

Removal of total ammonia nitrogen (TAN), nitrate and total organic carbon (TOC) from aquaculture wastewater using electrochemical technology: A review

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ABSTRACT

Protein rich wastes from aquaculture systems result in total ammonia nitrogen (TAN), total organic carbon (TOC) and biochemical oxygen demand (BOD). A number of conventional approaches have been adopted for the removal of these wastes in aquaculture ponds and hatcheries with varying degrees of success but they face critical problems such as membrane fouling, high cost or the generation of toxic by-products. To overcome such issues, electrochemical technology is commonly employed. The advantages of electrochemical treatment include high efficiency, ambient operating conditions, small equipment sizes, minimal sludge generation and rapid start-up. An even better system involves bio-electrochemical reactors (BERs), which have the potential to generate energy from wastewater (by means of microbial fuel cells) or a valuable product such as hydrogen (using microbial electrolysis cells). Mechanisms of cathodic nitrate reduction and anodic oxidation in electrochemical and bio-electrochemical technology are reported in this review. Also some work on the simultaneous removal of nitrate and organic matter by Electro-Fenton and microbial fuel cells are elaborated upon. It is apparent that BERs can remove contaminants at high efficiencies ($\approx 99\%$) whilst giving least impact upon the environment.

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1. Introduction

Aquaculture globally has undergone tremendous growth during the last 50 years from a production of less than a million tons in the early 1950s to over 50 million tons during the present time. Aquaculture in Malaysia has developed greatly from small scale family oriented businesses to large scale operations. Exports of aquaculture have recorded positive growth rates as much as RM 1,323,280 (US\$ 440,000) to RM 1,769,305 (US\$ 587,120) from 2007 to 2008 [1,2]. The main categories of fish involved have been shellfish, freshwater fish, marine prawn, marine fish and giant freshwater prawn [3]. Fish or fish based products are a cheap source of animal protein for human growth. Due to Malaysia being surrounded by sea and an ocean, it is easy to have access to fish and fish based products [2]. The total consumption of fish has increased from 49 kg/capita/year to 56 kg/capita/year from year 2000 to 2010. Hence, Malaysia has the highest fish consumption rate in the world [1,2]. Current local production of fisheries, which has increased from 89% in year 2000 to 94.3% in 2010 [1], is unable to achieve the goal of self sufficiency in the future. This is due to an increase in health awareness and rise of population in the country. Thus, in year 2009, through National Aquaculture Development Plan, the Ministry of Agriculture has roughly allocated RM 358 million (US\$ 118,796,770) to establish an aquaculture industrial zone and provide the necessary assistance, including infrastructure to cope with the rising demand [3].

The intensive development in the aquaculture industry has caused major environmental impacts. Wastewater discharged from aquaculture contains nitrogenous compounds (ammonia, nitrite and nitrate), phosphorus and dissolved organic carbon, which cause environmental deterioration at high concentrations [4]. Ammonia (NH_3) is the product of fish respiration and decomposition of excess organic matter. Chemoautotrophic bacteria (Nitrosomonas and Nitrobacter) tend to oxidize ammonium ions (NH_4^+) to nitrite (NO_2^-) and nitrate (NO_3^-) ions. Nevertheless, these ions are removed by aquatic plants, algae and bacteria since they assimilate them as a source of nitrogen [5].

These nitrogen compounds are nutrients for generating eutrophication which disrupt aquatic ecosystems in a severe manner [6] as shown in Fig. 1. Animal farming, urban and agricultural runoff, industrial wastes, and sewage effluents also increase the concentration of ammonium, nitrate and nitrite ions in aquatic ecosystems [5]. Several studies have been conducted on the toxicity of nitrate on aquatic animals and results indicate that nitrate reacts with hemoglobin causing shortage of oxygen in their body (methaemoglobin) and finally death [5]. When nitrate enters in human intestines, it is also converted into nitrite under anaerobic conditions and this may lead to methaemoglobinaemia in infants [4,5]. Besides that, formation of nitrosoamines from nitrite can give rise to cancers of the digestive tract since nitrosoamines are the most efficacious carcinogens in mammals [7]. Therefore, World Health Organization (WHO) established the limit for nitrate in drinking water to 10 mg $\text{NO}_3\text{-N/L}$ [7,8].

Total organic carbon (TOC) is defined as any compound containing carbon atoms except CO_2 and related substances such as carbonate, bicarbonate and the like [10]. Various natural and man-made activities result in the presence of dissolved organic carbon in aquaculture wastewater. The major compositions of dissolved organic carbon in aquaculture wastewater are humic-like substances, carbohydrates, protein-like substances, low molecular weight aldehydes, fulvic acids, phenols and organic peroxides [11]. Organic carbon is the energy substrate for many microorganisms and its consumption contributes to the problem of inadequate dissolved oxygen in water bodies that become a threat to aquatic life. In addition, treatment costs increase when dissolved organic carbon in wastewater is high [4,11–13]. In this article, the removal of conventional TAN, nitrate and organic matter is reviewed in detail. In addition, the review attempts to compare both electrochemical and bio-electrochemical methods used for TAN or nitrate and total organic removal. Finally, an effective method for simultaneous denitrification and TOC removal in synthetic contaminated water and actual aquaculture wastewater is surveyed and recommendations are put forth with some emphasis on a novel bio-electrochemical reactor.

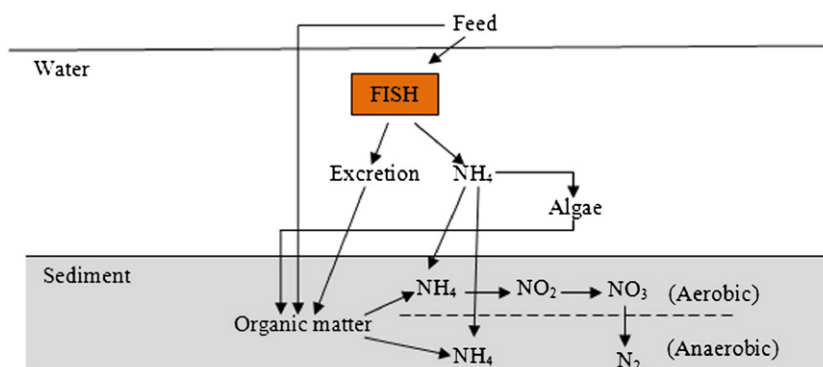


Fig. 1. Nitrogen transformation in fishpond [9].

2. Conventional TAN and nitrate removal methods

Coagulation, filtration, chlorination, UV and ozone treatment are the common methods applied in wastewater treatment but are not considered advanced enough for TAN and nitrate ions removal. So, there are a few techniques available to remove TAN and nitrate ions that are divided into two main categories: physicochemical and biological (Table 1).

2.1. Physicochemical treatments

Physicochemical treatment methods include ion exchange (IE), reverse osmosis (RO), electrodialysis (ED) and activated carbon adsorption. Reverse osmosis (RO) has potential to remove ions, proteins and organic chemicals in brackish water and seawater [29–31]. The advantages of using reverse osmosis include high permeability efficiency of selective ions, low production costs, environmental friendly consequences, unchanged molecular structure in separation process at room temperature and no product accumulation in the membrane [32]. However, the cost of RO operation is higher due to energy expense. The renewable energy sources such as wave, solar, and wind energy have been investigated during the past decade to overcome this problem [14,33]. Wind driven RO membrane process is successful for nitrogen removal from aquaculture wastewater [14]. The limitation of RO technique, however, is that the wastewater requires further treatment as the nitrate removed is accumulated in the brine system [16]. Efficiency of permeability becomes limited when soluble salts such as calcium carbonate (CaCO_3) and calcium sulphate (CaSO_4), from the feed solution, precipitates on the membrane [34]. Fouling problem is also an issue as it affects the membrane performance and increases complexity in the membrane operations [31,35–38].

Ion exchange resins are initially bonded to functional groups in chloride ions. The chloride ions are exchanged with anions and flow out from the system when contaminated water passes through the resin beads. The resin beads can be regenerated with sodium chloride solution by displacing the anions by chloride ions. However, this is not always a straightforward task as the anions (which are not only nitrate but also sulphate ions) have more affinity to the resin than the chloride ions [39–41]. This contributes to higher operation cost since extra steps have to be taken to eliminate these two anions before being discharged to the environment [42,43].

ED is a well established process for the desalination of brackish water to produce potable water [44]. The main advantages of ED compared to RO are that very little feed pre-treatment is required since membrane fouling and scaling is reduced to a minimum due to reverse polarity operation. Also much higher brine concentration can be achieved in ED than in RO since there are no osmotic pressure limitations [44]. ED has lower energy and incurs less investment costs for certain feed and product water compositions when compared to distillation processes. In comparison to IE, ED does not require the regeneration of chemicals, which makes IE a more costly process. However, ED has disadvantages such as the removal of ions and not other harmful microorganisms or organics during the production of potable water. Another disadvantage involves relatively high energy consumption when solutions with high salt concentrations have to be processed [44]. Likewise, the investment costs are prohibitively high when very low salt concentrations need to be achieved in the effluent because of the low limiting current density which requires a large membrane area.

Activated carbon is an adsorbent with large porous surface area, controllable pore structure, high thermo-stability and low acid/base reactivity [45]. Owing to its low initial cost, simplicity of design, insensitivity to toxic substances, high adsorption capacity and regenerability, activated carbons appeared to be the most versatile and suitable candidate for the removal of micropollutants from

wastewaters. However, commercial activated carbon remains an expensive material. In addition, if the activated carbon is not regenerated then it becomes a solid waste that ends up being dumped ultimately in landfills. If regenerated, the process can be very expensive.

2.2. Biological treatment

Biological treatments are carried out by bacteria that convert TAN and nitrate to nitrogen gas. There are no by-products formed and further treatment is not required for this method. Therefore, the operation cost is lower than physicochemical methods. Many researchers have investigated different operating conditions to achieve higher TAN and nitrate removal in aquaculture wastewater and these are reviewed below in brief.

2.2.1. Trickling filters

Trickling filters consist of a fixed media bed through which pre-filtered wastewater trickles downwards over an aerobic biofilm. The main parameter involved here is the filter medium. Void ratio, specific surface area and homogeneous water flow are the main characteristics of selecting a good filter medium. Void ratio affects the contact time between trickling water and biofilm and also affects pore clogging. The specific surface area indicates the surface required for biofilm growth as well as the homogeneous water flow related to dead zones and channels in the system [17]. Various materials and sizes have been investigated for TAN and nitrate removal by using this method (Table 1).

Lekang and Kleppe [17] used four different types of filter media, which are Leca (2–10 mm), Kaldnes rings, Norton rings and a rolled mat of Finturf artificial grass, to treat 1.5 mg TAN-N/L. The highest denitrification rate was 100% in Leca fraction columns since Leca has larger surface area and longer retention times in the columns. These four filter media are most frequently used [46]. Eding et al. [47] report that the bulk phase concentration of total ammonium nitrogen (TAN), dissolved oxygen, organic matter (COD), nitrite, temperature, HCO_3^- , pH and the hydraulic loading are the other parameters that influence the performance of trickling filters. Although high TAN removal rate is observed in trickling filters, it causes biofilm shedding and high risk of clogging during operation [47]. This may be the reason for imperfect nitrate elimination.

2.2.2. Fluidized bed reactor

Fluidized bed reactor may be one of the solutions for clogging problems in trickling filters and can provide an efficient method for removing dissolved wastes from recirculating aquaculture systems compared to rotating biological contactors, trickling filters and bed filters [46,48]. There appear to be few researchers who have performed TAN or nitrate removal in this type of reactor. Particle size of the medium is the most influential variable in the removal process [49]. Other parameters such as the medium and bed management techniques also affect the performance of this system (Table 1).

Davidson et al. [23] carried out a comparative experiment on two sand sizes (0.11 mm and 0.19 mm) and bed moving techniques (siphoning from top portion of the bed and biofilm shearing), to remove carbonaceous biochemical oxygen demand (cBOD), TAN, total phosphorous, total suspended solids (TSS) and total coliform bacteria from wastewater. The effective sand size, D_{10} was 0.11 mm which gave greater removal of TAN. The biofilm shearing method was more advanced in bed growth and less sand loss occurred compared with the siphoning technique, which resulted in a reduction in sand replacement costs. 88% of TAN removal was achieved when sand size of 0.11 mm and biofilm shearing were applied. Schnell et al. [18] investigated efficiency of TAN removal in a combination of screen filter, trickling filter and fluidized bed reactor using 260 m^2/m^3 PVC strips and 0.7 mm particle sand size as medium in trickling filter

Table 1
Conventional methods to remove TAN, nitrate and nitrite.

Reactor system	Wastewater	Carrier	Experiment conditions	Results	References
Ultra-low pressure asymmetric polyethersulfone (PES) membrane	Aquaculture wastewater	PES Radel A300	Pressure: 4–8 bar flux ($\times 10^{-6}$)(m^3/m^2s): 4.83–7.75	TAN removal: 75.42–85.30% phosphorus removal: 83.85–96.49%	[4]
Wind driven reverse osmosis (RO) system	Culture water of <i>Oreochromis niloticus</i> (tilapia)	RO membrane: 7.40 m ²	Flow rates: 230–370 L/h	TAN-N removal: ~92%	[14]
Wind driven reverse osmosis (RO) system	Culture water of tilapia	RO membrane: 7.40 m ²	Wind speed: 2.9 to 6.0 m/s permeate flux: 228 to 366 L/h	Nitrogen removal : 90–97% nitrate concentration: UD or <0.02 mg/L nitrite concentration: UD or sometimes around 0.002 mg/L	[15]
Ion exchange membrane bioreactor	Oceanarium	Mono-anion perm selective anion: 39 cm ²	HRT: 28 h F/A: 0.9 HRT: 17 h F/A: 1.5 HRT: 3 h F/A: 7.7	Nitrate removal: 89.36% Nitrate removal: 76.89% Nitrate removal: 41.61%	[16]
Trickling filter	Synthetic wastewater	Leca Kaldnes Norton	HRT: 0.057 h HRT: 0.02 h HRT: 0.0058 h	Nitrite removal: ~100% Nitrite removal: ~80% Nitrite removal: ~60%	[17]
Combination of microscreen filter, fluidized bed column and trickling filter	Tilapia recirculating	Finturf artificial grass Micro screen filter: 40 μ m Fluidized bed sand: 0.7 mm Trickling filter media: PVC strips, 260 m ² /m ³	HRT: 0.016 h HRT: 0.028 h HRT: 0.208 h	Nitrite removal: ~40% TAN removal: ~65.21%	[18]
Rotating biological contactor	Tilapia wastewater	–	HRT: 0.267 h	TAN removal: ~40%	[19]
Combination of bead filter and rotating biological contactor	Tilapia wastewater	Bead filter: 178 m ²	Flow rate: 146.8 L/min	Nitrite removal: 51.7% TAN removal: 30.7%	[20]
Floating microbead filters	Tilapia wastewater	RBC: 246 m ² /m ³ , 3 rpm Polystyrene bead porosity: 36 to 40% Diameter: 1–3 mm	Flow rate: 75.9 L/min Fish feeding rate: 239 kg/d	TAN area removal rate: 0.30 g/m ² d	[21]
Combination of floating microbead and trickling media biofilters	Tilapia wastewater	Microbead filter microbead diameter: 1 mm specific surface area: 3936 m ² /m ³	Influent TAN concentration: 0.81–4.63 mg/L	Areal nitrification rate: 0.45–0.60 g/m ² d	[22]
Fluidized sand biofilters	Rainbow trout wastewater	D_0 : 0.11 mm	Flow rate: 120 L/min	<u>Siphon bed management</u> TAN removal: 63% cBOD ₅ : 63% TSS removal: 24% phosphorous removal: 41% <u>Shear bed management</u> TAN removal: 88% cBOD ₅ : 79.5% TSS removal: 25% Phosphorous removal: 18%	[23]
		D_0 : 0.19 mm	Flow rate: 120 L/min	<u>Siphon bed management</u> TAN removal: 30% cBOD ₅ : 60% *TSS removal: -4.6% Phosphorous removal: 28% <u>Shear bed management</u> TAN removal: 86% cBOD ₅ : 66% TSS removal: 12% Phosphorous removal: 21%	
Bio-floc technology	Tilapia ponds	–	C/N ratio: 20 23% protein C/N ratio: 20 23% protein + starch	*TAN removal: –80.49% *Nitrite removal: –78.79% TAN removal: ~95% Nitrite removal: 83.33%	[24]
Bio-floc technology	Tilapia pond Shrimp culture	– –	C/N ratio: 20	TAN removal: 88.57%	[25]
Wetlands system (combination of free water surface and subsurface flow)	Culture water of milkfish (<i>Chanos chanos</i>)	Gravel 10–20 mm	HRT: 0.6 d HLR: 0.27 m/d area of application: 5 m ² total wetland volume: 3 m ³	Nitrate and nitrite removal: 42.64% TAN removal: 86–98% Nitrate removal: 82–99% Nitrite removal: >99% TIN: 95–98% Phosphate removal: 32–71%	[26]

Table 1 (continued)

Reactor system	Wastewater	Carrier	Experiment conditions	Results	References
Wetlands system (six subsurface flow)	Culture water of trout farm	Gravel: 4–8 mm	HRT: 0.014 d HLR: 10.6–28.9 m/d area of application: $6 \times 35.8 \text{ m}^2$ wetland volume: 215 m^3	TSS removal: 34.6–68% TAN removal: 87.8% nitrite removal: 35.3–41.6% COD: 24.3–52.2% BOD ₅ : 37.1–48.6%	[27]
6 subsurface wetlands with different filter materials	Synthetic aquaculture wastewater	Steel slag, limestone, gravel, peat 5–10 mm	HRT: 4 d HLR: 0.03 m/d wetland volume: 5 m^3 area of application: $20 \times 1 \text{ m}^2$	Nitrate removal: 44.1–69.7% COD: 52.8–91.1% BOD ₅ : 68.3–99% TSS: 96.8–100%	[28]

UD: undetectable.

LR: loading rate. F/A (L/m²h): ratio of feed water flow rate per membrane area.

D₀: effective diameter. HLR: daily hydraulic load rate.

* Negative sign: increase of concentration. TIN: Total inorganic nitrogen.

and fluidized bed reactor respectively. The overall TAN elimination was approximately 65.21%. Selection of the particle size used in the system was dependent on the cross sectional area and bed depth of the biofilter. However, this type of reactor required an additional aeration system to launch the treatment [46,48].

2.2.3. Rotating biological contactor

In a rotating biological contactor (RBC) system, microorganisms attach to an inert support medium and form a biological film. The support medium is attached to a central horizontal shaft and is partly or totally submerged in the wastewater [19,50]. The advantages of an aerobic RBC are short hydraulic retention times (HRT), high specific surface area, low chances of clogging, insensitivity to toxic substrates, low energy consumption and simple operation [50,51]. Mass and hydraulic loading, rotational speed and organic loading have great influence on the system performance. Brazil [19] has carried out an industrial scale air driven RBC in rearing tilapia at 28 °C. Each RBC system has been divided into three stages where total surface area of stage 1 and 2 are the same (4880 m²), while stage 3 is 25% smaller than the other. Average TAN removal rate is 0.42 g/(m² d) when the rotating speed and hydraulic loading rate of every RBC is approximately 1 rpm and 407 m³/m² respectively. Reyes and Lawson [20] have used a combination of a floating bead filter (FBF) and RBC in treating tilapia wastewater. Total surface area of RBC used is 197 m² and it rotates at 3 rpm. RBC shows that percentage of TAN and nitrite removal is higher than FBF, which means that FBF contributes less in the elimination process. The average TAN and nitrite removal is 30.7% and 51.7% of the influent loading respectively. Easter [52] has concluded that the mass removal of nitrate is linearly related to the influent nitrate loading. However, Brazil [19] indicates that no detectable relationship between the feed loading rate and nitrate removal can be ascertained. The overall nitrification is better than other biofilter types but the RBCs inability to remove solids and its need to be combined with other solid removal treatments to increase its efficiency for wastewater treatment limit its performance [20].

2.2.4. Bio-floc technology

Bio-floc technology (BFT) involves the development and control of dense heterotrophic microbial bio-flocs in the water column by adding carbohydrates to water [24]. This suspended growth consists of phytoplankton, bacteria, aggregates of living and dead particulate organic matter and grazers of the bacteria. Organic nitrogenous waste is converted to bacterial proteinaceous biomass when carbon and nitrogen are well balanced. As a result, bio-floc becomes a feed source for aquatic organisms [24]. The uptake of inorganic nitrogen by bacteria only occurs when the C/N ratio is higher than 10 [53]. Crab et al. [24] has carried out an experiment about maintaining water quality in a wintering pond of tilapia by applying BFT. Temperature in the pond is maintained between 0.4 °C and 4.9 °C and C/N ratio is controlled by the quantity of starch added or carbohydrates in the feed

stream. 95% of TAN is successfully removed when C/N ratio is 20 and protein and starch are added to the system. However, maintaining a constant C/N ratio is not easy despite the high denitrification rate obtained in this technology (Table 1).

Besides that, addition of organic carbon may promote heterotrophic bacterial growth, resulting in limitation of the denitrification process [54]. The bio-floc technology only measures the conversion of TAN to nitrite, but does not account for O₂ consumption by bacteria that converts nitrite to nitrate [55]. This may cause other environmental issues related to nitrate accumulation.

2.2.5. Wetlands

Natural wetlands can remove suspended solids, nitrogen, phosphorous, trace elements and microorganisms contained in wastewater [56,57]. Constructed wetlands have been used to replace the loss of natural wetlands and to treat municipal, industrial and agricultural wastewater [26]. Verhoeven and Meuleman [58] have found that ammonium ions decrease exponentially with longer residence times. Lin et al. [26] have investigated a combination of free water surface wetlands (FWS) and subsurface wetlands (SSF), to remove nitrate and phosphorus from aquaculture wastewater and the results indicate that nitrate removal reaches between 82 and 99%. Naylor et al. [28] have reported 44.1 to 69.7% removal of nitrate by six subsurface wetlands. However, nitrate is insignificantly affected during wetland treatment due to high oxygen saturation in aquaculture effluents [27,59,60]. Wetland wastewater treatment has a high potential to remove nitrate, but requires longer treatment times than other traditional approaches [61].

3. Conventional TOC removal methods

Lowering organic carbon concentrations in recirculating aquaculture systems can enhance denitrification since bacteria that consume organic carbon compete directly for space and oxygen with those bacteria that consume ammonia and nitrite [62]. There are a few practical approaches for removal of low levels of TOC (<10 ppm) in water, which are adsorption and oxidation. Oxidation treatments include ozonation and UV radiation. These processes are briefly reviewed below.

3.1. Adsorption

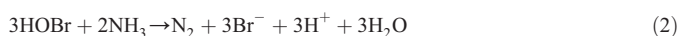
Adsorption process has been extensively used in recirculating aquaculture systems to remove organic chemicals and TOC [63]. The most important parameters in this method are porosity and BET surface area.

Aitchison et al. [64] investigated adsorption onto granular activated carbon of dissolved organic carbon (DOC) that was categorized into two groups, therapeutants and D-glucose. The therapeutants included Malachite Green, formalin, Chloramine-T and Oxytetracycline

which were used in controlling fish parasites and diseases. The characteristics of activated carbon utilized were: BET surface area of 1000 m²/g and porosity of 0.46. The experiment was carried out under various pH, temperature and ionic strength conditions which were similar to real aquaculture effluents' characteristics. The efficiency of overall adsorption of therapeutants was between 24 and 99%, while that for D-glucose was *c.a.* 44–58%. This proved that adsorption had a good ability for organic carbon elimination. However, activated carbon had higher porosity, and could become a breeding ground for microorganisms [65]. Hence, adsorption process is usually a poor choice for TOC removal.

3.2. Ozone and ultraviolet irradiation

Ozone is commonly used to disinfect water supplies, industrial effluents such as textiles, pharmaceuticals, pulp and paper as well as aquaculture systems [66]. Ozone has been used in recirculating aquaculture systems to control pathogens and to oxidize NO₂ to NO₃, organic matter, TAN, or fine suspended particles [67,68]. By adding approximately 3–25 g O₃ per kg of feed to a recirculating aquaculture system, it is possible to improve water quality and result in higher growth rates of fish [68,69]. The ozone reactions are as follows if sufficient bromide is present in marine water [66]:



Krumins et al. [62] has examined the effect of adding the same total amount of ozone (15 g ozone per kg feed) for 24, 12, and 6 h per d, and has found that TOC drops by about 2–4 mg/L during the first 6 h after feeding and then rises steadily for the next 12 h. Tango and Gagnon [66] reported a reduction of 15% of total organic carbon (TOC) by ozonation treatment. However, ozonation by-products are toxic to fish and humans and include species such as bromate [69,70]. Therefore, the application of ozone in aquaculture systems requires further studies.

UV irradiation is used to destroy ozone residuals and to denature the DNA of microorganisms, causing the microorganisms to die or lose their function [71]. Sharrer and Summerfelt [72] investigated a combination of ozone and ultraviolet radiation and found that nearly complete inactivation of heterotrophic and coliform bacteria is possible in recirculating aquaculture system. However, both ozone and UV don't last long in the aquatic system in a similar manner to chlorine thus allowing re-growth of harmful microorganisms with the passage of time [13].

4. Electrochemical technology

The conventional methods do help with nitrate and organic carbon removal but the disadvantages include sludge production, high energy demand, unstable performance and frequent maintenance requirements [15,26]. Hence, research on new methods for nitrate and organic carbon removal in aquaculture wastewater is under way. The past few decades has seen the emergence of electrochemical technology for wastewater treatment. The particular advantages of electrochemical treatment include high efficiency, ambient operating conditions, small equipment sizes, minimal sludge generation and rapid start-up [73–77].

4.1. Electrochemical reduction of nitrate

Electrochemical technology can be applied to reduce nitrate ions to nitrite and finally to nitrogen gas on the cathode surface. The

efficiency of this process is dependent on a few parameters which will be discussed in Section 4.1.2.

4.1.1. Mechanisms of cathodic nitrate reduction

Hydrogen and oxygen gasses are evolved when water undergoes electrolysis. Nitrate (NO₃⁻) and nitrite ions (NO₂⁻) are very soluble in water and form several types of products. Nitrite ions act as intermediate products and further react with water to generate nitrogen gas, ammonia and hydroxylamine (NH₂OH). Reduction of nitrate to nitrogen gas is the desired process but ammonia is usually formed. The eight electrons involved in the reaction are balanced by anodic water electrolysis. Sodium bicarbonate (NaHCO₃) is required to maintain the pH during electrochemical reduction of nitrate since the electrolyte gradually becomes alkaline [78,79]. High alkaline environments prompt the generation of precipitates of magnesium hydroxide and calcium carbonate around the cathode when soluble calcium and magnesium salts are present in the water [80]. Ammonia and nitrite are the two main end products generated and are considered as major limitations to the efficacy of electrochemical denitrification. Chloride-salt is widely added to overcome this issue. In this process, chlorine is oxidized at the anode and reacts with water to form hypochlorous acid (HOCl). The hypochlorite ions then react with nitrite and ammonia to produce nitrate and nitrogen [75,76]. Sodium chloride salt is usually selected [77,81,82]. The general mechanism of the electrochemical reduction of nitrate is summarized in Table 2 [76–79,81,82].

4.1.2. Performance of electrochemical technology

The operating parameters that have significant influences upon electrochemical denitrification processes include electrode material, current input, pH, conductivity, sodium chloride (NaCl) concentration and initial concentration of TAN or nitrate ions. The electrochemical denitrification technique has been applied by many researchers to remove nitrate and a summary of their results are presented in Table 3.

Li et al. [83] have investigated the influence of NaCl addition, current density, initial pH, temperature and nitrate concentration by using Fe and Ti/IrO₂ as cathode and anode. In the absence and presence of 0.5 g/L NaCl, the nitrate removals are 92.8% and 87.1% in 180 min, respectively. There is no ammonia and nitrite detected in the presence of NaCl since they are oxidized by hypochlorite as shown in Table 2. Moreover, nitrate removal rate increases linearly with current density but decreases with increasing NaCl concentration. Nitrate elimination is more advanced at high temperatures and at initial pH values of either 3.0 or 11.0. Li and co-workers [75] have used different types of materials as anodes to perform high efficiency nitrate reduction. The authors have found that high nitrate removal is

Table 2

General mechanisms involved in the electrochemical reduction of nitrate.

Process	Reaction steps
Cathodic water electrolysis	2H ₂ O + 2e ⁻ → H ₂ + 2OH ⁻
Anodic water electrolysis	4OH ⁻ → O ₂ + 2H ₂ O + 4e ⁻
Reactions of nitrate ion and water molecules	NO ₃ ⁻ + H ₂ O + 2e ⁻ → NO ₂ ⁻ + 2OH ⁻ NO ₃ ⁻ + 3H ₂ O + 5e ⁻ → ½ N ₂ + 6OH ⁻ NO ₃ ⁻ + 6H ₂ O + 8e ⁻ → NH ₃ + 9OH ⁻
Reaction of nitrite ion and water molecules	NO ₂ ⁻ + 2H ₂ O + 3e ⁻ → ½ N ₂ + 4OH ⁻ NO ₂ ⁻ + 5H ₂ O + 6e ⁻ → NH ₃ + 7OH ⁻ NO ₂ ⁻ + 4H ₂ O + 4e ⁻ → NH ₂ OH + 5OH ⁻
Reduction of nitrate (especially sodium nitrate) to produce ammonia	NO ₃ ⁻ + 2H ₂ O → NH ₃ + 2O ₂ + OH ⁻
Sodium bicarbonate added to maintain pH of electrolyte	NaNO ₃ + NaHCO ₃ + H ₂ O → NH ₃ + 2O ₂ + Na ₂ CO ₃
Chlorine formed in anodic electrolysis	2Cl ⁻ → Cl ₂ + 2e ⁻
Reaction of chlorine and water molecules	Cl ₂ + H ₂ O → HOCl + H ⁺ + Cl ⁻
Reaction of nitrite and hypochlorite ions	NO ₂ ⁻ + HOCl → NO ₃ ⁻ + Cl ⁻ + H ₂ O
Reaction of ammonium and hypochlorite	2NH ₄ ⁺ + 3HOCl → N ₂ + 5H ⁺ + 3Cl ⁻ + 3H ₂ O

Table 3

A summary of results obtained by various workers in the electrochemical reduction of TAN and Nitrate.

Process	Electrode material		Composition of electrolyte	Experiment conditions	Results	References
	Anode	Cathode				
Batch	Ti/Pt	Cu/Zn plate	Nitrate and 0.5 g/L Na ₂ SO ₄	NaCl: 0.75 g/L N/A	Nitrate removal: ~74% NH ₃ -N generated: ~1.5 mg/L	[75]
	Ti/IrO ₂ -Pt			NaCl: 0.5 g/L	Nitrate removal: ~86.7% NH ₃ -N generated: ~20 mg/L	
				NaCl: 0.75 g/L N/A	Nitrate removal: 82.7% NH ₃ -N generated: 14.7 mg/L	
	Ti/RuO ₂ -Pt		N/A	Nitrate removal: 77.4% Nitrate removal: ~66.7% NH ₃ -N generated: ~46.7 mg/L		
Batch	Ti/IrO ₂ -Pt	Cu-Zn	Synthetic nitrate solution with 0.5 g/L Na ₂ SO ₄	Current density: 40 mA/cm ² NaCl: 0.5 mg/L	Nitrate removal: 90.3%	[79]
Batch	Graphite	TiO ₂	Synthetic aquaculture wastewater (sodium nitrite and ammonium chloride)	Initial NO ₂ - N: 5 mg/L NaCl Concentration: 2000 mg/L Current input: 1.5 A pH: 7 Removal time: 30 min	Nitrite removal: ~99%	[81]
Batch	Ti/IrO ₂ -Pt plate	Fe plate	Nitrate and 0.5 g/L Na ₂ SO ₄	Current density: 20 mA/cm ² Initial pH: 7 NaCl: 0.5 g/L	Nitrate removal: 87.1%	[83]
Batch, divided two electrode cell with cation and anion permeable membrane	Ti	Ti	Aquaculture wastewater	Current density: 0.06 mA/cm ² Electrolysis time: 48 h Fenton reagent: 40 mM	Nitrate removal: 94.8%	[84]

obtained using Ti/IrO₂-Pt and Ti/Pt as anode material with negligible formation of ammonia and nitrite. The efficiency of nitrate removal is higher without NaCl, but ammonia and nitrite tend to accumulate in the treated solution. Therefore some experimental variations are necessary to avoid such conditions. As a result, by increasing the sampling time from 180 min to 300 min, Li et al. [79] have achieved 90.3% of nitrate reduction using the same reactor configuration and without the accumulation of nitrite and ammonia.

Electrochemical technique can also be applied for nitrite removal [76]. Lin and Wu [81] have used two pairs of graphite and Ti/O₂ as anodic and cathodic electrodes with inter-electrode gap of 1.5 cm. The total effective surface area and initial pH of the solution are 22.6 cm² and 7, respectively. They have found that the time for total nitrite removal is directly proportional to initial nitrite concentration when 1.5 A current is applied. Chloride ion present in the system enhances the electrochemical nitrite removal. Conductivity and current input are the most important operating variables in comparison to pH in the electrochemical process. pH control may result in other by-products which can limit nitrite and ammonia removal. NaCl is used to eliminate ammonia and nitrite by-products, but it tends to decrease nitrate removal efficiency. Hence, an optimum dose of NaCl has to be determined before varying other parameters [76].

4.2. Electrochemical oxidation of organic compounds

TOC can be eliminated by electrochemical oxidation at the anode. Electrochemical oxidation of TOC is divided into direct and indirect anodic oxidation methods which have been discussed in the following section.

4.2.1. Mechanisms of direct anodic oxidation

Direct anodic oxidation is used to treat wastewater containing non-biocompatible pollutants such as phenol to form biocompatible organics such that biological treatment can be employed [84–86]. In electrochemical conversion, organic compounds can be oxidized directly at anode surfaces through physically adsorbed hydroxyl radicals, MO_x(•OH) that produce carbon dioxide as the final product. This hydroxyl radical also produces higher oxide species (MO_{x+1})

on dimensionally stable anodes (DSA). DSA is an inert metal coated with noble metal oxides such as RuO₂ and IrO₂. The mechanism of direct anodic oxidation is illustrated in Table 4 [84–86].

Meanwhile, the hydroxyl radical also enhances the production of oxygen. The oxygen evolution is considered as a factor that limits the efficiency of the electrochemical process [85,86]. Therefore, oxidizing agents are recommended to be used to increase the oxidation rate.

4.2.2. Mechanisms of indirect anodic oxidation

Oxidizing agents such as peroxide, Fenton's reagent, sodium chloride, chlorine, hypochlorite or peroxydisulfate are added in the case of indirect anodic oxidation to react with organic pollutants. Oxide electrodes are very active for Cl₂ evolution, so this agent is commonly used in oxidation of organic matter [85,87,88]. Chloride oxidizes to form chlorine (Cl₂) which further reacts with water to produce hypochlorous acid (HOCl) and hypochlorite ions (OCl⁻). Then, hypochlorite ions oxidize the organic matter to produce carbon dioxide and organochlorine compounds (RCl) which can be considered to be mutagenic and carcinogenic [89–91]. The major reaction mechanisms of indirect anodic oxidation are given in Table 5 [87–91].

Another effective means of oxidation of organic compounds involve the electro-Fenton method. In general, the Fenton's reagent is a mixture of hydrogen peroxide and ferrous ion (Fe²⁺) in acidic medium. The ferrous ion can be regenerated by reducing the ferric

Table 4

General mechanism of direct anodic oxidation of organic compounds.

Process	Reaction steps
Water is electrolyzed by anodic catalysis to produce adsorbed hydroxyl radicals	MO _x + H ₂ O → MO _x (•OH) + H ⁺ + e ⁻
Oxidation of organic compounds by MO _x (•OH)	R + MO _x (•OH) → CO ₂ + inorganic ions + MO _x + H ⁺ + e ⁻
Formation of higher oxide species	MO _x (•OH) → MO _{x+1} + H ⁺ + e ⁻
Oxidation of organic compounds by higher oxide	MO _{x+1} + R → MO _x + RO
Oxygen evolution	MO _x (•OH) → MO _x + ½ O ₂ + H ⁺ + e ⁻ MO _{x+1} → ½ O ₂ + MO _x

Table 5
General mechanism of indirect anodic oxidation of organic compounds.

Oxidizing agent	Reaction steps
Chloride	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$
	$\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^-$
	$\text{HOCl} \rightarrow \text{H}^+ + \text{OCl}^-$
	$\text{OCl}^- + \text{R} \rightarrow \text{CO}_2 + \text{inorganic ions} + \text{H}^+ + \text{e}^-$
	$\text{OCl}^- + \text{RCl} \rightarrow \text{R}$
	$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^\cdot$
Fenton reagent	$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^\cdot + \text{H}^+$

ion (Fe^{3+}) [92,93]. Electro-Fenton process is more economical and efficient in removing organic matter compared to the conventional Fenton process [94].

4.2.3. Performance of direct and indirect anodic oxidation processes

For direct anodic oxidation, the electrode material is the main figure of merit. RuO_2 has been widely used due to its mechanical resistance as well as its cheap and successful scale-up in the electrochemical industry. Boron doped diamond (BDD) is considered as a good material in electrochemical processes due to its feasibility of producing hydroxyl radicals. However, it is very expensive [85]. Feng et al. [88] appears to be the only researcher who has applied direct electrochemical oxidation of organic matter on actual aquaculture wastewater. They have investigated the production of hydroxyl radicals on three different anode materials and have found that hydroxyl radicals are detected in larger quantities on Ti/ RuO_2 - TiO_2 in comparison to platinum and titanium anodes (no radicals are detected for titanium anodes). In a pilot plant electrochemical system, iron and Ti/ RuO_2 - TiO_2 are combined for use as an anode material to treat pond water. COD and BOD are successfully decreased as much as 92.4% and 78%, respectively after treatment. There are a few researchers who used indirect anodic oxidation for treating aquaculture wastewater and these have been highlighted in Table 6.

Removal of organic substances is directly proportional to the concentration of the oxidizing agent used, but an excess of peroxide (exceeding toxicity limits) is found to remain in the wastewater after treatment [84,95]. Diaz et al. [96] have used chloride as an oxidizing agent with boron doped diamond (BDD) electrodes to treat and reuse seawater in recirculating aquaculture systems. They have found that about 88% of COD has been removed at a current density of 50 A/m^2 . Virkutyte and Jegatheesan [84] have used 40 mM of Fenton's reagent in an electrodialytic reactor to remove 9.2–11.2 mg/L of TOC. The authors have proved that Fenton's reagent is more advanced in organic oxidation and 97.3% of TOC has been removed in 48 h.

Organic matter is eliminated with high efficiency by applying direct and indirect anodic oxidation methods. However, these techniques are more dependent on the cost of electrode materials and

Table 7
Mechanism of denitrification with hydrogen gas as electron donor.

Process	Reaction steps
Water electrolysis at cathode	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$
Nitrate reduction	$\text{NO}_3^- + \text{H}_2 \rightarrow \text{NO}_2^- + \text{H}_2\text{O}$
Nitrite reduction	$\text{NO}_2^- + \text{H}^+ + 0.5\text{H}_2 \rightarrow \text{NO} + \text{H}_2\text{O}$
Nitric oxide reduction	$2\text{NO} + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$
Nitrous oxide reduction	$\text{N}_2\text{O} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$
Overall denitrification	$2\text{NO}_3^- + 5\text{H}_2 + 2\text{H}^+ \rightarrow \text{N}_2 + 6\text{H}_2\text{O}$

oxidizing agents. Detailed information is reported on the performance of direct and indirect anodic oxidation of organic matter in Table 6.

5. Bio-electrochemical technology

Bio-electrochemical systems (BESs) are divided into two major groups which are microbial fuel cells (MFCs) and microbial electrolysis cells (MECs). They have great potential for simultaneous production of energy as well as for wastewater treatment. These systems use microorganisms for catalysis of electrochemical reactions [97,98]. In MFCs, chemical energy of organic material in wastewater is converted into electrical energy, while in MECs, external electricity is utilized to generate a product (e.g. hydrogen) at the cathode [97]. BESs have been widely used for the removal of organic materials (anodic oxidation) with a lower sludge generation yield (ranges from 2.4 to 26.5 times lower) compared to aerobic activated sludge processes [98]. Thus, BESs are known as a clean technology for wastewater treatment.

5.1. Bio-electrochemical reduction of nitrate

BESs can be used to eliminate nitrate through a cathodic reduction process. This process is similar to electrochemical nitrate reduction, but denitrifying microorganisms are added to increase nitrate removal efficiency.

5.1.1. Mechanisms of cathodic nitrate reduction

In BESs, autotrophic denitrification gives a higher efficiency than heterotrophic denitrification. Autotrophic denitrifying microorganisms utilize hydrogen gas as the electron donor that is produced on the cathode surface by electrolysis of water. These autotrophic denitrifying microorganisms are called autohydrogenotrophs [99]. Hydrogen gas is used to reduce nitrate to nitrite (NO_2^-) which further reacts with hydrogen to form nitric oxide (NO). Then, this compound continues to be reduced to nitrous oxide (N_2O) and finally forms nitrogen gas (N_2). The reaction mechanism of this denitrification process is given in Table 7 [99] and a schematic representation of the process is shown in Fig. 2.

Table 6
Direct and Indirect Electrochemical Oxidation of Organic Compounds.

Cell operation and configuration	Electrode material		Type of wastewater	Experimental Conditions	Results	References
	Anode	Cathode				
Divided two electrodes with cation and anion permeable membrane	Ti	Ti	Aquaculture wastewater	Input current: 30 mA (0.06 mA/cm^2) pH: 2.2–2.4 Electrolysis time: 48 h	TOC removal: 97.3%	[84]
Combination of two batch electrolysis methods	Iron	Stainless steel	Pond water	Fenton's reagent: 40 mM Flow rate: $0.3 \text{ m}^3/\text{h}$	Phosphorus removal: 89.86%	[88]
	Ti. RuO_2 - TiO_2	Stainless steel		Current density: 3 mA/cm^2	COD removal: 92.4% BOD removal: 78% Suspended solids removal: 97.1%	
Divided recirculation batch electrolysis	BDD	BDD	Seawater containing chloride ion	Flowrate: 6 L/min Current density: 5 mA/cm^2	TAN removal: ~100% COD removal: ~88%	[96]

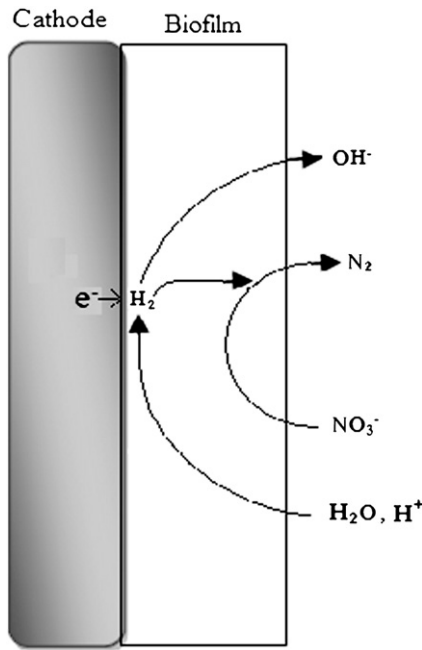


Fig. 2. Schematic of denitrification reaction within biofilm [100].

5.1.2. Factors controlling nitrate removal

There are limited publications regarding nitrate removal from real aquaculture wastewater by using BES. Hence, synthetic wastewater has been assumed to represent aquaculture wastewater. Some important parameters have been investigated in denitrification processes and these are cathodic material, initial pH, current density and nitrate loading rate.

5.1.2.1. Cathodic material. Graphite granules have been used recently in treating wastewater due to its large surface area that allows the bacteria to attach quickly and act as a third bipolar electrode [7,101]. Abiotic electrode such as graphite, carbon, platinum and stainless steel are usually used in conventional BESs. Platinum and stainless steel are commonly used but expensive and unsustainable when applied on bacterial solutions [97,102]. Another disadvantage of the platinum electrode is that their activities are disrupted by the formation of a platinum oxide (PtO) layer at the cathodic electrode surface [103]. Biological electrodes have become popular as they are inexpensive and also possess sustainable properties. In conventional BESs, anodic and cathodic compartments are colonized by bacteria that oxidize hydrogen gas and organic substrate or reduce TAN to nitrogen gas. For bio-electrode, these microorganisms are used as an inert electrode to accept electrons [102]. Gregory et al. [104] state that these andophilic microorganisms have an ability

to use an inert electrode to take up electrons from graphite electrodes without needing hydrogen gas for nitrate reduction. Clauwaert et al. [105] have proved that the bio-anode oxidizing acetate could be combined with a bio-cathode for reducing nitrate to nitrogen gas. Graphite and carbon are the most popular materials for bio-anodes and bio-cathodes as they are inexpensive and suitable for growing electrochemically active biofilms. However, these materials have high electrical resistivity which causes larger electrode ohmic losses when the system is scaled-up. Hence, graphite or carbon electrodes are supported by a conductive metal current collector such as a stainless steel mesh [97].

5.1.2.2. pH. The pH of the wastewater is the main influencing factor on the performance of hydrogenotrophic denitrification [106]. The optimum pH for denitrification is dependent on the cultures used as well as the operating conditions [43,107]. When pH value is higher than 8.6, it can cause nitrite accumulation problems, whereas when pH is lower than 7.0, carbonate ions are decomposed thereby decreasing the denitrification rate [43]. Carbon dioxide is popularly used to adjust the pH of wastewater to neutral conditions by capturing hydroxyl ions by means of H₂CO₃ and HCO₃⁻ [7,101]:



In the research of Clauwaert et al. [107], pH of anolyte and catholyte is adjusted by adding NaOH and HCl respectively. Without continuous pH adjustment, only 26.3% nitrate is removed and this further improves to 74% when the pH is maintained at 7.2. The authors conclude that the optimal pH for denitrification is between 7 and 8. This optimum pH value is also supported by Wan et al. [108] who conclude that a suitable pH range for denitrification is in between 7.05 and 7.20.

5.1.2.3. Current density. Current density influences hydrogen formation at the cathode, which also affects the efficiency of nitrate reduction since hydrogen supply is important in hydrogenotrophic denitrification. Increasing current density input from 21.1 mA/cm² to 23.4 mA/cm² enhances the nitrate reduction efficiency from 72% to 74% [107]. The result of Sakakibara and Nakayama [109] also shows a similar trend, which indicates that increasing current density input from 0.46 mA/cm² to 0.82 mA/cm² improves average current-denitrification efficiency (η) from 61% to 70%. The current-denitrification efficiency (η) can be calculated from Eq. (7)

$$\eta = \frac{Q(C_{f, \text{NO}_3^-} - C_{\text{NO}_3^-})}{I/5F} \tag{7}$$

Table 8
Bio-electrochemical reduction of nitrate.

Cell operation and configuration	Electrode material		Type of wastewater	Experimental conditions	Results	References
	Anode	Cathode				
Divided electrolysis cell with graphite granules and cation exchange membrane connected to a Ag/AgCl reference electrode	Bio-anode	Bio-cathode	Synthetic wastewater	pH: 7.2 Current density: 23.4 mA/cm ² Flowrate: 0.35 L/h	Nitrate removal: 74%	[107]
Divided electrolysis cell with proton exchange membrane	DSA	Cu	Synthetic wastewater	Current input: 50 mA Initial NO ₃ -N: 22.13 mg/L pH: 7.05–7.20	Nitrate removal: 98.5%	[108]
Cell with 8 cathodes and 2 anodes separated by a porous water permeable plastic foam	Pt	Titanium	Synthetic wastewater	Current density: 0.82 mA/cm ² pH: 6–7 HRT: 6 h	η: 70%	[109]
Batch bio-electrolysis cell divided by cation selective membrane	DSA	Graphite	Synthetic wastewater	Current input: 200 mA Temperature: 30 °C	Nitrate removal: ~93%	[111]

Note: η is the current-denitrification efficiency. HRT: Hydraulic Residence Time. DSA: Dimensionally Stable Anode.

Table 9
Bio-electrochemical oxidation of organic matter.

Cell operation and configuration	Electrode material		Type of wastewater	Experiment conditions	Results	References
	Anode	Cathode				
Divided electrolysis cell with graphite granules and cation exchange membrane	Graphite	Graphite	Synthetic wastewater	Flow rate: 200 mL/min resistance: 5 Ω pH: 7	OM removal: 93.59%	[114]
Divided electrolysis cell with proton exchange membrane	Graphite	Graphite	Synthetic wastewater (ferricyanide catholyte)	Flow rate: 100 mL/min pH: 6 operation period: 131 h	COD removal: 74.2%	[118]
			Synthetic wastewater (aerated catholyte)	Flow rate: 100 mL/min pH: 6 operation period: 154 h	COD removal: 74.15%	
Combining oxidic-biocathode MFC (O-MFC) and anoxic-biocathode MFC (A-MFC)	Graphite	Bio-cathode	Synthetic wastewater	Recirculation ratio: 1:1 pH: 7–7.5 resistance at A-MFC: 5 Ω resistance at O-MFC: 20 Ω	TAN removal: 97.4% total nitrate removal: 97.3% COD removal: 98.8%	[119]

N.B. Recirculation ratio: ratio between recirculated flow rate and the total influent flow rate; OM: organic matter.

Where, C_f , NO_3^- and $C_{NO_3^-}$ are influent and effluent concentrations of nitrate (mol/cm^3),

Q is volumetric flow rate (cm^3/s),

I is current (mA)

F is Faraday's constant (C/mol).

Wan et al. [108] use a combination of membrane and bio-electrochemical techniques to eliminate nitrate in synthetic wastewater. A proton exchange membrane is used to separate anodic and cathodic compartments and autotrophic denitrifying microorganisms are inoculated into the cathodic half-cell. The authors have found that a current input from 30 to 100 mA does not influence the denitrification rates since hydrogen gas generated by water electrolysis is saturated in the cathodic half-cell. Therefore, hydrogen supply rate has no effect on the denitrification process. Moreover, nitrate removal rate reaches 42.5% when the current input is 15 mA because hydrogen gas generated is inadequate for denitrification purposes. However, Flora et al. [110] conclude that larger current densities yield excess of hydrogen gas, which remains in the biofilm and decreases the denitrification rate.

5.1.2.4. Initial nitrate loading rate. An investigation was carried out by Clauwaert et al. [107] that showed that nitrate removal rate was directly proportional to nitrate loading rate until an optimum value was reached. Wan et al. [108] used a proton exchange membrane

electro dialysis cell attached with autotrophic microorganisms to compare nitrate removal rate with three different initial nitrate-nitrogen concentrations (22.13, 15.76 and 11.31 mg/L NO_3^- -N respectively). The trend of the results was similar to that reported by Clauwaert et al. [107] since the quantity of hydrogen generated by the cathode was sufficient for nitrate reduction. In conclusion, hydrogen affected the nitrate reduction rate indirectly (Table 8).

5.2. Bio-electrochemical oxidation of TOC

Total organic compounds are oxidized by microorganisms to form carbon dioxide and protons as final product [7,97,112]. It is assumed that the growth of the microorganisms is stable when the growth parameters such as temperature and organic carbon source are maintained in a relatively constant manner [7]. There are limited publications regarding the application of BESs for the removal of TOC in actual wastewater and thus it is assumed that the chemical compounds used in synthetic wastewater are similar to those in real aquaculture wastewater.

5.2.1. Factors controlling TOC removal

There are two main parameters that influence bio-electrochemical TOC removal and these are electrode material and pH. These two factors are discussed in the following sub-sections.

5.2.1.1. Electrode material. Performance of BESs is variable on different electrode materials because these affect activation polarization losses.

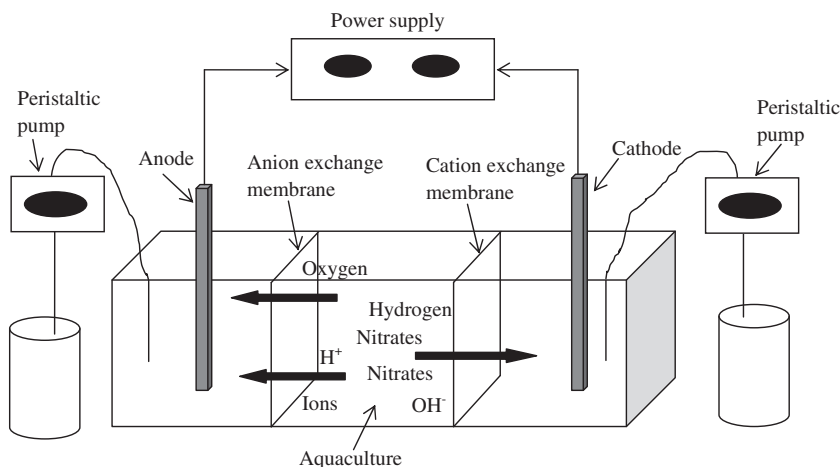


Fig. 3. Schematic set-up of an electro-Fenton wastewater treatment system for simultaneous denitrification and TOC removal from synthetic wastewater [84].

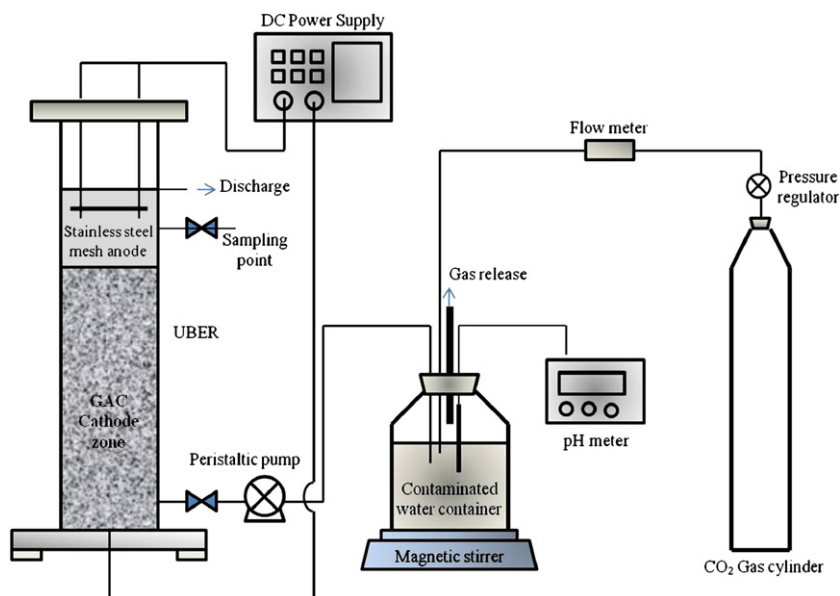
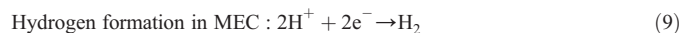
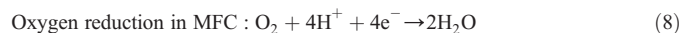


Fig. 4. Schematic set-up of an upflow bio-electrochemical wastewater treatment system for denitrification purposes [120,121].

Activation polarization is an energy barrier that must be overcome by the reacting species before current and ions flow through the electrode [103]. Electrodes also should be highly conductive, non-corrosive, possess high specific surface area, should be non-fouling, inexpensive and the materials must be suitable for bacterial growth [113]. Viridis et al. [114] reported that 93.59% of organic matter removal can occur when carbon is used as anode and cathode material.

5.2.1.2. pH. The protons produced in anodic TOC oxidation can acidify the biofilm and affect BESs performance [97]. Picioreanu et al. [115] reported that pH decreases when microorganisms convert organic matter and then remains constant when the organic matter is depleted. The cathodic oxygen reduction in MFCs and cathodic hydrogen formation in MECs are both proton consuming reactions, resulting in an increase in pH value at the cathodic compartment. Consequently, the overall driving force (E.M.F.) of the BESs and TOC oxidation rate also decrease. The electrical energy output of MFC is reduced, while more energy input is required in MEC operation [97,98,109]. The influence of pH on the reactions involved in both MFCs and MECs is shown below.



Mohan et al. [116] found that bacteria under neutral pH are susceptible to methanogenic activity where the electron and H^+ are reduced to form methane. The ideal pH range is 5.5–6.0 to limit the methanogenic bacterial activity [116,117]. However, Viridis et al. [114] have found that 93.59% removal of organic matter could be achieved when the pH of the wastewater is 7.0. The main differences between these two results are due to the differences in the cell configuration and wastewater recirculation rates. This proves that the interaction between the initial pH of electrolyte and other parameters has a strong effect on TOC removal in aquaculture wastewater. Some recent information in this connection is highlighted in Table 9.

5.3. Simultaneous removal of nitrate and organics

Simultaneous removal of nitrate and TOC from aquaculture wastewater has recently gained some popularity due to its cost effective

advantage. This process is commonly applied on electro-Fenton and bio-electrochemical systems. Virkutyte and Jegatheesan [84] have focused on the simultaneous removal of both organics and nitrate by means of the Electro-Fenton process (Fig. 3). Organic pollutants are attacked by hydroxyl radicals and nitrate is reduced to nitrogen at the cathode. Efficiency of nitrate and organic removals has been reported to be 94.8% and 97.3%, respectively. Microbial fuel cells (MFC) have been used by Viridis et al. [114] for simultaneous removal of these two compounds and it is found that nitrate and organic matter removal are 70% and 93%, respectively. In another study on MFC conducted by Xie et al. [119] nitrate and organic matter removal efficiency is reported to be 97.3% and 98.8%, respectively. Fenton's reagent is discouraged from being used in wastewater treatment due to the formation of toxic intermediates [7]. Hence, further research is required on simultaneous removal of nitrate and organics by bio-electrochemical methods using reactor configurations as shown in Fig. 4. The application of actual aquaculture wastewater in such systems is also necessary in future research endeavors.

6. Conclusion

The literature reports several physicochemical and biological methods for the removal of TAN, nitrate and TOC. However, they face critical issues such as membrane fouling or generation of toxic by-products that limit their successful application in the field. The electrochemical method could be a good alternative due to its high efficiency, ambient operating conditions, small equipment sizes, minimal sludge generation and rapid start-up. However, the generation of ammonia and nitrite limit its efficiency. Addition of chloride salts partially solves the problem but the nitrate removal efficiency remains poor.

As a consequence, bio-electrochemical reactors (BERs) have evolved, which have the potential to generate energy from wastewater (by means of microbial fuel cells) or a valuable product such as hydrogen (using microbial electrolysis cells). The main parameters that affect denitrification in bio-electrochemical systems are cathodic material, pH, current density and initial nitrate loading rate, while for TOC removal, electrode material and pH have the greatest influence on the operating variables. The bio-electrochemical method is more beneficial for simultaneous nitrate and TOC elimination since it is known as a green technology that generates less sludge and by-

products. However, applications of real aquaculture wastewater have been limited in such systems and more work is encouraged in this area.

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