al.* 2019; Ye *et al.* 2019c; Singh & Kaushik 2021).

The increase in the population has resulted in an increased demand for food production, which in turn increased the demand for constant fertilizer supply (Sun *et al.* 2018; Patel *et al.* 2020). Phosphate is a non-renewable resource that is mainly derived from phosphate-based rocks that can only serve the market demand for the next 50–100 years, while ammonium is commercially produced by energy-intensive Haber–Bosch process (Ye *et al.* 2019c). Elevated levels of nitrogen and phosphorus are present in different types of wastewaters including municipal wastewater, swine wastewater, dairy wastewater, beverage wastewater, and coke wastewater (Kumar & Pal 2015). The higher concentrations of nitrogen and phosphorus in the aquatic environment can cause eutrophication and related problems (Yetilmezsoy *et al.* 2017). As phosphate and nitrogen are essential for the growth of food crops, recovering them from wastewater has a crucial economic and environmental impact and is a sustainable approach (Santos & Pires 2018). Chemical processes like precipitation and adsorption, biological uptake by living organisms and membrane systems are generally used for nutrient recovery from wastewater (Ye *et al.* 2020b).

Phosphate recovery from sludge formed from biological treatment is banned in several countries because recovered phosphate may contain pathogens and heavy metals (Ye *et al.* 2020a). Magnesium ammonium phosphate, also known as struvite is extensively used as a fertilizer in soil of low pH (Tao *et al.* 2015). Struvite recovery from wastewater by conventional precipitation method requires additional chemicals that increases the cost, while recovery by adsorption process requires desorption, which results in additional complexity and cost (Ye *et al.* 2020a). If phosphate alone is present, it can be precipitated by the addition of magnesium as cattiite (Hirooka & Ichihashi 2013). Ammonia can be recovered by air stripping and adsorption of volatile ammonia into acid solutions (Ye *et al.* 2018). Membrane technologies such as forward osmosis, membrane distillation, and electrodialysis are also being investigated for nutrient recovery (Ye *et al.* 2020a).

MFCs are now considered a promising technology to recover nutrients from wastewater along with the generation of electricity (Al-Mamun *et al.* 2017; Mukherjee *et al.* 2021). Applying aeration in cathode chambers is considered beneficial as it increases oxygen availability in the cathode chamber, leading to more hydroxyl production resulting in an alkaline pH, which helps in precipitation of struvite without the addition of chemicals (Ye *et al.* 2019c). Phosphate is partly removed by microbial absorption during their growth, and ammonium accumulated in the cathode chamber by diffusion caused by concentration gradients and migration by current field generation is precipitated along with phosphate (Ye *et al.* 2019c). Therefore, MFC can be regarded as a feasible approach for nutrient removal and can simultaneously convert the energy stored in chemical bonds of organic compounds to electricity (Tao *et al.* 2015). The microalgal-based photosynthetic MFCs are also getting increased attention as they can assimilate nutrients into algal biomass, which can be used for downstream biodiesel production, CO_2 sequestration, and the recovery of other value-added products (Wang *et al.* 2019a; Arun *et al.* 2020). Oxygen produced by these microalgae acts as an electron acceptor in the cathode chamber and saves the cost of mechanical aeration (Arun *et al.* 2020).

The application of MFCs over other technologies has advantages such as lower sludge production compared to other aerobic and anaerobic technologies, and direct generation of electricity by providing an external circuit (Asai *et al.* 2017). Lower power density and higher operating costs are the major constraints that limit its application on a larger scale (He *et al.* 2017). Aeration cost in the cathodic compartment is a major issue that needs to be solved. Integration of MFCs with various other existing techniques may be a suitable approach to overcome these drawbacks. For example, decolorization of about 98% was reported by a novel MFCs coupled with a peroxicoagulation system (Jayashree *et al.* 2019). The energy generated from MFCs can make them a neutral or positive energy system (Ye *et al.* 2019c). The study conducted by Rahimnejad *et al.* (2012) demonstrated that stack arrangement of MFC was able to produce current required for 10 LED lamps and a digital clock. The scaled-up models can produce more current, which may reduce the energy required for aeration in the case of dual-chamber MFCs. In hybrid systems, MFCs have been explored widely as biosensors for *in situ* detection of BOD, metals and toxicity (Tan *et al.* 2021).

Some studies have been reported in the literature in recent years on the use of different configurations of MFCs for nutrient removal from wastewater. Although a few review papers have been published on the application of MFCs for wastewater treatment (He *et al.* 2017; Saravanan *et al.* 2021; Verma *et al.* 2021) and nutrient recovery (Kelly & He 2014; Paucar & Sato 2021), a review report focusing exclusively on nutrient removal using MFCs and their modifications is missing in the literature. This review focuses on nutrient removal and recovery using the emerging technology of MFCs. The paper first discusses the different configurations available for MFCs. Mechanisms of nitrogen and phosphorus removal in MFCs are then described. In an MFC, nutrient removal is affected by different parameters and these parameters are discussed next. Finally, challenges of this technology for nutrient removal and the future research needs are presented.

2. COMPONENTS AND CONFIGURATIONS OF MFCS FOR NUTRIENT REMOVAL

MFCs are bio-electrochemical systems in which the microbes transfer electrons produced in the anode chamber by oxidizing the organic substrate to the anode via an extracellular electron transfer mechanism generating electron flow through the external circuit, which is utilized to reduce oxygen to water in the cathode chamber (Zhang *et al.* 2014; Jaiswal *et al.* 2020). According to the application and arrangement of the components, there are different types of MFCs and these are discussed in this section.

2.1. Components of MFC

In general, MFCs consist of an anode and a cathode in one chamber or in separate chambers. Usually, an IEM is used to separate the two chambers (Huang *et al.* 2011; Zinadini *et al.* 2017). A schematic diagram of a dual-chamber MFC is presented in Figure 1.

An anode chamber is a critical component of MFCs where oxidation of the organic compound takes place along with electron transfer from microbial cells to the anode electrode (Ieropoulos *et al.* 2005). Therefore, this chamber can be described as the heart of the MFC (Jaiswal *et al.* 2020). The anode chamber consists of an anode substrate, electrodes, and microbial culture. Organic matter is mainly removed in this chamber along with electricity generation, sulphate reduction, fermentation and methanogenesis (Wang *et al.* 2019a). The chemical reaction that takes place for a simple organic molecule containing carbon, hydrogen and oxygen is given below:

$$\text{Organics} \rightarrow CO_2 + H^+(\text{ to cathode chamber via IEM}) + e^- \text{ (to cathode via external circuit)}$$

The wastewater is added to the anodic chamber as a substrate, which is degraded by the microorganisms to simpler molecules. The electrons produced by these microorganisms are then flowed through an anode electrode to cathode generating electricity (Huang *et al.* 2011). In the early development stage of MFC, mediators were used in the anode chamber where bacterial species do not readily release electrons, but now this has become outdated following the discovery of electroactive bacteria (Ieropoulos *et al.* 2005; Ieropoulos *et al.* 2008). Redox mediators help in transferring electrons from within the microbial cell to electrodes. They can be either internally produced or externally applied. Generally, non-metallic materials, such as graphite rods, carbon paper, and carbon cloth, are used as the anode. Materials having characteristics such as low

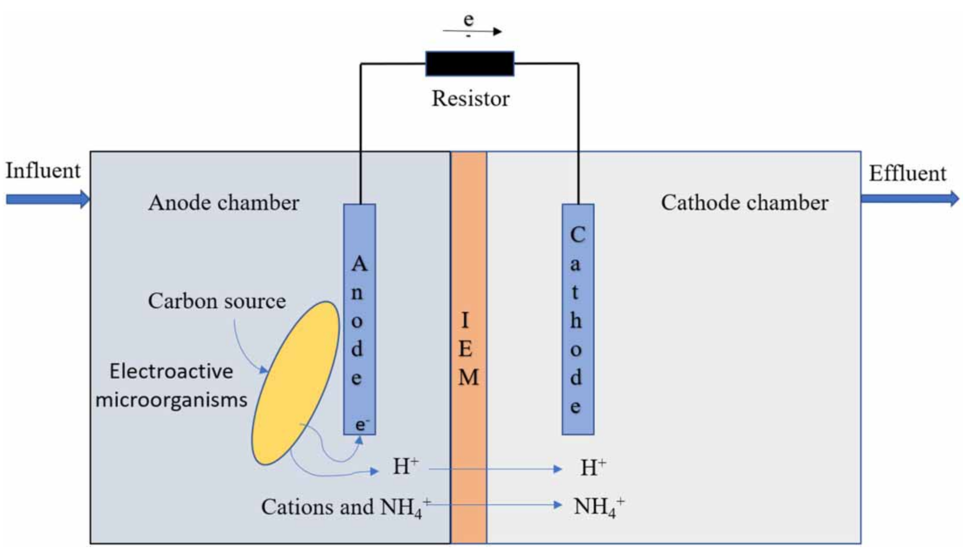


Figure 1 | Components of a dual-chamber microbial fuel cell.

cost, high stability, high conductivity, low resistance and biocompatibility are generally considered for use as electrodes (Kusmayadi *et al.* 2020). Therefore, anode material, substrate characteristics, microbial species, and the electron transfer mechanism to the anode are the main factors that influence the overall efficiency of the system.

The electrons that are transferred from the anode are received by an electrode in the cathode chamber and the electron is taken by the electron acceptor in the cathode chamber completing the electron cycle. The cathode chamber acts as proton/cation receiver in a dual-chamber MFC (Jaiswal *et al.* 2020). The general reaction that occurs in cathode is given below:

$$O_2 + H^+ \text{ (via IEM)} + e^- \text{ (via external circuit)} \rightarrow H_2O$$

External aeration or an aqueous solution containing dissolved oxygen or any other electron acceptor is generally provided in the cathode chamber. In a single-chamber MFC, the air cathode acts as an electron acceptor. Carbon cloth, graphite fiber brush, and a mesh of carbon or stainless steel can be used as cathode. Cathode electrodes are usually coated with platinum or other catalyst to improve the oxygen reduction reaction (Mustakeem 2015).

A conventional dual-chambered MFC has two compartments that are separated by an IEM. A cation exchange membrane (CEM) (also known as a proton exchange membrane (PEM)) is used as an IEM. The CEM facilitates the transfer of protons and cations at high concentrations from anode chamber to cathode chamber, which helps nutrient recovery through precipitation (Rozendal *et al.* 2008; Ye *et al.* 2019c). Chen *et al.* (2015) has proposed the use of both anode exchange membrane (AEM) and CEM to recover nutrients in multistage operations. The most commonly used material in laboratory-scale studies is Nafion 117 membrane. An efficient membrane should not transfer oxygen from the cathode to the anode chamber and it should transfer protons very effectively (Jayashree *et al.* 2019). The IEM alone constitutes approximately 60% of the overall cost of the MFC systems in field-scale applications (Ge & He 2016).

2.2. Types of MFCs

Dual-chamber MFC, single-chamber MFC, up-flow MFC and stacked-type MFCs are some of the different types of popular MFCs used in laboratory-scale applications for nutrient removal. Schematics of these types of MFCs are presented in Figure 2.

2.2.1. Dual-chamber MFC

This is the simplest form of MFC with anode and cathode chambers separated by an IEM. In some cases, anode effluent is used as an influent for the cathode chamber to increase efficiency and to further treatment (Don & Babel 2021). Dual-chamber MFCs working based on pH static control by adding a base to the anode chamber and an acid to the cathode chamber has also been reported by a few authors (Cord-Ruwisch *et al.* 2011).

2.2.2. Single-chamber MFC

The MFC system, which consists of only one chamber that has both cathode and anode, is known as a single-chamber MFC. The single-chamber MFC provides a simple and economic design (Kumar *et al.* 2017). In most cases, one side of the cathode faces towards the separator and the other side to the atmosphere. The cathode facing the liquid side requires a catalyst, binder material, and cloth separators for proper functioning (Ichihashi & Hirooka 2012; Hirooka & Ichihashi 2013). This configuration has many advantages over a dual-chamber system. The overall volume of the system can be decreased and the cost of air sparging in the cathode chamber is eliminated. The lack of a PEM between anode and cathode can increase oxygen diffusion, but this can reduce the cost of construction. The formation of an aerobic biofilm on the cathode surface can reduce the oxygen diffusion to a certain extent (Liu *et al.* 2005).

2.2.3. Up-flow MFC

In this type of arrangement, the anode is at the bottom, and the cathode is at the top, and the substrate is supplied from the bottom of the system towards the upper portion or separately to each chamber. Both portions may be separated by glass wool or glass bead layers as in an integrated constructed wetland–MFC system or by an IEM as in a dual–chamber MFC (He *et al.* 2006; Ma *et al.* 2016). The main advantage of this type of MFCs is that they can be scaled up easily compared to other models with emphasis on wastewater treatment than power generation (Kumar *et al.* 2017). A study conducted for the treatment of produced water from an oil and gas industry with up-flow MFC documented a best power density of 227 mW/m^2 (Cabrera *et al.* 2022).

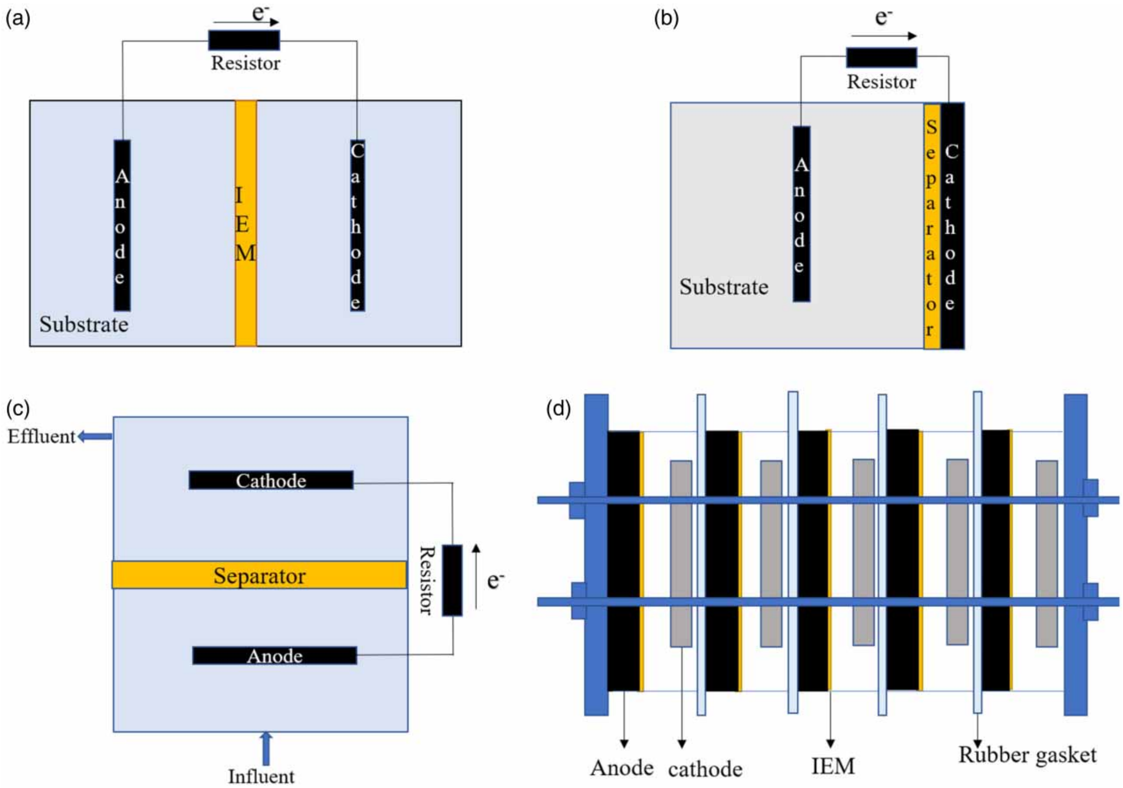


Figure 2 | Schematic representation of different types of MFCs. (a) Dual-chamber MFC. (b) Single-chamber MFC. (c) Up-flow MFC. (d) Stacked MFC.

2.2.4. Stacked MFC

MFCs can be arranged either in series or in parallel to increase the efficiency of the system (Kumar *et al.* 2017; Tan *et al.* 2021). However, there is the possibility of a decrease in efficiency due to ohmic losses (Ieropoulos *et al.* 2008). To avoid voltage reversal and high-power output, all the cells connected should be in proper working condition (Gurung & Oh 2012). In a study with stacked MFCs using synthetic wastewater it was found that series connection produces lower power compared to parallel arrangement due to a cross-conduction effect. Thus, to obtain high COD removal and current density, a parallel stack arrangement is preferred (Aelterman *et al.* 2006). Based on power output from 10 small units and its theoretical projection for 80 small units stacked together, Ieropoulos *et al.* (2008) suggested that the projected output could be 50 times higher than that of a single MFC of the same volume.

3. NUTRIENT REMOVAL AND RECOVERY MECHANISMS IN MFCS

Domestic wastewater as well as wastewater such as swine wastewater, landfill leachate, urine waste, dairy manure, coke wastewater, and beverage wastewater are rich in nutrient content (Kumar & Pal 2015). Most of the reported studies on nutrient removal using MFCs are performed using synthetic domestic wastewater (Chen *et al.* 2015; Wang *et al.* 2019a, 2019c; Ye *et al.* 2019a, 2019b, 2020b), real domestic wastewater (Chen *et al.* 2017; Sun *et al.* 2018; Yang *et al.* 2018), swine wastewater (Ichihashi & Hirooka 2012; Doherty *et al.* 2015a, 2015b; Kim *et al.* 2015; Li *et al.* 2021a), dairy wastewater (Mansoorian 2016), slaughter house wastewater (Mohammed & Ismail 2018), leachate (Nguyen & Min 2020), and urine (Sharma & Mutnuri 2019; Sharma *et al.* 2021). Different mechanisms/pathways involved in nutrient removal and recovery by MFCs along with the efficiency of different systems are described in this section.

3.1. Nutrient removal and recovery by precipitation

In MFCs, precipitation of nutrients in a cathode chamber by pH control is a common method for removal of nutrients from wastewater. The precipitates generally show the elemental composition of struvite ($MgNH_4PO_4.6H_2O$) or cattiite

($Mg_3(PO_4)_2.22H_2O$) in spectroscopy (Santoro *et al.* 2013; Ye *et al.* 2020a). Vivianite ($Fe_3(PO_4)_2{\cdot}8H_2O$) precipitation also can be expected if there is the presence of iron (Liu *et al.* 2018). Struvite precipitation is considered as one of the methods to recover nutrients (Yetilmezsoy *et al.* 2017). Figure 3(a) shows the mechanisms in a dual-chamber MFC that remove nutrients as struvite.

In dual-chambered MFCs, wastewater is treated in two stages. Initially, it is treated by electroactive microorganisms for removing organics and recovering energy in the anode chamber and later by conducting ion migration to recover phosphorus and nitrogen in the cathode chamber (Ye *et al.* 2019c). It has been observed that the concentration of ammonium in deionized water in the cathode chamber increases with time (Ye *et al.* 2019c). The ammonium ion passes through the IEM to the cathode chamber by diffusion and the electric field generated by MFC (Mohammed & Ismail 2018; Samrat *et al.* 2018). A cathode chamber can be provided with or without aeration. Aeration can significantly influence the nutrient removal efficiency in the cathode chamber, while the removal efficiency of the anode chamber is negligibly affected. In the cathode chamber, nitrogen and phosphorus are removed by the combined action of chemical precipitation and air stripping (Ye *et al.* 2019c). Struvite crystal precipitation occurs when the concentrations of Mg^{2+}, NH_4^+, and PO_4^{3-} exceed the solubility limit. The solubility decreases with an increase in pH value and the solubility is also affected by the ionic strength of the solution (Ichihashi & Hirooka 2012). The pH value near the cathode is found to be higher than other sites in the chamber due to hydroxyl ion formation. Even though the pH of the effluent is found to be less in some cases, researchers have suggested this possibility of local pH increase for the precipitation (Zhao *et al.* 2006). The pH in the cathode chamber is increased due to hydroxyl ions produced in the cathode according to the following chemical reactions:

anode reaction: $C_6H_{12}O_6 + 6H_2O \rightarrow 6\ CO_2 \uparrow + 24\ H^+ + 24\ e^-$

cathode reaction: $2H_2O + O_2 + 4e^- \rightarrow 4OH^-$

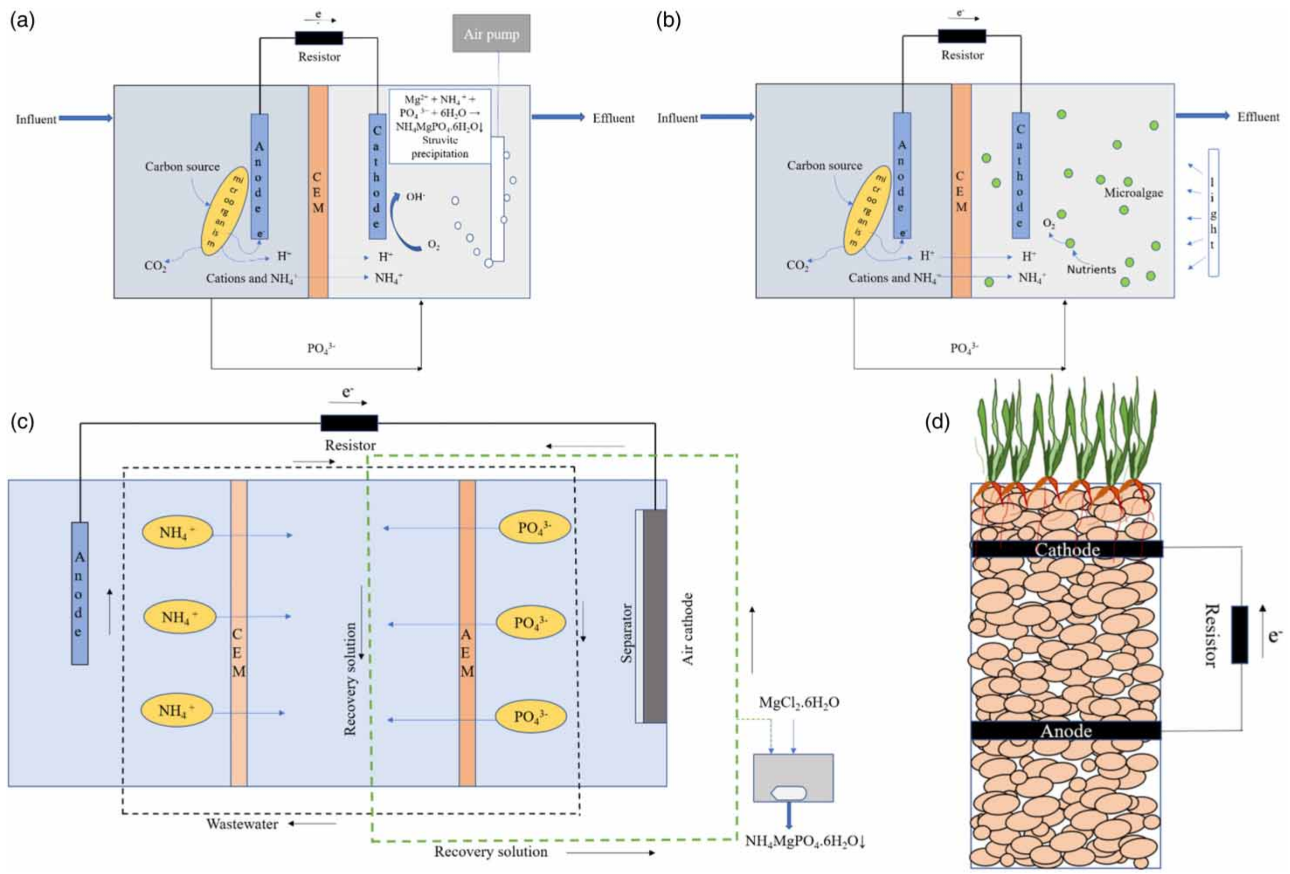


Figure 3 | Schematic representation of nutrient removal in (a) dual-chamber MFC by struvite precipitation, (b) microalgae-based MFC, (c) microbial nutrient recovery cell (MNRC), and (d) MFC integrated with constructed wetland.

Therefore, it has been suggested that the local pH increase near the cathode induced by the cathode reaction is the main reason for struvite precipitation. When the pH value is between 8.0 and 8.4, ammonium and phosphate can be precipitated with magnesium as per following reaction (Ye *et al.* 2019c):

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow NH_4MgPO_4.6H_2O\downarrow$$

Since there is an increase in pH without adding external chemicals and generation of direct electricity, MFC can be a more economical and sustainable approach. Apart from precipitation, some amounts of nutrients are consumed by the bacterial consortium present in the anode chamber. In a single-chambered MFC with an air cathode, the crystals are obtained on the surface of the liquid side of the cathode.

A summary of different studies reported on the nutrient removal by precipitation using MFCs is presented in Table 1. It can be seen from this table that the removal efficiencies vary widely with respect to the membranes and electrode used, surface area of electrodes and membrane, and the characteristics of wastewater. The best removal/recovery of 94.9 and 97.58% for PO_4^{3-} -P and NH_4^+-N, respectively was reported by Ye *et al.* (2019c) while treating synthetic municipal wastewater. A study conducted by Tao *et al.* (2015) reported that the maximum power density of a single chamber MFC was higher than that of the dual-chamber MFC. This study also concluded that single-chamber and dual-chamber MFCs can effectively remove phosphate, but their nitrogen removal efficiency varies considerably (Tao *et al.* 2015).

3.2. Nutrient removal and recovery by using photosynthetic microalgae

Microalgae-based wastewater treatment technology has been getting much attention currently as it is a green technology and is conceptualized on circular bioeconomy (Sharma *et al.* 2022). The algal biomass can assimilate nutrients and further can create economic benefits by producing value-added products like biodiesel and pigment (Yang *et al.* 2018; Arun *et al.* 2020). The removal efficiency also depends upon the type of microalgae used, and *Chlamydomonas reinhardtii* and *Pseudokirchneriella subcapitata* can be used to remove nutrients (Xiao *et al.* 2012). Adsorption, accumulation, biodegradation and immobilization are the important mechanisms adopted by microalgae for the remediation of pollutants in wastewater (Sharma *et al.* 2022).

A photosynthetic microalgal-based MFC is a promising technique that can be employed in nutrient removal. Microalgal application in MFC can reduce greenhouse gas emissions (Bolognesi *et al.* 2021). The schematic representation of a microalgae-based MFC is given in Figure 3(b). The predominant method of struvite precipitation in an MFC might negatively impact electricity generation and can be overcome by this alternative. Since microalgae can produce oxygen, the external aeration process can be eliminated, which increases the economic benefit. Photosynthesis, nitrification, aerobic denitrification, and autotrophic denitrification in the cathode chamber and their collaborative interactions play a significant role in nitrogen removal (Wang *et al.* 2019a). In general, microalgae-based MFCs remove phosphorus through both abiotic precipitation and biotic assimilation, while nitrogen is removed by assimilation and electron acceptor in the cathode (Yang *et al.* 2018). Li *et al.* (2020) based on studies on microalgae-based MFC found that microalgae present in the cathode chamber alone can remove up to 55.8% of total nitrogen (TN) and 48.7% of total phosphate (TP). The presence of microalgae can also increase power generation in MFCs (Yang *et al.* 2018).

A summary of various studies conducted to remove nutrients from wastewater using microalgae-based MFCs is given in Table 2. The ammonia or nitrogen recovery of microalgae-based MFCs is higher than those systems that recover nutrients by precipitation. A complete removal of ammonia from synthetic wastewater was also reported (Don & Babel 2021). A study on nutrient removal in swine wastewater using airlift type photosynthetic MFCs by Li *et al.* (2021) has been reported to achieve COD, NH_4^+-N, and TP removal efficiencies of 96.3, 99.1 and 98.9%, respectively, using *Chlorella vulgaris*.

3.3. Other mechanisms of nutrient removal by MFCs

Other than precipitation and absorption by microalgae, nutrients are removed by various other mechanisms in MFCs. The high pH at the cathode causes the production of volatile ammonia, which can be removed by air stripping and it can be recovered by adsorbing it in acid solution to produce ammonium salts (Kuntke *et al.* 2012; Ye *et al.* 2020a). Autotrophic nitrification and denitrification, and ammonia stripping are the two main mechanisms of removal of ammonia other than precipitation in a single-chamber MFC. Littfinski *et al.* (2022) reported that ammonia volatilization alone contributes 22 to 63% of total ammonia nitrogen (TAN) removal in a single-chamber MFC. In biocathode MFCs, autotrophic denitrifying

Table 1 | Summary of reported studies on single-chamber and dual-chamber MFCs by precipitation

SI No.	Type of wastewater	Wastewater characteristics	Type of MFC	Anode chamber	Cathode chamber	Ion exchange membrane/ Separator	HRT	COD removal	Phosphate removal	Ammonia removal	Maximum power density/ voltage/ current generation	Reference
1	Synthetic municipal wastewater	COD-300 ± 15 mg/L NH_4^+-N-5.0 ± 0.15 mg/L PO_4^{3-}-P-1.0 ± 0.05 mg/L	Double-chambered MFC (self-circulation mode)	350 mL, Cylindrical shaped graphite felt anode (3 cm diameter and 6 cm thickness)	350 mL, Carbon fiber brush coated with titanium bar cathode (approximately 3 cm length and 3 cm diameter)	CEM (CMI7000) FO membrane nonwoven	24 h 24 h 24 h	– – –	>94.9% 83.18% 90.6%	>97.58% 98.81% 97.2%	641.4 mV – –	Ye *et al.* (2019c)
2	Synthetic domestic wastewater	COD- 600 mg/L	Double chamber MFC (continuous)	350 mL, graphite felt anode (3 cm diameter and 6 cm thickness)	350 mL, Carbon fiber brush coated with titanium bar cathode (3 cm length and 3 cm diameter)	CEM (CMI7000)	0.69 days	70%	71.5% removal in anode chamber, 24.4% average recovered in cathode chamber.	75.13% removal in anode chamber, 24.34% recovery in cathode chamber	253.84 mW/m^3	Ye *et al.* (2019a)
3	Synthetic domestic wastewater	COD- 300 mg/L	Double chamber MFC (continuous)	350 mL, Graphite felt anode (3 cm diameter and 6 cm thickness)	350 mL, Carbon fiber brush coated with titanium bar cathode (3 cm length and 3 cm diameter)	CEM (CMI7000)	0.35–0.69 days	>92%	12–14% removal in anode chamber, ~83% recovered in cathode chamber	13–15% removal in anode chamber, ~85% recovered in cathode chamber	253.84 mW/m^3	Ye *et al.* (2020b)
4	Industrial wastewater (Coors WWTP, Golden Colorado)	COD-total-1,243 ± 55 mg/L COD-dissolved -989 ± 21 mg/L Phosphate-18 ± 2 mg/L Ammonia-24 ± 3 mg/L	Biochar-based microbial fuel cell	Waste wood-derived biochar	Waste wood-derived biochar	CEM (CMI-7000)	-	95%	TP -88%	NH_4-73%	6 W/m^3	Huggins *et al.* (2016)
5	Urine	pH-6.3 COD-5,628 ± 52 mg/L Ortho-P-305 ± 14 mg/L NH_4-N-440 ± 32 mg/L	Three-stage system (MFC-struvite precipitation-MFC system)	0.5 L, Stainless steel mesh (projected surface area of 255 cm^2)	0.5 L, Stainless steel mesh (projected surface area of 255 cm^2)	CEM (CMI-7000)	48 h	75.55 ± 2.8%	90 ± 1.5% recovery	46 ± 2.16% recovery	14.5 mW/m^2	Sharma *et al.* (2021)

(*Continued.*)

Table 1 | Continued

Sl No.	Type of wastewater	Wastewater characteristics	Type of MFC	Anode chamber	Cathode chamber	Ion exchange membrane/ Separator	HRT	COD removal	Phosphate removal	Ammonia removal	Maximum power density/ voltage/ current generation	Reference
6	Synthetic wastewater	NH_4^+-N-55.0 mg/L PO_4^{3-}-P-122.9 mg/L	Single-chamber MFC aeration	4 cm long 3 cm diameter, Carbon paper anode (projected area of 4 cm^2)	Carbon cloth with platinum catalyst (0.5 mg Pt/cm^2, liquid side) with four PTFE layers and one carbon base layer (air side) cathode	–	–	70%	–	–	560 mW/m^2	Tao *et al.* (2015)
			Dual-chamber MFC	4 cm long, 3 cm diameter, carbon paper anode (projected area 7 cm^2)	4 cm long, 3 cm diameter, carbon cloth containing 0.5 mg Pt/cm^2 cathode (projected area of 7 cm^2)	Nafion 117 (7 cm^2)	–	79%	–	–	528 mW/m^2	
7	Swine wastewater	COD- 60,000 mg/l phosphorus (SS)-670 mg/l	Air-cathode single-chamber MFC	70 mL, Carbon felt anode (47 cm^2 projected surface area)	Carbon paper coated with platinum cathode (0.5 mg/cm^2 of Pt/C) (effective surface area 47 cm^2)	Polyester nonwoven cloth separator placed against both cathode and anode (7.7 cm diameter,0.5 mm thickness)	-	76–91%	79–82%	-	1.7 mW/m^2	Ichihashi & Hirooka (2012)
8	Synthetic wastewater	-	Air cathode single-chamber MFC	70 mL, Carbon felt anode (projected area 47 cm^2)	Wet porous carbon paper with coating of mg/cm^2 of pt/C catalyst (projected area 47 cm^2)	Nonwoven polyester separating cloth (2 × 3.5 0.5 cm thickness)	–	–	55% (as struvite)	–	–	Hirooka & Ichihashi (2013)
9	Synthetic domestic wastewater	COD-300 ± 15 mg/L NH_4^+- N-5 mg/L PO_4^{3-}1 mg/L	Dual compartment MFC	Cylinder shaped graphite felt anode (3 cm diameter and 6 cm thickness)	Carbon fiber brush cathode (3 cm length 3 cm diameter)	CEM (CMI7000)	0.69 day	85.56%	11.37–13.33% removal and 76.03–83.23% recovery rate	85.11% recovery rate	230.17 mW/m^2	Ye *et al.* (2019b)
10	Urine	pH- 6.3 ± 0.6 Conductivity- 11.14 ± 0.12 mS/cm COD- 11,876.23 ± 22 mg/L Ortho-P-201 ± 15 mg/L NH_4^+-N-674 ± 23 mg/L NO_3^-- 246 ± 42 mg/L	Dual-chambered MFC	230 mL, Stainless steel mesh (8 × 8 cm)	Stainless steel mesh (8 × 8 cm)	CEM (Ultrex CMI7000)	22 h	69.97 ± 2.2%	Ortho-P-94.2 ± 2.3%	49.96 ± 0.9%	0.24 ± 0.15 W/m^2	Sharma & Mutnuri (2019)

Table 2 | Summary of reported studies on microalgae-based MFCs for nutrient removal

SI No.	Type of wastewater	Wastewater characteristics	Type of MFC	Microalgae	Anode chamber	Cathode chamber	Ion exchange membrane/ Separator	HRT	COD removal	Phosphate removal	Ammonia removal	Maximum power density/ voltage/ current	Reference
1	Synthetic domestic wastewater	–	Immobilized microalgal-based photosynthetic MFC (PMFC)	*Chlorella vulgaris*	400 mL, Carbon brush (7.5 × 4 cm)	400 mL, Carbon brush (7.5 × 4 cm)	PEM (Nafion 117–8.5 cm^2)	12 h	sCOD -93.2%	82.7%	NH_4^+-N-95.9% TN-95.1%	466.9 mW/m^3	Wang *et al.* (2019a)
2	Synthetic wastewater	NH_4^+-N-90 mg/L	Dual-chambered MFC assisted with algae in cathode chamber	*Chlorella* sp. (single celled), *Desmodesmus sp* and *Scenedesmus* sp.	205 mL, Carbon fiber brush (3 × 2.5 cm)	20 mL, Carbon fiber brush (3 × 2.5 cm)	PEM (Nafion 117)	–	–	–	99.6%	0.35 A	Kakarla & Min (2019)
3	Swine wastewater	COD -7,786 mg/L TOC-2,094 mg/L TN-2,048 mg/L TP-124.7 mg/L NH_4^+-N-1,820 mg/L pH -7.68	Airlift-type photosynthetic microbial fuel cell (APMFC)	*Chlorella vulgaris*	400 mL, Carbon brush (length of 9.0 cm, diameter of 3.5 cm)	400 mL, Carbon fiber cloth (6 cm × 8 cm ¼ 48 cm^2) containing Pt catalyst	PEM (Nafion 117)	–	96.3%	TP-98.9%	NH_4^+-N-99.1% TN-98.3%	3.66 W/m^3	Li *et al.* (2021a)
,4	Domestic wastewater	COD-186.8 to 327.9 mg/L TN-25.3 to 52.5 mg/L TP- 2.9 to 8.3 mg/L	Algae biofilm microbial fuel cell (ABMFC)	*Scenedesmus quadricauda*	Carbon cloth cathode (diameter 90 mm, thickness 8 mm) interwoven with titanium wire in the lower chamber of the MFC.	Carbon cloth cathode (diameter 90 mm, thickness 8 mm) woven with titanium placed on the water surface	Glass wool (thickness 20 mm, diameter 110 mm)	12days	81.9%	96.4 %	95.5%	162.93 mW/m^2	Yang *et al.* (2018)
,5	Leachate and wastewater mix	NH_4^+-N- 403.4 ± 27.9 mg/L	Algae cathode microbial fuel cell	Mixed algal bioreactor	260 mL, Carbon fiber brush (L × D = 3 × 2.5 cm^2)	230 mL, Carbon fiber brush (L × D = 3 × 2.5 cm^2)	CEM (CMI-7000)	60 h	–	Soluble phosphate -86.3%	TN-58.85% NH_4^+–N-76%	1.4 ± 0.4 mV (current generation almost zero)	Nguyen & Min (2020)
,6	Synthetic wastewater	COD-1,500 mg/L NH_4^+-N-50 mg/L	Photosynthetic MFC	*Chlorella vulgaris* and *Scenedesmus quadricauda*	Carbon fiber cloths (surface area of 204 cm^2)	Carbon fiber cloths (surface area of 204 cm^2)	CEM (CMI-7000)	–	–	–	100%	16.72 mW/m^2	Don & Babel (2021)
,7	anaerobically digested effluent from kitchen waste	COD- 6,015 ± 280 mg/L NH_4^+-N-2,365 ± 160 mg/L TP- 95 ± 3 mg/L	Photosynthetic microbial fuel cell stack	*Golenkinia* sp.	0.36 L, Carbon brush	16 L, Carbon cloth	CEM	–	–	–	98%	2.34 W/m^3	Yang *et al.* (2019)

bacteria can reduce nitrate to nitrogen gas (Al-Mamun *et al.* 2017). However, the recovery of ammonia is mostly reduced due to nitrification and denitrification processes (Ye *et al.* 2019a). It has been reported that electrogenesis also promotes denitrification, and species like *Dechloromonas* and *Geobacter* have the capacity for denitrification (Li *et al.* 2021b).

Wastewater discharged from industries such as tanneries and mining and swine wastewater contains both ammonium and sulphide. In such wastewaters, the S/N molar ratio is an important parameter with a desirable value of 3 for coupled system of nitrifying sulphide removal MFC (N-MFC) and denitrifying sulphide removal MFC (D-MFC). N-MFC consists of an oxic-cathode and D-MFC consists of an anoxic-cathode, and sulphide can act as electron donor in both cases. This coupled system was able to achieve $58.7 \pm 1.3\%$ TN removal efficiency (Chen *et al.* 2019). The dual MFC system developed to remove the dye Victoria blue R (VBR) achieved complete ammonia removal (Jayashree *et al.* 2019). In this system, two MFCs were coupled together. For anaerobic decomposition of VBR in the first MFC, the anode chamber was inoculated with *S. putrefaciens*, and *A. calcoaceticus* was cultured in the biocathode of a second MFC for aerobic decomposition (Wu *et al.* 2020). The use of a seawater bacterial consortium for denitrification in MFCs was also explored by researchers and found it to be a feasible approach that needs further studies (Samrat *et al.* 2018; Pepè Sciarria *et al.* 2019). The incorporation of a bioactive oxygen consuming unit (OCU) as separator in a single-chamber MFC has a higher oxidation peak value which increases with increase in thickness of OCU. This is because OCU creates an oxygen gradient between the anode and cathode, thus reducing oxygen diffusion to the anode and enhancing the electrochemical reaction (Elmaadawy *et al.* 2020). The microbial desalination cell (MDC) is a technology in which some aspects of MFCs and electrodialysis are amalgamated (Gujjala *et al.* 2022). This consists of three chambers (anode, cathode and desalination chambers) which are separated by a CEM on one side and an AEM on the other side. A modified version with four chambers with an acid production chamber that is separated from the anode chamber by a bipolar membrane has also been explored by various researchers (Rahman *et al.* 2021).

The microbial nutrient recovery cell or MNRC represented in Figure 3(c) is a type of modified MFC for nutrient recovery (Shahid *et al.* 2021a). More than 95% nutrient removal efficiency was possible by using nutrient recovery cell (Chen *et al.* 2017). These three chambered nutrient recovery cell reactor systems containing a middle recovery chamber separated by a CEM on the anode side and an AEM on the cathode side show a high nutrient removal efficiency. In this system, nutrients from the wastewater are collected by the influence of bioelectricity produced from the decomposition of organic matter. The wastewater circulates between the anode and cathode chambers and the recovery solution, which receives nutrients circulates individually. Ammonium ions and phosphate ions are pushed from the anode and cathode sides, respectively, into the recovery chamber. Concentrated nutrient ions in the recovery solution are recovered in the form of struvite. The concentration of recovery solution also has a significant influence on the overall performance of the MNRC (Chen *et al.* 2015).

Studies on various modified MFC systems for removal of nutrients are summarized in Table 3. The MNRC system was reported to achieve removal efficiencies of 99.5, 98.27, and 99–100% of COD, ammonium and phosphate respectively using a heat-treated carbon brush as the anode and a carbon cloth coated with platinum as the cathode, achieving a power density of 1,000 mW/m^2 (Shahid *et al.* 2021b). In this study it was concluded that the carbon brush anode was able to achieve higher power production compared to a stainless steel anode with other experimental conditions remaining the same.

3.4. Integrated systems for nutrient removal

MFCs can be integrated with various other treatment technologies to overcome the limitations of the existing technologies or to improve the nutrient recovery/removal. Results of various MFC-integrated systems reported for removal of nutrients from different types wastewater are summarized in Table 4. MFCs integrated with constructed wetlands, aerobic and anoxic bioreactors, biofilters, membrane bioreactor and anaerobic digestors were used in different studies. The most explored integrated system is constructed wetland–MFC due to minimal construction and operational costs.

Constructed wetland treatment systems are naturally aerobic near the surface, which is suitable for the cathode reaction and are anaerobic as depth increases, providing suitable conditions for anode reactions (Doherty *et al.* 2015b). A 99.7% removal of ammonia was reported in constructed wetland–MFC with corncobs to enhance the performance (Tao *et al.* 2022). In these systems, nitrogen removal can take place by oxidation by nitrifiers combined with aerobic denitrification, bio-electrochemical oxidation, reduction or by ammonia volatilization (Xu *et al.* 2021). Many studies have utilized constructed wetland–MFC-integrated systems for nutrient removal. The schematic representation of a constructed wetland–MFC-integrated system is given in Figure 3(d). *Canna indica, Phragmites australis*, *Chrysopogon zizanioides* and *Typha latifolia* are used as plants in different constructed wetland–MFC-integrated systems (Doherty *et al.* 2015a; Lu *et al.* 2015; Oon

Table 3 | Summary of reported studies on modified MFC systems

SI No.	Type of wastewater	Wastewater characteristics	Type of MFC	Anode chamber	Cathode chamber	Ion exchange membrane/ Separator	HRT	COD removal (%)	Phosphate removal (%)	Ammonia removal (%)	Maximum power density/ voltage/ current	Reference
1	Synthetic waste water	NH_4^+-28.9 ± 0.7 mg N/L (oxic cathode chamber) Sulphide-(64, 128, 192 and 256 mg S/ L)	Two dual-chambered MFC coupled (nitrifying sulphide removal N-MFC and denitrifying sulphide removal D-MFC)	200 cm^3, Carbon brush prepared with carbon fiber filaments twining on a titanium wire anode	200 cm^3, Carbon brush prepared with carbon fiber filaments twinning on a titanium wire cathode	PEM (Nafion 117)	–	–	–	TN-58.7 ± 1.3%	13.59 ± 0.31 W/m^3	Chen *et al.* (2019)
2	Landfill leachate	COD-2,005.5 mg/L Ammonia nitrogen -251.4 mg/L	Cathodic algal biofilm (*Chlorella vulgaris*) MFC equipped with a bioactive oxygen consuming unit (AB-OCU-MFC)	Circular piece of carbon felt anode (diameter of 25 mm and thickness 10 mm.)	Air cathode electrode (diameter of 48 mm) prepared from stainless steel mesh loaded with catalyst	Circular carbon felts (28 mm diameter and 10- or 20-mm thickness) OCUs	–	86.0 ± 1.25%	–	89.4 ± 0.85%	0.39 V	Elmaadawy *et al.* (2020)
3	Synthetic wastewater	COD-322 mg/L PO_4^{3-}-P-20 mg/L NH_4^+-N-20 mg/L NO_3^--N-20 mg/L	Three chamber microbial nutrient recovery cell (MNRC)	Carbon brush with heat treatment (projected area of 19.6 cm ^{2})	Carbon cloth (Pt coating at water side and PTFE coating at air facing side)	CEM (CMI7000S), AEM (AMI7001S)	–	99.5% (*t = 120 h)	99–100% (*t = 168 h)	NH_4^+-N-98.27%(*t = 144 h) NO_3^-N-90.06% (*t = 168 h)	1,000 mW/ m^2	Shahid *et al.* (2021b)
				Carbon brush with APTES modification				99%(*t = 120 h)	99–100% (*t = 168 h)	NH_4^+-N-97.98%(*t = 144 h) NO_3^-N-91% (*t = 168 h)	850 mW/m^2	
				Stainless steel brush with heat treatment				80% (*t = 120 h)	78.77% (*t = 168 h)	NH_4^+-N 97.16%(*t = 144 h) NO_3^-N 73.28% (*t = 168 h)	370 mW/m^2	
4	Municipal wastewater	–	Microbial nutrient recovery system (MNRS)	Carbon brush and	Air-cathodes 30% wet proofed carbon cloth with an inside catalyst layer of 0.5 mg/cm2 Pt on carbon black with 5 wt %	CEM(CMI7000S) AEM(AMI-7001S)	–	82.3 ± 4.1%	83% (recover)	80% (recover)	800 mW/m^2	Shahid *et al.* (2021a)
				Stainless-steel brush				63 ± 3.1%	70%(recover)	70% (recovery)	~400 mW/m^2	
5	Synthetic domestic wastewater	COD-369 ± 21 mg/L NH_4^+-N-23.8 ± 1.3 mg/L PO_4^{3-}-P-6.4 ± 0.6 mg/L	Microbial nutrient recovery cell (MNRC) (3.6 mL recovery chamber)	21.2 mL, Granular activated carbon.	3.6 mL, The air cathode made of carbon cloth (30% wet-proofing) with 0.5 mg/cm2 platinum catalyst and four polytetrafluoroethylene (PTFE) diffusion layers.	CEM (Ultrex CMI7000), AEM (Ultrex AMI-7001)	–	>82%	>64%	>96%	0.56 A/m^2	Chen *et al.* (2015)
6	Domestic wastewater	COD = 463 mg/L, PO_4^{3-}-*P* = 7.6 mg/ L, NH_4^+-*N* = 47.4 mg/ L	Enlarged microbial nutrient recovery cell (EMNRC)	Granular activated carbon (~1 mm in diameter, ~2–5 mm in length) anode	30% wet-proofing carbon cloth with a platinum loading of 0.5 mg/cm^2 and four diffusion layers of polytetrafluoroethylene cathode	CEM, (Ultrex CMI7000) AEM, (Ultrex AMI-7001)	–	> 70%	> 55% (89% Recovered as struvite)	> 80% (62% Recovered as struvite)	2.3–3.1 mA	Sun *et al.* (2018)
7	Sludge reject water samples and livestock wastewater	Sludge reject water: livestock wastewater = 70%:30% (v: v)	Microbial nutrient recovery cell (MNRC)	220 mL, Carbon-fiber anode	220 mL, Air cathode made of carbon cloth	CEM-(CMI-7000) AEM- (AMI-7001)	–	–	–	79.8 ± 7.7%	14.10 ± 1.14 A/ m^3	El-Qelish & Mahmoud (2022)

(*Continued.*)

Table 3 | Continued

SI No.	Type of wastewater	Wastewater characteristics	Type of MFC	Anode chamber	Cathode chamber	Ion exchange membrane/ Separator	HRT	COD removal (%)	Phosphate removal (%)	Ammonia removal (%)	Maximum power density/ voltage/ current	Reference
8	Domestic wastewater	COD-331 ± 25 mg/L, TN-84.4 ± 7.9 mg/L, NH_4^+-N-58.2 ± 6.7 mg/L, TP-9.4 ± 0.2 mg/L	Advanced microbial nutrient recovery cell (AMNRC)	4 L	4 L	CEM AEM	10 h	95.8 ± 0.5%	TP- 96.9 ± 0.3%	96.9 ± 0.2%	~40 mA	Chen *et al.* (2017)
9	Primary effluent from wastewater treatment plant	TCOD- 155 ± 37 mg/L SCOD-73 ± 23 mg/L NH_4^+-25.7 ± 5.5 mg N/L TSS- 72.9 ± 16.6 mg/L	96 tubular MFC modules, which were placed as 12 × 8 arrays with 12 MFCs in each row and 8 rows in total	Carbon brush	Carbon cloth coated with nitrogen doped activated carbon powder	CEM, (Ultrex CMI7000)	18 h	>75%	–	68%	~200 mW	Ge & He (2016)
10	Dairy industrial wastewater	COD-3,620 mg/L BOD_5–2,115 mg/L Total P-187 mg/L NH_3-167 mg/L NH_4^+- 174 mg/L TSS -1,430 mg/L VSS- 647 mg/L SO_4^{2-}-835 mg/L EC-2,176 ms/cm pH -8.5–10.3	Catalyst less mediator less dual-chamber MFC, continuous mode	2 L, Graphite plate (14 × 6 × 0.5 cm^3)	2 L, Graphite plate (14 × 6 × 0.5 cm^3)	PEM (Nafion 117)	5days	90.46%	Dissolved phosphate-31.18% Phosphate in suspends solid-72.45%	NH_3-73.22% NH_4^+ -69.43%	621.17 mW/m^2	Mansoorian (2016)
11	Synthetic wastewater (simulate eutrophic wastewater)	COD- 20 ± 3 mg/L NH_4^+-N- 3.2 ± 0.1 mg/L NO_3-N- 3.1 ± 0.1 mg/L PO_4^{3-}-P- 0.63 ± 0.02 mg/L	Photomicrobial nutrients recovery cell (PNRC) *(Chlorella vulgaris)*	Carbon brush (3 cm diameter, 3 cm length)	Carbon cloth (with 5 cm2 projected surface area) coated with Pt 0.5 mg /cm^2)	CEM, AEM	–	94.5%	94.4%	91.8%	472.3 mW/m^2	Jiang *et al.* (2019)

*Time of operation.

Table 4 | Summary of reported studies on different MFC-integrated systems for nutrient removal

SI No.	Type of wastewater	Wastewater characteristics	Type of MFC	Anode chamber	Cathode chamber	Ion exchange membrane/ Separator	HRT	COD removal	Phosphate removal	Ammonia removal	Maximum power density/ voltage/ current	Reference
1.	Swine slurry	COD- 411–854 mg/L TN-63 ± 7.5 mg/L NH_4^+-N-40 ± 5.3 mg/L TP -8.9 ± 2.1 mg/L Reactive phosphorus (RP)- 6.2 ± 1.5 mg/L	Alum sludge-based constructed wetland incorporating microbial fuel cell technology	1.1 ± 0.09 L, packing granular graphite anode (diameter 8–13 mm, initial porosity of 0.38)	1.1 ± 0.09 L, packing granular graphite cathode (diameter 8–13 mm, initial porosity of 0.38)	Glass wool	1day	80%	85%	75%	0.268 W/m^3	Doherty *et al.* (2015b)
2	Swine wastewater	COD-583 ± 92 mg/L TN- 63 ±7.5 mg/L NH_4^+-N-40 ± 5.3 mg/L TP -8.9 ± 2.1 mg/L PO_4-P-6.2 ± 1.5 mg/L	Constructed wetland -MFC	Graphite granule with graphite rod anode	Graphite granule with graphite rod cathode	Glass wool	1 day	64 ± 4.6%	PO_4-P-90 ±2.2% TP- 85 ± 4.0%	NH_4^+-N-75 ± 3.1% TN- 58 ± 3.1%	0.276 W/m^3	Doherty *et al.* (2015a)
3	Municipal wastewater	NH_4^+-N-21.3 ± 7.5 mg/L TP-10.1 ± 3.6 mg/L	MFC-based horizontal flow constructed wetland (*Phragmites australis* and *Chrysopogon zizanioides*)	Aluminium plate anode	Aluminium plate cathode	–	–	80–100%	≥93%	55 t-92%	38.6 mW/m^2	Saeed *et al.* (2022)
4	Synthetic wastewater	COD-200 mg/L, NO_3^-N-40–80 mg/L, TP -4–8 mg/L	Pyrite-based constructed wetland-microbial fuel cell (PCW-MFC) (*Canna indica* plant)	Carbon fiber felts anode (12 cm in diameter, 1 mm in thickness)	Carbon fiber felts cathode (12 cm in diameter, 1 mm in thickness)	–	6 h	71.9 ± 3.6%	TP-89.2 ± 2.7%	NO_3^--N -67.5 ± 4.4%	2.67 mW/m2	Ge *et al.* (2020)
5	Synthetic domestic wastewater	NH_3-N-25 mg/L NO_2–N-0.1 mg/L, NO_3–N-0.5 mg/L, organicN-15 mg/L TN-40.6 mg/L PO_4^{3-}-P-4 mg/L $P_3O_{10}^{5-}$P-1 mg/L, TP-5 mg/L. COD- 50–360 mg/L	Constructed wetland-MFC (*Canna indica*)	Carbon fiber brush anode	Graphite plate cathode	–	1.5 day	–	–	TN- 90.30–91.46%	3.25 mW/m^3	Wang *et al.* (2019c)
6	Synthetic wastewater	COD-314.8 ± 13 mg/L	Up-flow constructed wetland-MFC (UFCW-MFC) (*Typha latifolia*)	Carbon felt anode (total surface area 280 cm^2)	Carbon felt cathode (total surface area 280 cm^2)	–	1 day	100%	–	91%	6.12 mW/m^2	Oon *et al.* (2015)
7	Secondary effluent from WWTP -synthetic WW	COD-58.0 ± 2.2 mg/L, TN-14.7 ± 1.5 mg/L, NH_4^+-N-5.6 ± 1.1 mg/L NO_3^--N-10.8 ± 1.4 mg/L	Constructed wetland -MFC (corncobs were added to enhance the performance)	Graphite plate anode (200 × 100 × 8 mm)	Graphite plate cathode (200 × 100 × 8 mm)	–	48 h	89.9%	–	NH_4^+-N-99.7% NO_3^-N- 100%	1.92 mW/m^2	Tao *et al.* (2022)
8	Synthetic wastewater	COD-150 mg/L, NH_4^+-N-30 mg/L	Tidal flow constructed wetland – MFC (TFCW-MFC) (*Canna indica)*	Layer of Activated carbon granules and graphite felt (20 cm length × 10 cm width × 0.6 cm thickness)	Carbon felt (14 cm outer diameter × 7 cm inner diameter × 0.6 cm thickness)	–	7 Days	>85%	–	TN- 52.89 ± 3.16%	–	Xu *et al.* (2021)
9	Swine wastewater	TCOD-73,828 ± 1,804 mg/L SCOD-43,489 ± 1,146 mg/L T-N-5,152 ± 266 mg/L TAN-4,199 ± 27 mg/L T-P -818 ± 19 mg/L	Anaerobic digestor-MFC (3 identical air cathode MFCs)	320 mL, carbon felt anode	Carbon cloth coated with a Pt catalyst (0.5 mg/ cm^2) cathode	Nafion NAF NR212	–	–	–	TAN- 77.5%	33 mW/m^2	Kim *et al.* (2015)
10	slaughterhouses wastewater	COD-980–1,000 mg/L NH_4^+-150–250 mg/L NO_3^--15–20 mg/L NO_2^--6–12 mg/L Electrical conductivity (EC)- 920–1,280 μS/cm pH – 6.3–7.1	Microbial fuel cell, aerobic bioreactor, and anoxic bioreactor (MFC-AB-ANB)	Uncoated plane graphite rod (effective surface area of 185.35 cm^2)	Graphite granules (specific surface of 0.0832 m2 /g, and granular size diameter range of 2–4 mm)	CEM (CMI-7000 s)	–	99%	–	99.3%	162.55 mW/m2	Mohammed & Ismail (2018)

(*Continued.*)

Table 4 | Continued

Sl No.	Type of wastewater	Wastewater characteristics	Type of MFC	Anode chamber	Cathode chamber	Ion exchange membrane/ Separator	HRT	COD removal	Phosphate removal	Ammonia removal	Maximum power density/ voltage/ current	Reference
11	Municipal wastewater	COD-266.7 mg/L NH_4^+-N-52.3 mg/L PO_4^{3-}-P-6.2 mg/L	Integrated photo bio-electrochemical system (Microbial fuel cell inside an algal bioreactor-*Pseudokirchneriella subcapitata*)	~300 mL, 20 cm long carbon brush anode	Layer of carbon cloth with Pt/C as catalysts cathode	CEM, Ultrex CMI7000	12.5 h	92.4%	82.3%	98.6%	2.2 ± 0.2 W/m^3	Xiao *et al.* (2012)
12	Synthetic wastewater	NaAc- 600 mg/L NO_3 – 95.0 mg/L	MFC coupled with up-flow denitrification biofilter (BF)	Graphite particle filter as bioanode	Air cathode made of stainless steel	–	24 h	87.50–90.86%	–	denitrification efficiency - 89.31–98.60%	0.48 mA	Li *et al.* (2021b)
13	Synthetic wastewater	COD-1,505.61 ± 681.54 mg/L NH_4^+-21.72 ± 7.99 mg/L Phosphate-17.13 ± 5.77 mg/L	Algal (*Chlorella vulgaris*) assisted constructed wetland (*Canna indica*)-MFC integrated with sand filter	600 mL, Graphite granules anode	750 mL, Carbon felt cathode	Earthen membrane	5 days	96.37 ± 2.6%	69.03 ± 10.14%	85.14 ± 10.73%	33.14 mWm^{-3}	Gupta *et al.* (2021)
14	Domestic wastewater	NH_3-N-32 ± 4.28 mg/L SCOD-1,080 ± 160 mg/L	MFC-MBR	Graphite brush anode (2.5 cm diameter × 2.5 cm length)	Conductive UF membranes biocathodes prepared by dispersing multiwalled carbon nanotubes (MCNTs) (specific surface area of 117 m^2/g)	–	2–3 days	SCOD-97.3 ± 1.1%	–	97.3 ± 1.6%	0.38 W/m^2	Malaeb *et al.* (2013)
					Platinum-based MCNT/ polyester UF membrane cathode	–	2–3 days	96.9 ± 0.6%	–	95.2 ± 2.9%	0.82 W/m^2	
15	Domestic wastewater	COD_{total} 323 mg/L Ammonia 41 mg/L Sulphate 102 mg/L Orthophosphate9 mg/L	Horizontal subsurface constructed wetland	20 cylindrical graphite rods wrapped in stainless steel (1 cm length and 0.5 cm diameter each)	20 cylindrical graphite rods wrapped in stainless steel (1 cm length and 0.5 cm diameter each)	–	2.6 days	61%	–	58%	36 mW/m^2	Corbella *et al.* (2015)

et al. 2015; Ge *et al.* 2020; Saeed *et al.* 2022). A study conducted by Doherty *et al.* (2015b) with different configurations on swine slurry in constructed wetland–MFC showed an efficiency of about 80, 85, and 75% for COD, phosphorus and ammonia removal, respectively. This study also suggested that, by varying the inflow conditions, the efficiency can be increased. Wang *et al.* (2019c) was able to achieve a TN removal efficiency of 91.46% in a constructed wetland–MFC while treating synthetic domestic wastewater. Ge *et al.* (2020) reported that compared with the traditional constructed wetland–MFC system, the pyrite-based constructed wetland–MFC can give higher removal efficiencies under similar conditions since pyrite can enhance the N and P removal efficiency along with bioelectricity generation treating synthetic wastewater. An up-flow constructed wetland–MFC system using *Typha latifolia* has been reported to achieve 91% removal of NH_4^+-N while treating synthetic wastewater (Oon *et al.* 2015).

The tests conducted by Pepè Sciarria *et al.* (2019) coupling microbial electrochemical technologies with crystallization process gave approximately 90% overall phosphate reduction efficiency. The system consisted of an MFC followed by a precipitation process. The removal efficiency of this MFC system was 10–15% higher than microbial electrolysis cells (Pepè Sciarria *et al.* 2019). Complete nitrate removal was reported by using an integrated system with MFC, an aerobic bioreactor, and an anoxic bioreactor (Mohammed & Ismail 2018). Compared to a biofilter working alone to treat municipal sewage with a denitrification efficiency of 71.34%, a higher denitrification efficiency of 89.31% was reported when MFC was coupled with an up-flow denitrification biofilter (Li *et al.* 2021). Nutrient removal from nitrogen-rich swine wastewater was studied using an anaerobic digestor–MFC-integrated system to overcome low COD removal efficiency due to high TAN in the anaerobic digestor (Kim *et al.* 2015). An MFC–membrane bioreactor system was reported to have an ammonia removal efficiency of 97.3% while treating domestic wastewater (Malaeb *et al.* 2013).

4. PARAMETERS AFFECTING NUTRIENT REMOVAL IN MFCS

Recovering nutrients from wastewater is a promising approach with an economic benefit. To achieve high removal and recovery efficiency, the operation at optimum conditions for different parameters affecting the overall MFC performance is required (Sivakumar 2021). Temperature, pH, electrodes, membrane, organic loading rate (OLR), hydraulic retention time (HRT), light intensity, light and dark cycles, initial nutrient concentration, dissolved oxygen concentration, and resistance are some of the important factors that affect the performance of MFCs used for nutrient removal and recovery. These factors are discussed here.

4.1. Temperature

A higher operating temperature can increase the microbial activity which can improve the reaction kinetics, mass transfer, coulombic efficiency, and power density (Kusmayadi *et al.* 2020). Increasing the electrolyte temperature from 37 to 45 °C can increase the COD removal efficiency and can result in higher voltage output (Anam *et al.* 2020). In a catalyst and mediator less dual-chamber MFC, the maximum voltage and current intensity was obtained at 35°C compared to 15, 20, 25, 30, and 40°C, along with NH_3, NH_4^+, dissolved phosphorus, and phosphorus particulate removal of 73.22, 69.43, 31.18, and 72.45% respectively (Mansoorian 2016). In a study conducted by varying the temperature of microalgae-based MFC, maximum oxygen production and ammonium removal efficiency of 99.6% were obtained at 27°C, by enhancing both anode bacterial and cathode microalgae metabolisms compared to 19 and 35°C (Kakarla & Min 2019). Exposure to a higher temperature above the mesophilic range can cause cell damage to anaerobic bacteria (Anam *et al.* 2020).

4.2. pH

In an MFC, the microbial activity, precipitation of nutrients and growth of microalgae are all directly dependent on the pH. Microbial growth in an anode chamber is affected by extreme pH values. An unstable supply of electrons, protons and oxygen can affect the pH of the system resulting in physical ammonium loss and organic matter loss, and disrupt the physiology of the cell (Kusmayadi *et al.* 2020). A neutral pH is considered as optimum for maximum power generation. A pH between 6.5–7.0 is best for the microbial growth in the anaerobic chamber (Mansoorian 2016). An acidic pH or alkaline pH of anolyte shows a lower COD removal efficiency (Anam *et al.* 2020). The nutrient precipitation in the form of struvite requires a pH range of 8.0–8.4 in the cathode chamber (Ye *et al.* 2019c). The traditional dual-chambered MFC is capable of maintaining different pH values in two chambers to attain optimum activities in individual chambers. Single-chambered MFCs do not have this capability which makes dual-chambered MFC more efficient in nutrient removal (ElMekawy *et al.* 2013).

4.3. Electrodes

The bio-electrochemical reactions usually take place on the surface of the electrodes and hence the selection of electrodes is very important. Electrodes that are used as anode and cathode should have chemical stability, biocompatibility, high conductivity, large potential range, and a reproducible surface (Jain *et al.* 2015; Jayashree *et al.* 2019). The cost of an electrode is an important factor for nutrient removal with MFCs. Several types of cathodes and anodes have been used by different researchers in their studies. They can be classified into mainly two groups as metal-based electrodes and carbon-based electrodes. Carbon-based electrodes were found to be more efficient in energy production and more biocompatible compared to metal-based electrodes (Zhuang *et al.* 2012; Shahid *et al.* 2021b). Metal-based electrodes have more conductivity but less surface area (Shahid *et al.* 2021a). The composite of these carbon-based and metal-based electrodes can enhance efficiency much more. Optimum spacing depends on the design configuration, type of substrate and oxygen permeability of the membrane (Arun *et al.* 2020). Giving pretreatments such as heat treatment and silanization treatment can improve the performance of electrodes (Shahid *et al.* 2021b). A study conducted by Huggins *et al.* (2016) on industrial wastewater, used a biochar-based electrode that was able to remove 95% COD. A study by Shahid *et al.* (2021b) showed that carbon-based APTES pretreated electrodes can achieve 99 and 98% total phosphorus and ammonia removal efficiency in a microbial nutrient recovery cell while treating municipal wastewater. The coulombic efficiency can be increased by increasing the electrode surface area per reactor volume. This also increases anode biofilm growth (Bose *et al.* 2018). It has been reported that platinum-based carbon cloth gives approximately 65% higher power than a platinum-free carbon cloth cathode (Santoro *et al.* 2013). A complete nitrate removal was achieved with a biocathode containing seawater bacteria (Samrat *et al.* 2018).

4.4. Membrane

The transfer of cations from anode to cathode takes place through the membrane due to the concentration gradient. Different membranes such as CEM, AEM, bipolar membrane and ceramic membrane salt bridge have been used in MFCs. The membranes which can conduct protons and prevent fuel crossover are ideal membranes for MFCs (Ramirez-Nava *et al.* 2021). The CEM increases the pH, which further helps in nutrient precipitation in the cathode chamber. Nazia *et al.* (2020) synthesized a new cost-effective ionically crosslinked nanocomposite membrane made up of cationic aniline-treated polysulfone (APSf) doped with an anionic sulfonated multiwalled carbon nanotube (SMWCNT) to lower the oxygen crossover and enhance the chemical, tensile and thermal stabilities. This membrane was able to produce a power density of 304.2 mW/m^2, which was higher than the power density of 197 mW/m^2 with Nafion 117, while treating kitchen wastewater. Nafion and Ultrex membranes are commonly used in MFC studies (Kumar *et al.* 2017). CEM shows more removal efficiency compared to non-woven and forward osmosis membranes (FO) in nutrient recovery (Ye *et al.* 2019c).

4.5. Microorganisms

Anaerobic microorganisms present in the anode chamber play a vital role in removing organic matter present in wastewater (Saravanan *et al.* 2021). Certain bacteria can transfer electrons produced by the oxidation of organic matter directly to the anode without electron mediators. Anode biofilms are usually covered with microbial species of different shapes and sizes (Sharma *et al.* 2021). The bacterial species affects the performance of MFC. The presence of methanogens in the system can decrease the coulombic efficiency and therefore pretreatments of inoculum to reduce methanogens can increase the power generation (Wang *et al.* 2019a; Raychaudhuri & Behera 2020). The electroactive organisms that present in the anode chamber include *Geobacter*, *Rhodobacter* and *Turicibacter* (Lu *et al.* 2015; Wang *et al.* 2019a). Sharma & Mutnuri (2019) while monitoring power generated from four different cultures of microorganisms found a higher maximum power density of 99 $mW/\ m^2$ from the pure culture of *Proteus vulgaris*. However, mixed bacterial culture showed better performance (Sharma & Mutnuri 2019). Even though several studies have shown an increase in COD removal with an increase in mixed liquor suspended solids (MLSS), the study conducted by Fazli *et al.* (2018) found the opposite. The microorganisms that belong to Proteobacteria are very helpful in nitrification and denitrification processes (Wang *et al.* 2019b). Certain bacteria belonging to Planctomycetes can remove nitrogenous pollutants by converting ammonia and nitrate into nitrogen. *Nitrospira* is considered very helpful in the nitrification process and *Acinetobacter* in the aerobic denitrification process (Xu *et al.* 2021). In photosynthetic microalgal–MFC the Proteobacteria concentration decreased with increase in algal biomass (Yang *et al.* 2018). The presence of Cyanobacteria in the cathode can produce reactive oxygen species that are beneficial for electricity generation (Wang *et al.* 2019a). The presence of microbial flora like *Bacillus*, *Pseudomonas*, *Achromobacter*, *Acinetobacter*, *Flavobacterium*, *Azospirillum* and *Bdellovibrio* in the MFC can remove nitrate and phosphate effectively (Shahid *et al.*

2021b). It has been reported that the presence of Zn(II) can reduce some functional genera in the microbial community, thereby reducing the nutrient removal efficiency of constructed wetland–MFC systems (Wang *et al.* 2020).

4.6. Organic loading rate

The wastewater characteristics and OLR influence the overall performance of an MFC. In a study conducted by Mansoorian (2016) using dairy wastewater, the maximum current density and power density were obtained at an OLR of 53.22 kg COD/m^3.d and showed a decreasing effect above and below this value. The MFC performance highly depends upon the catalytic reaction of anaerobic bacteria for the substrate, electron transport to the anode, proton transfer to the cathode, and electron acceptor in the cathode chamber. These processes are highly dependent on the OLR. The removal of NH_4^+-N and PO_4^{3-}-P in the anode chamber can be enhanced by increasing the OLR, as a specific COD:N:P ratio is required for growth of microorganisms in an anaerobic chamber. It has been concluded that the amount of nutrients needed for high-strength organic wastewater with COD >4,000 mg/L is higher, which increases nutrient removal in the anode chamber, reducing the struvite precipitation in the cathode chamber (Ye *et al.* 2019a). Therefore, the nutrient recovery rate decreases with increase in OLR. For this reason, dual-chamber MFC is a more suitable technology to recover nutrients from low-strength wastewater (Ye *et al.* 2019a). A higher OLR can also decrease coulombic efficiency due to a decrease or saturation in bacterial activity (Tamilarasan *et al.* 2017). At high OLRs, organic matter is taken up for bacterial growth instead of electricity generation and the electrons are accepted by receptors present in the solution itself (Mansoorian 2016). In addition, a higher COD value can cause membrane fouling, which adversely affects the performance of MFCs. In MNRC systems, high NH_4^+-N recovery was observed when bioavailable COD was higher and wastewater with high COD/NH_4^+ ratio was favorable for high current density production (El-Qelish & Mahmoud 2022).

4.7. Hydraulic retention time

Hydraulic retention time is an important parameter that influences the efficiency of the system. A study conducted by Ye *et al.* (2020b) on synthetic domestic wastewater with HRT ranging from 0.35 to 0.69 days concluded that a longer HRT produces maximum power density. However, the average nutrient removal efficiency was approximately the same in HRT range studied, which indicates that HRT can be reasonably reduced if economic nutrient recovery is the major objective (Ye *et al.* 2020b). In another study to understand the influence of HRT on bioelectricity production, Mansoorian (2016) changed HRT values between 2 and 8 days. The maximum power density of 621.13 mW/m^2 was obtained at an HRT of 5 days. The increase in voltage when the HRT was increased from 3 to 5 days might be due to a longer contact time between the substrate and microorganisms. In an another study when the HRT was increased from 8 to 12 days in an algal biocathode MFC, TN and phosphorus removal efficiency increased from 82.9 and 86.3% to 95.5 and 96.4%, respectively (Yang *et al.* 2018). Therefore, increase in HRT can increase nutrient removal (Fazli *et al.* 2018; Nguyen & Min 2020). However, a longer HRT may limit power production and coulombic efficiency due to insufficient substrate (Ma *et al.* 2016).

4.8. Initial ammonia concentration

A higher concentration of ammonia in influents can cause cytotoxic impacts on the microbial community. The ammonia concentration can influence the activity of cytosolic enzymes and intracellular pH. A study by Ye *et al.* (2019b) suggested that there is a decrease in coulombic efficiency and power density as the influent ammonia concentration increased from 5 to 40 mg/L. However, the recovery rate of phosphate was insignificantly influenced at a wider influent ammonia concentration. The larger amount of ammonia conversely helps in the precipitation of phosphorus in the cathode chamber as struvite along with magnesium (Hirooka & Ichihashi 2013). Hiegemann *et al.* (2018) showed that the impact load of a total ammonia concentration greater than 800 mg/L can lead to the instant collapse of power generation due to the inhibition of exoelectrogenic biofilm. A study by Kim *et al.* (2015) demonstrated that the COD:TAN ratio is an important parameter in the anaerobic digestor–MFC system in terms of COD and nitrogen removals. Higher COD:TAN ratio is favorable to attain higher removal efficiency. An influent COD:TN ratio of $\geq$3 resulted in a TN removal of 90.30 to 91.46% in a constructed wetland–MFC system (Wang *et al.* 2019c). Complete removal of ammonia was observed in a photosynthetic MFC with an influent ammonia concentration of 50 mg/L within 210 h and the removal efficiencies decreased when ammonia concentration was increased further (Don & Babel 2021).

4.9. Dissolved oxygen concentration

An optimum level of dissolved oxygen (DO) should be maintained in the anode and cathode chambers to obtain the optimum performance of MFCs. In a study conducted by Ye *et al.* (2019c), the DO concentration in the anode chamber was kept below 0.02 mg/L to maintain the anaerobic condition, while a DO concentration around 6.22 mg/L was maintained in the cathode chamber by aeration to enhance the nutrient removal efficiency of MFC. In the case of algae-based MFCs, there was no need for external aeration, and the oxygen required for electron acceptance was produced by photosynthesis (Arun *et al.* 2020). The cathodic DO is a very important factor for nutrient removal. The efficiency of removal decreases as the DO concentration declined in the cathode chamber (Tao *et al.* 2014). High DO concentration conversely causes back diffusion to the anode chamber and decreases power density. Bazdar *et al.* (2018) reported a 53.4% decrease in power density when the DO concentration was increased from 7.8 to 9.5 mg/L in photosynthetic MFC using the microalgae *Chlorella vulgaris*.

4.10. Light intensity and light and dark cycle

There is optimum light intensity for algal-based MFCs. A long illumination period may increase oxygen production and thus electricity generation, but an extended illumination can decrease electricity production, since a dark period is required to maintain a healthy community of microorganisms (Xiao & He 2014). Bazdar *et al.* (2018) conducted tests under light intensities varying between 3,500 and 10,000 lx and a light/dark regime of 24/00, 12/12 and 16/8 h to investigate the performance of photosynthetic microalgae–MFCs. Their results suggest that light intensity between 5,000 and 6,500 lx is the optimum range for the growth of *Chlorella vulgaris*. Biomass growth is directly related to the nutrient removal in microalgae-based MFCs. In another study the optimum ammonia removal efficiency was obtained at 12/12 h light/dark cycles (Kakarla & Min 2019). With respect to the illumination characteristics, the energy production capacity also varies for different types of microalgae. Artificial light can increase the efficiency of MFC but it can increase the operational cost. For *Chlamydomonas reinhardtii*, power generation increased when red LED light was used (Lan *et al.* 2013). Increase in photon flux density also increases the ammonia removal rate and efficiency in photosynthetic MFCs. In an MFC with a microalgal cathode, illuminated with 92 $\mu E/m^2 s^1$ photon flux achieved complete ammonium removal within 96 h, while the cathode illuminated with 47, 27, or 13 $\mu E/m^2 s^1$ attained only 95, 63, or 70% ammonium removal, respectively (Kakarla & Min 2019).

4.11. Effect of resistance

In a fuel cell the maximum power transfer is achieved when loading resistance equals the internal resistance (Ieropoulos *et al.* 2008; Al-Mamun *et al.* 2017). Electrode spacing, electrode material, ionic strength and pH of the electrolyte, type of microbes and membrane are the main factors that can affect the internal resistance (Ieropoulos *et al.* 2005; Kumar *et al.* 2017). A study conducted by Huggins *et al.* (2016) using biochar electrodes and adsorption of nutrients to their surface suggested that biochar electrodes can reduce the internal resistance, while it can attain a removal efficiency of 88 and 73% for phosphate and ammonia, respectively. Reducing the electrode separation and increasing the DO concentration in the cathode can reduce the internal resistance and increase the power output in constructed wetland–MFC systems (Doherty *et al.* 2015a). The type of microorganisms and their metabolic products also affect the conductivity of the anolyte, thereby effecting the internal resistance (Ieropoulos *et al.* 2008).

5. FUTURE PERSPECTIVES

Conventional nutrient removal/recovery techniques include precipitation, adsorption, and biological processes (Ye *et al.* 2020a; Rout *et al.* 2021). The biological processes face limitations in removing organic matter and nutrients simultaneously. The precipitation technique depends on the solution pH, while the adsorption technique needs effective desorption process to recover the adsorbed nutrients. Conversely, MFC is a self-sustainable and promising technique that can simultaneously produce electricity and treat wastewater (Logan *et al.* 2006; Wang *et al.* 2010). This technology can elevate the pH in the cathode chamber due to their inherent mechanism and without additional chemicals, which indicates their high economic feasibility to precipitate struvite (Ye *et al.* 2020a). The local pH near the cathode can precipitate nutrients, and ammonia can also be removed by air stripping. Modification of conventional MFCs with biocathode, algal photobioreactors, etc., can help to produce more value-added products such as biodiesel and pigments, simultaneously fixing CO_2 and eliminating the cost of aeration in the cathode chamber (Arun *et al.* 2020). A recent study on ghee wastewater showed a COD removal efficiency of 90% for MFC that was significantly higher than that of conventional anaerobic treatment (73%), and biomass production in the anode chamber of MFC was 0.7 g/20 mL, which was much less than that in anaerobic treatment system (1.2 g/20 mL) (Elakkiya & Niju 2021).

While a number of studies showed the feasibility of MFCs for nutrient removal, most of these studies were conducted on a laboratory scale. To understand more about real applications, full-scale studies analyzing the relationship between various parameters are essential (Verma *et al.* 2021). Scale-up can be done by enlarging a single system or by stacking multiple reactors into one system (Ge & He 2016). But the modularized model shows more efficiency than simply enlarging the size of MFC (Ge & He 2016; Liang *et al.* 2018). A pilot-scale study with a 90 L stackable MFC treating brewery wastewater showed that MFCs can be employed for real wastewater treatment with zero energy input (Fitzgerald *et al.* 2015). A 1,000 L modularized MFC generated a maximum power density of 7–60 W/m^3 while treating municipal wastewater (Liang *et al.* 2018). Only very few studies have reported in the scaled-up model study of MFC to remove nutrients. A study conducted by Ge & He (2016) on a 200 L modularized MFC system with 96 tubular MFCs gave 68% nitrogen removal efficiency. Even though air-cathode microbial electrochemical systems use energy for aeration, in a pilot-scale study it was found that the energy requirement was only about 12% of that of activated sludge process (He *et al.* 2019). In another pilot-scale study on an air-cathode MFC of 1,400 L liquid volume the system was able to achieve 9% columbic efficiency (Rossi *et al.* 2022).

Despite the advantages of MFCs, there are still many challenges that need to be resolved before successful commercial application. A better understanding of various parameters that affect the performance of MFCs is necessary to arrive at the optimum operating conditions. Since the coulombic efficiency is related to the internal resistance, which in turn depends upon various other factors, comprehensive studies focusing on improving the efficiency is required. The high cost of materials used in an MFC is one of the main limitations of this technology (Pepè Sciarria *et al.* 2019). However, a cost analysis by Ge & He (2016) indicates that the impact of cost factors can be reduced by applying this technology to an appropriate small treatment system with cost-effective methods. Membrane fouling, low power density, and high cost are the main issues faced during field applications. Microalgae-based systems are energy-consuming for their cultivation and harvesting (Gajda *et al.* 2015; Jaiswal *et al.* 2020). In the algal cathode chamber, another issue is the light penetration while there is the chance that the growth of microalgae can hinder the light reaching evenly affecting further growth of microalgae. The main advantages and constraints of MFCs for nutrient removal are summarized in Figure 4.

The development of low resistant economic membranes and more efficient electrodes are needed for large-scale application. Even though the use of microalgae can reduce the aeration cost and carbon footprint, separation of algae from treated wastewater remains a challenge. Optimizing the arrangements of modules is crucial in the field-scale application (Ge & He 2016). Thus, to become a superior technology over current nutrient recovery techniques, future MFC research

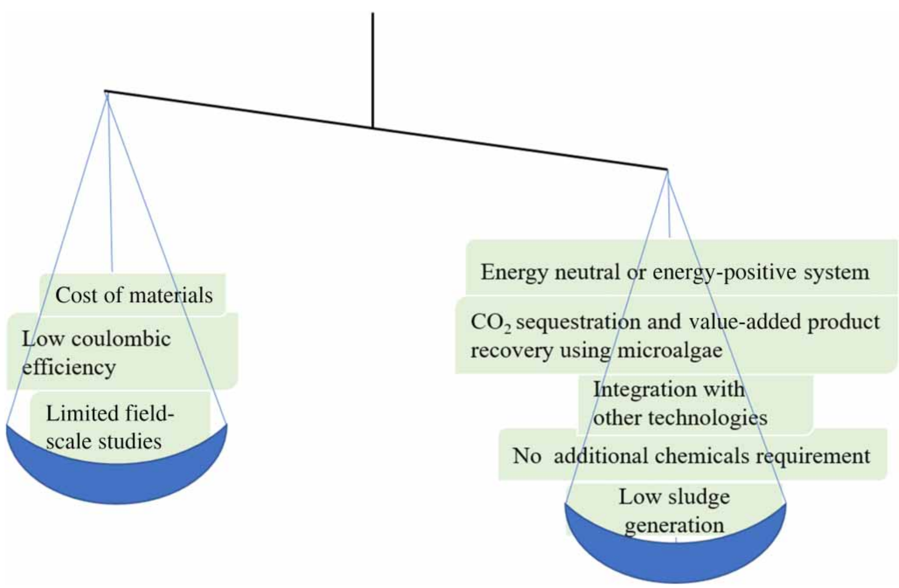


Figure 4 | Advantages and constraints of MFCs in nutrient removal/recovery from wastewater.

should focus on reducing the electrochemical energy loss, improving nutrient removal efficiency, and optimizing the operating conditions.

6. CONCLUSIONS

MFCs are bio-electrochemical systems in which microorganisms degrade organic matter in the wastewater to produce electrons simultaneously generating electricity and treating wastewater. Struvite, cattiite or vivianite precipitation, nutrient assimilation by microalgal biomass in the system, ammonia stripping, nitrification and denitrification are the different types of mechanisms through which MFCs remove and recover nitrogen and phosphate. The nutrient removal efficiency and power generation are affected by various parameters such as temperature, pH, type of electrode, type of membrane, OLR, HRT, light intensity and light and dark cycles, initial ammonium concentration, dissolved oxygen concentration, and resistance. For the large-scale application of MFCs for nutrient removal, high removal/recovery without compromising the electricity generation capacity has to be achieved at a low cost of construction. Full-scale field studies, and analysis of various process parameters affecting the nutrient recovery to establish relationships between them are required to develop efficient MFC systems for nutrient removal and recovery from different types of wastewaters.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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