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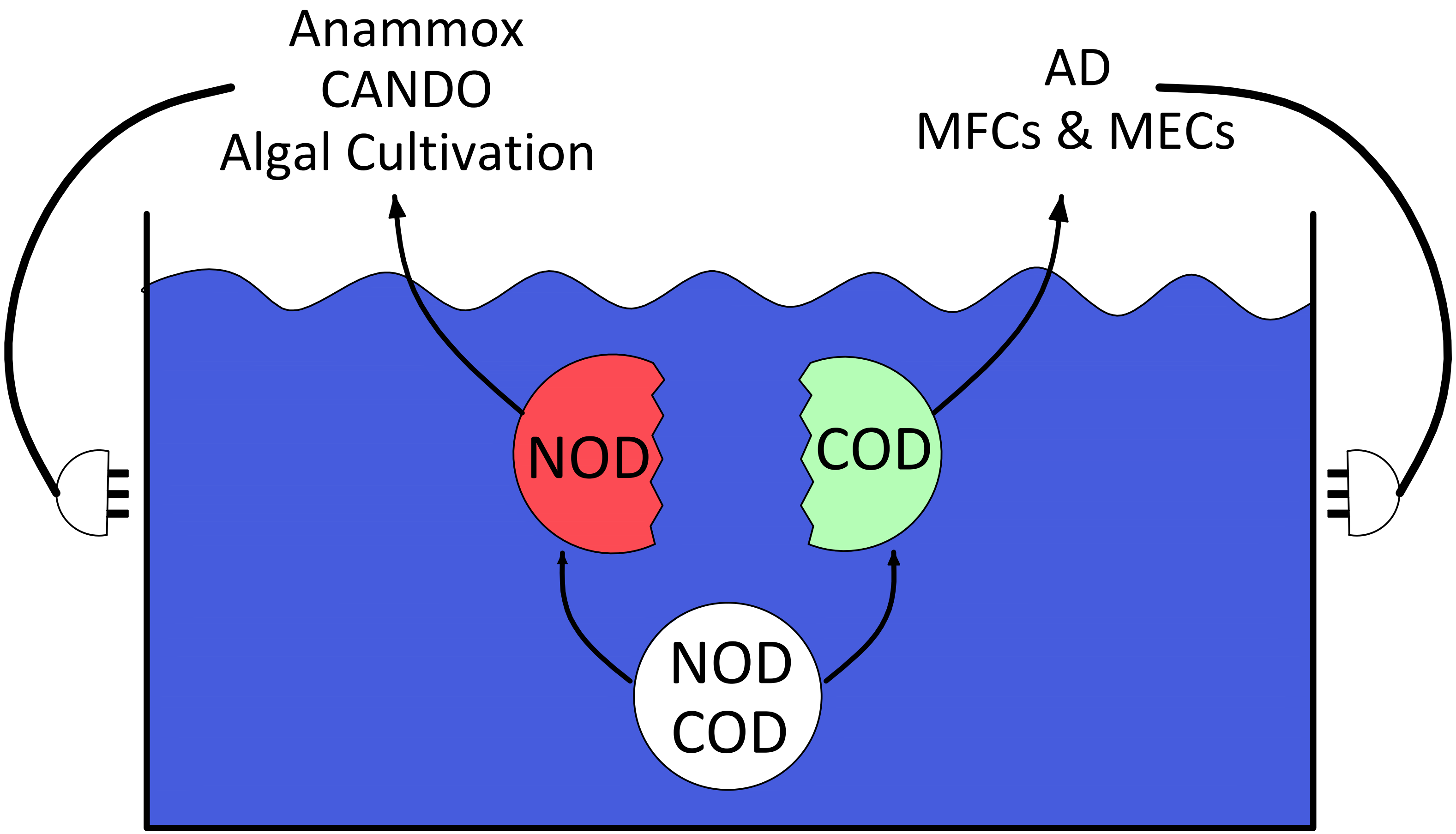

An optimal way to maximize energy recovery from wastewater treatment is to separate carbon and nutrient (particular N) removal processes.

Environmental Impact Statement:

Municipal wastewater treatment accounts for approximately ~3% of the electricity load in the US. Much of this electricity is used for aeration in bioprocesses that remove deleterious organic matter and reactive nitrogen. However, organic matter and reactive nitrogen have substantial embedded chemical energy. Water utilities, engineering firms, and researchers are now transitioning to a paradigm of viewing wastewater as valuable feedstock for resource and energy recovery. Here, we critically review five emerging bioprocesses at the leading edge of a movement towards energy neutral or even energy positive wastewater treatment. We emphasize the importance of separating nitrogen and organic waste streams to maximize energy capture, and we focus specifically on innovative routes for low energy or energy yielding nitrogen management strategies.

Towards Energy Neutral Wastewater Treatment: Methodology and State of the Art

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ABSTRACT

Conventional biological wastewater treatment processes are energy-intensive endeavors that yield little or no recovered resources and often require significant external chemical inputs. However, with embedded energy in both organic carbon and nutrients (N, P), wastewater has the potential for substantial energy recovery from a low-value (or no-value) feedstock. A paradigm shift is thus now underway that is transforming our understanding of necessary energy inputs, and potential energy or resource outputs, from wastewater treatment, and energy neutral or even energy positive treatment is increasingly emphasized in practice. As two energy sources in domestic wastewater, we argue that the most suitable way to maximize energy recovery from wastewater treatment is to separate carbon and nutrient (particularly N) removal processes. Innovative anaerobic treatment technologies and bioelectrochemical processes are now being developed as high efficiency methods for energy recovery from waste COD. Recently, energy savings or even generation from N removal has become a hotspot of research and development activity, and nitritation-anammox, the newly developed CANDO process, and microalgae cultivation are considered promising techniques. In this paper, we critically review these five emerging low energy or energy positive bioprocesses for sustainable wastewater treatment, with a particular focus on energy optimization in management of nitrogenous oxygen demand. Taken together, these technologies are now charting a path towards to a new paradigm of resource and energy recovery from wastewater.

1. INTRODUCTION

Wastewater can be thought of as a "misplaced resource" well-suited for recovery of energy, valuable materials, and clean water. It has been estimated that the total energy content of municipal wastewater is approximately 23 W/capital contained in organic C, and 6 and 0.8 W/capital embedded in ammonium-N and phosphate-P[1], respectively. Although complete capture of this energy potential may be unrealistic, emerging technologies are now enabling recovery of significant energy resources from waste. Conventionally, engineers have focused on energy recovery from organic carbon in wastewater via anaerobic digestion or, more recently, bio-electrochemical systems. Increasingly stringent nitrogen and phosphorous effluent standards have now put nutrient removal or recovery during wastewater treatment on level footing in terms of treatment goals with organic carbon removal for many wastewater treatment plants, and traditional nutrient removal methods require substantial energy inputs. A suite of anammox-based processes that rely on autotrophic nitrogen removal have made great progress in nitrogen removal and energy consumption reduction. Recently, direct energy recovery from waste nitrogen has proven feasible using the CANDO process. And an innovative method that combines microalgae production and nutrient removal has the potential to produce clean water and biofuel feedstock simultaneously. Combined with energy generation from organic carbon, these innovative low energy nitrogen removal methods now enable us to approach self-sufficient wastewater treatment. In this paper, we review cutting-edge bioprocesses that may enable energy neutral or even energy positive wastewater treatment processes.

2. LOW ENERGY OR ENERGY POSITIVE APPROACHES FOR NOD REMOVAL

Besides the removal of COD, nutrient removal, especially the removal of nitrogen (N), is also of increasing concern during the wastewater treatment process. In 2008, the US National Academy of Engineering included management of the N cycle as one of fourteen grand challenges facing the engineering community in the 21st Century[2]. Indeed, of nine "planetary boundaries" identified by Rockstrom and colleagues[3] delimiting unacceptable environmental change, human interference with the N cycle was one of three boundaries to have already been exceeded. It is thus clear that anthropogenic production of reactive nitrogen has significantly disrupted the natural nitrogen cycle. This disruption has led to an array of environmental and public health problems, including ammonia toxicity to aquatic life, oxygen depletion and eutrophication of nutrient-limited water bodies resulting in vast dead zones in the ocean margins, increasing atmospheric concentrations of the potent greenhouse gas nitrous oxide, stratospheric ozone depletion, and direct adverse effects to human health (e.g. methemoglobinemia caused by nitrates)[2]. Nitrification/denitrification, which is the most common biological nitrogen removal (BNR) method in conventional wastewater treatment plant (WWTP), is an energy intensive process that couples chemical oxygen demand (COD) and nitrogenous oxygen demand (NOD) removal. High NOD increases the need for oxygen supply and aeration, which is the dominant the energy consuming process (～50%) in typical WWTPs with N removal[4,5]. Therefore, it is unlikely that energy-positive wastewater treatment can be achieved without innovative management of nutrient removal processes.

Decoupling COD and NOD removal is a promising strategy to decrease energy demand for nutrient removal and divert carbon sources to energy production[6]. We summarize three emerging strategies for NOD management:

1. **Nutrient recovery or direct reuse:** This is potentially the most sustainable, yet challenging future strategy for N management. Direct irrigation of crops or landscapes with nutrient-rich effluent from anaerobic secondary treatment of municipal wastewater may be a particularly attractive in rural, water-scarce locales[7], but is challenging in urban environments where transport distances to agricultural lands are long. Another promising option is source separation of urine, the dominant reservoir of nutrients in domestic wastewater, and treatment specifically for N and P recovery. Promising research and implementation efforts in this direction are reviewed elsewhere[8,9].
2. **Low-energy NOD removal:** Innovative N removal bioprocesses that "short-circuit" the conventional nitrification-denitrification paradigm offer the opportunity to dramatically decrease aeration and COD requirements for N removal, thereby conserving energy and offering the opportunity to route additional COD to energy production. Likely the most promising short-circuit N removal process leverages the combined microbial processes of nitritation and anammox.
3. **Energy recovery from NOD:** Energy can be recovered from NOD bound in reactive forms of nitrogen if the nitrogen can be removed from wastewater and processed to generate heat or electricity. Ammonia and nitrous oxide are two nitrogen species found in wastewater that meet these criteria[10]. Promising methodologies in this direction include the CANDO process for energy recovery from nitrous oxide, and a suite of emerging high-rate algal bioprocesses.

In this section, we focus on strategies 2 and 3 by reviewing three promising and rapidly developing methods for energy reduction, or even recovery from NOD removal: nitritation-anammox (aerobic ammonium oxidation coupled to anaerobic ammonium oxidation), CANDO (Coupled Aerobic-anoxic Nitrous Decomposition Operation), and algae biomass cultivation for biofuels production combined with wastewater treatment.

2.1 Nitritation-Anammox Based Processes

First reported in 1995 by Mulder et al.[11], the application of anaerobic ammonium oxidizing bacteria (anammox) during BNR is considered a promising way to reduce energy consumption. In conventional nitrification-denitrification processes, oxygen is consumed by aerobic ammonium oxidizing bacteria (AerAOB), ammonium-oxidizing archaea (AOA), and nitrite oxidizing bacteria (NOB), thereby oxidizing all ammonium (NH_4^+) to nitrate (NO_3^-). NO_3^- is then reduced to N_2 by heterotrophic denitrifiers, with organic carbon as the electron donor. With the suppression of NOB, nitritation-denitritation (also called the nitrite shunt), a short-cut process compared with nitrification-denitrification that involves NH_4^+ oxidation only to nitrite (NO_2^-), is possible. However, nitritation-denitritation still involves completely aerobic NH_4^+ oxidation, as well as substantial COD for NO_2^- reduction. In contrast, anammox can directly oxidize NH_4^+ to nitrogen gas using NO_2^- as the electron acceptor. By combining partial nitritation (oxidation of NH_4^+ to NO_2^- by AerAOB or AOA) and anammox, a shortcut BNR scheme is possible that reduces requirement for O_2 by 60%[12,13](with associated saving in electrical power need for aeration). In addition, organic carbon requirements for heterotrophic denitrification are reduced by ~90%, thereby eliminating the need for often-costly external organic electron donor supply (such as methanol) or allowing a rerouting of wastewater COD to anaerobic digestion for methane production[13,14]. Moreover, waste biomass production decreases substantially due to the lower biomass yield of anammox compared to heterotrophic denitrification[15]. Based on stoichiometry, a ratio of 1.32:1 of NO_2^- to NH_4^+ is necessary for anammox metabolism[16], and partial nitritation of NH_4^+ to NO_2^- by AerAOB or AOA is a common way to produce the requisite nitrite[17]. Till now, the three pathways of conventional nitrification-denitrification, nitritation-denitritation (or nitrite-shunt) and nitritation-anammox are the major practical nitrogen removal processes (Figure 1). Below, we review existing applications of anammox processes, and highlight new trends in development and implementation of this promising route for sustainable N removal.

2.1.1 Sidestream Nitritation-anammox Processes

Despite critical remaining challenges to adoption by practitioners, nitritation-anammox processes have seen an explosion of interest and application in recent years. Currently there are over 100 full-scale combined nitritation-anammox installations treating high-strength nitrogen wastestreams, with the majority (~75%) applied to sidestream treatment in municipal wastewater[18]. Such sidestream systems treat anaerobic digester centrate resulting from dewatering of stabilized waste biomass. Absent such dedicated sidestream treatment processes, sidestreams are recirculated to the mainstream, thereby generally representing about 1% of the mainstream flow but 15%-20% of the nitrogen loading in a typical municipal wastewater treatment plant[19]. Dedicated sidestream treatment is thus desirable to significantly reduce the nitrogen load to mainline processes. The low nitrogen effluent from sidestream treatment processes is recycled to the mainline for further polishing (Figure 1a). Both a two-stage treatment process, known as SHARON®-Anammox Process, and the one-stage treatment process have been installed at full-scale. For the two-stage treatment plant, nitritation and anammox steps are performed in separate reactors, and research has demonstrated that the SHARON® (nitritation) reactor can effectively convert ~50% of influent NH_4^+ into NO_2^- through the control of aeration rate[17,20,21]. Compared with the two-stage unit, the one-stage configuration (also known as CANON[22]: Completely Autotrophic Nitrogen removal Over Nitrite process, OLAND[13]: Oxygen-limited Autotrophic Nitrification-Denitrification, aerobic/anoxic deammonification[23], or combined nitritation-anammox[24]) is used more widely in practice[12]. The terminology “combined nitritation-anammox” is used here to represent the one-stage configuration. Under oxygen-limiting conditions, the co-culture of aerobic and anaerobic ammonium oxidizing bacteria makes it possible to accomplish combined nitritation-anammox in a single reactor[25]. Research, development, and full-scale implementation of combined nitritation-anammox processes have occurred almost entirely in Europe over the past decade. However, recent years have seen a dramatic increase in testing and construction of sidestream nitritation-anammox processes in North America as well as other parts of the world. The first full-scale combined nitritation-anammox process in the US came online in 2012 at the Hampton Road Sanitation District’s York River Treatment Plant in Seaford, VA[26], and has been followed by full-scale operations in James River, VA[18] and Alexandria, VA[27]. Pilot-scale nitritation-anammox studies have been performed in the Robert W. Hite Treatment Facility (Denver, CO)[28], the John E. Egan Water Reclamation Plant (Chicago, IL)[29], the Blue Plains Advanced Wastewater Treatment Plant (Washington, DC)[30], and

Pierce County Chambers Creek Regional WWTP (Pierce, Washington)[31].

Rapid accumulation of anammox biomass in a short time during process startup is an important engineering challenge from a practical standpoint, and several process control and startup strategies have been developed and applied in WWTPs by different companies and institutions. The attached growth ANITA® Mox Moving-Bed Biofilm Reactor (MBBR) and hybrid suspended and attached growth Integrated Fixed-Film Activate Sludge (IFAS) (Veolia Water, Inc) processes use real-time DO control and bioaugumentation for process control and rapid startup, respectively. The initial bioaugumentation is accomplished via a so-called "BioFarm Concept", in which new reactors are seeded with a small fraction of colonized carriers[32]. Suspended-growth DEMON® systems (World Water Works, Inc) combine pH, time and DO control to optimize process performance in a suspended growth system, and employ a novel hydrocyclone device to maximize retention of biomass with high anammox activity[33]. Granular sludge nitritation-anammox systems (Paques) are also applied at several WWTPs[34]. Several full-scale suspended growth sidestream systems in Switzerland employ continuous aeration and online NH_4^+ monitoring as effective control strategies[35,36].

It is clear that tremendous progress has been made in recent years on sidestream nitritation-anammox process development in academia, industry, and at water utilities. Sidestream nitritation-anammox processes are now commercially available from a number of different companies, and these processes are rapidly becoming an "established" technology. It should be emphasized, however, that key challenges remain to practitioners. Key among these challenges is a susceptibility to process instabilities that can occur during startup or even after extended periods of stable operation[35,37-39]. Anammox have low growth rate, low cellular yield, and are sensible to adverse environmental conditions[40]. A variety of factors are toxic or inhibitory to anammox, including dissolved oxygen, several heavy metals, sulfide, salt, and toxic organic matters (antibiotics, phenol)[40-44]. Even its own substrates, NO_2^- and NH_4^+, can act as inhibitors. Studies have shown that free ammonium and free nitrous acid have negative effects on anammox bacteria[45]. Additional research is needed to clarify susceptibility and resilience of nitritation-anammox process variations to disturbances or routine fluctuating conditions, and to identify robust control strategies to counteract process instabilities.

2.1.2 Mainline Nitritation-anammox Processes

To date, full-scale anammox process implementation at municipal WWTPs is constrained to removal of N from digester supernatant (e.g sidestream treatment). Digester supernatant provides suitable conditions for the growth of AerAOB and anammox as well as suppression of NOB and heterotrophic denitrifiers: the low ratio of C/N ratio precludes high rates of heterotrophic denitrification; relatively high temperatures (~30^{o}C) enables effective outcompetition of NOB by AerAOB via DO control and increases both process (N-removal) and autotrophic growth rates (beneficial during startup); and supernatant generally provides enough bicarbonate alkalinity to maintain reasonable pH values[5]. We are on the way towards energy-positive wastewater treatment with the implementation of sidestream anammox[14]. However, previous calculations showed that the application of anammox in the mainline (treating primary effluent directly) would yield 24 watt hours per person per day (Wh/pd) (assuming COD savings are routed to mainline anaerobic treatment for methane generation), compared to a net consumption of 21 Wh/(pd) in sidestream treatment[14,46]. Recent research efforts have thus focused on the potential utilization of anammox in mainstream N treatment. Figure 2 shows simplified conceptual process schematics for sidestream combined nitritation-anammox (now in use at multiple full-scale locations), mainline combined nitritation-anammox preceded by a high-rate activated sludge system for COD removal (variations on this theme are undergoing testing at lab, pilot and full-scale plants, as detailed below), and mainline combined nitritation-anammox and AD (primarily at lab-scale). The mainline combination of nitritation-anammox and AD has the largest potential for energy generation and would be the most ideal treatment process, but substantial challenges to implementation for both processes remain.

We discuss key approaches and challenges to mainline anaerobic treatment technologies elsewhere in this manuscript. The primary challenges to mainline combined nitritation-anammox implementation include how to obtain high process rates and acceptable stability of under low temperature; how to out-select or suppress heterotrophic denitrifiers and NOB under elevated C/N ratios, low N concentrations, and low temperature[47]; and how to ensure sufficient and possibly selective anammox biomass retention to offset slow growth rates of anammox. Anammox activity declines with temperature, but many anammox processes are considered by several research groups to be feasible under moderate temperature conditions with careful process control. Recent studies focusing on the application of anammox at moderate or low temperatures are listed in Table 1. Although proof of adaptation of nitritation-anammox biomass to low temperature has been demonstrated in lab-scale studies, more pilot-scale and full-scale experiments are needed to demonstrate that anammox biomass can retain high activities treating more complex wastewater under real-world fluctuating conditions.

Compared with sidestream anammox processes, outcompetition of NOB and heterotrophic denitrifiers by anammox is significantly more challenging in the mainline. In sidestream nitritation-anammox, both high free ammonium (FA) and control of DO are helpful for the inhibition of NOB[48]. However, usually the ammonium concentration in mainline is not high enough to have a negative effect on the growth of NOB. Low temperature would also display a disadvantage for the out-selection of NOB. Moreover, heterotrophic denitrifiers compete for NO_2^- with anammox, particularly under elevated C/N ratios. Simultaneous partial nitrification, anaerobic ammonium oxidation and denitrification (SNAD) has been observed in several bioreactors when treating low C/N wastewater[49-52]. Although anammox were found to be the dominant mechanism for N removal in these studies, whether denitrifiers would play a more important role and out-compete anammox with higher COD should be evaluated. Several strategies have been discussed for NOB out-selection: residual ammonia, controlled operational DO, transient anoxia, controlled COD input and limiting aerobic SRT, and bioaugumentation from sidestream nitritation-anammox reactors[53]. Vlaeminck et al. have demonstrated that aggregate size and architecture can influence microbial activity balance in granular nitritation-anammox systems[54]. These results suggest that tightly controlling aggregate characteristics and residence time with, for example, screens to wash out undesired bacterial groups [55], may be of great use in selecting for dominance of AerAOB and anammox. Tight control of DO or of oxygen supply presents an intriguing and apparently critical NOB suppression strategy, with questions remaining about mechanism and optimal control methodology. Previous studies have suggested that infrequent and short-term increased O_2 supply would increase NOB abundance[35], and that low DO conditions coupled to short SRT was an optimal strategy for NOB suppression due to the higher oxygen affinity of AOB compared to NOB[56]. However, the same strategy may not be useful under mainline condition. Recent work at the Blue Plains Advanced Wastewater Treatment Plant in Washington, DC suggested that intermittent high oxygen conditions and transient anoxia rather than DO level itself may be critical to NOB suppression at low temperatures[5,57]. This innovative control strategy follows earlier work by Kornaros and colleagues, who demonstrated a time lag in adaptation to aerobic conditions by NOB relative to AOB[58]. Besides, Kwak et al.[59] demonstrated that tight control of oxygen supply rather than operational DO enabled autotrophic nitrogen removal from low strength wastewater. This mirrors to some extent the strategy of Joss et al.[35], who recommended control of oxygen supply rather than DO setpoint in sidestream nitration-anammox systems. While critical challenges remain to implementation, a full-scale demonstration of mainline nitritation-anammox treatment was successfully implemented at Strass WWTP, which is a net energy positive plant[57]. Being the first mainline nitritation-anammox without bioaugumentation, Changqi Water Reclamation Plant in Singapore has demonstrated that mainline anammox can be a suitable technique especially in tropical areas[60]. Mainline nitritation-anammox has been demonstrated to be feasible (at least as proof of concept) under lab-scale, pilot-scale and full-scale settings, as summarized in Table 2. Besides studies listed in the table, three promising pilot studies (in the United Arab Emirates, Sweden, and France) started in 2013 are under evaluation, using either pure MBBR or hybrid IFAS ANITA Mox systems developed by Veolia Water, Inc (personal communication, Veolia Water, Inc.). The pilot-scale study in Sweden employs innovative carrier recycling and flow switch schemes between sidestream and mainstream ANITA Mox reactors (patent pending, Veolia Water, Inc)[61].

With great opportunities for saving energy and reducing cost in wastewater treatment, anammox is still a rather new process, and innovative solutions are needed to optimize this process and overcome potential disadvantages. Besides practical application used for NOB suppression, some lab works are validating other potential methods. Yao et al.[62] tried to decrease the production of NO_3^- and enhance the performance of combined nitritation-anammox by addition of the key anammox intermediate hydrazine (N_2H_4). While likely not feasible at full-scale, this demonstration may provide insights into mechanisms for stimulating recovery from process instabilities in anammox processes. Isaka et al.[63] developed a novel autotrophic N removal system using gel carries to immobilize the growth of AOB and using heat-shock treatment to suppress the growth of NOB. Now mainly applied for treatment of high strength streams in domestic wastewater treatment, it would be also worth testing whether anammox would be suitable for refractory industrial wastewater treatment. Tang et al.[64] presented a promising application of a bioaugumentation scheme for application of an anammox process to treatment of a refractory ammonium-rich pharmaceutical wastewater. Dissolved methane from high-rate mainline anaerobic treatment processes could have a negative impact on anammox. However, recent studies have demonstrated a remarkable new connection between the N and C cycles, termed N-DAMO (nitrite-dependent anaerobic methane oxidation), that can simultaneously remove nitrogen (nitrite) and methane[65,66]. Potential application of N-DAMO in engineered systems – for example, to scavenge trace methane and thereby prevent both emissions of this potent greenhouse gas and inhibition of downstream anammox— is only beginning to be explored. We mention these recent developments to highlight innovative and creative problem-solving efforts to address potential drawbacks to anammox processes. We further suggest that future efforts are warranted to promote advances in process monitoring and control strategies, as well as a better understanding of the relevance of both microscale microbial aggregate characteristics and community structure, interactions, and dynamics to process performance and stability. Innovations and discoveries in these realms would greatly facilitate full-scale implementation of mainline nitritation-anammox processes.

2.2 CANDO for Direct Energy Recovery from NOD

NOD bound in reactive forms of N can be converted into renewable energy. But for this to occur, the N must be in a form that can be removed from water and usable for energy production. Two N species that fit these requirements are ammonia (NH_3) and nitrous oxide gas (N_2O)[10]. NH_3 is an energy source that releases electrons when oxidized or heat when combusted with oxygen (Eq. 1). NH_3 in wastewater can potentially generate power with electrochemical fuel cells[67]. Alternatively, NH_3 recovered from wastewater could be burned to generate power or used as a transportable fuel. However, this is generally impractical because the energy and costs associated with removing NH_3 often exceed the energy and value recovered. For this reason, it is more practical to use recovered NH_3, or NH_4^+ at neutral pH, as a fertilizer instead of a fuel. NH_3 recovery from particularly high concentration side-streams is in some cases economically feasible with physical/chemical processes such as gas stripping[68].

Eq. 1: The heat of reaction of NH_3 with O_2.

$$NH_3 + {}^3/_4\,O_2 \rightarrow {}^3/_2\,H_2O_{(l)} + {}^1/_2\,N_2 \quad \Delta\widehat{H}°_R = 382\,\frac{kJ}{mol{-}N}$$

N_2O, derived from reactive forms of N, can be removed from wastewater and used to recover energy. Recently, Scherson and colleagues[69] introduced a new N removal process that recovers energy from NOD nitrogen as N_2O. The process is called the Coupled Aerobic-anoxic Nitrous Decomposition Operation (CANDO) and converts reactive N to N_2O, then captures the gas and recovers energy from it by using it as a co-oxidant in CH_4 combustion or decomposing the N_2O over a metal oxide catalyst. The end product is N_2. The innovation is utilizing N_2O as a renewable energy source. Traditionally, N_2O has been viewed as an unwanted by-product of wastewater treatment because it is a GHG (Greenhouse Gas) 310 times more powerful than CO_2 and is a dominant ozone-depleting substance[70]. For this reason, studies have generally focused on understanding the pathways for N_2O production in order to minimize its production. But, N_2O is like CH_4: both are harmful if released to the atmosphere, or sources of renewable energy if captured and combusted. In fact, N_2O is a powerful oxidant - commonly used in propulsion and automotive applications - that can increase energy recovery from methane[71-73]. Combustion of CH_4 with N_2O releases roughly 30% more heat as compared to O_2 (**Eq 2**), and, mitigates the release of N_2O to the atmosphere.

Eq 2. Comparison of the heat of reactions of CH_4 with N_2O (top) and CH_4 with O_2 (bottom).

$$CH_4 + 4N_2O \rightarrow CO_2 + 2H_2O_{(l)} + 4N_2 \qquad \Delta\widehat{H}°_R = -1{,}219\,\frac{kJ}{mol{-}CH_4}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_{(l)} \qquad \Delta\widehat{H}°_R = -890\,\frac{kJ}{mol{-}CH_4}$$

CANDO involves three steps: (1) nitritation of NH_4^+ to NO_2^-; (2) partial anoxic reduction of NO_2^- to N_2O; and (3) N_2O conversion to N_2 with energy recovery. Step 1 has been demonstrated at full-scale with over 95% efficiency by the (SHARON) process[74], and step 3 is well documented[71-73]. Step 2, NO_2^- reduction to N_2O, was demonstrated by two methods: (1) abiotic reduction by Fe(II); and (2) partial heterotrophic denitrification. In the first method, Fe(II) precipitates with Fe(III) in the form of carbonate "green rust" ($Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3$) reduced NO_2^- (28 mM, ~400 mg/L-N) to N_2O within 2.5 hours and with over 90% conversion. In the second method, a feeding strategy in which acetate (electron donor) and NO_2^- (electron acceptor) delivered as alternating pulses selected for organisms that store polyhydroxybutyrate (PHB) after the acetate pulse, and produce N_2O after the NO_2^- pulse. Reducing equivalents for NO_2^- reduction were derived from the stored PHB. High N_2O conversion (62% NO_2^- to N_2O) over long-term operation (>200 cycles) with 98% N-removal was reported in a lab-scale study treating synthetic wastewater (250 mg-N/L)[69]. CANDO is currently being evaluated at pilot-scale and with real wastewater.

Alternative methods for N_2O production can improve CANDO. At present, CANDO relies on heterotrophic organisms that consume biodegradable COD to reduce NO_2^- to N_2O. In some applications, the COD that is consumed could otherwise be used for energy recovery as CH_4 or electricity. But, autotrophic denitrification to N_2O with, for example H_2, CH_4, or NH_4^+, does not consume biodegradable COD and produces less biomass than heterotrophic denitrification. If NH_4^+ is the source of reducing equivalents, then only a fraction of the influent NH_4^+ is oxidized to NO_2^-, with the balance oxidized for NO_2^- reduction, thus reducing aeration energy (like nitritation-anammox). Autotrophic production of N_2O with NH_4^+ oxidation has been reported by both AerAOB and AOA. AerAOB are capable of N_2O production by either oxidation of hydroxylamine, or by so-called nitrifier-denitrification, in which NO_2^- is sequentially reduced via NO to N_2O[75-77]. However, further studies are needed to evaluate this strategy.

Energy recovery from NOD nitrogen as N_2O offers several benefits. First, N_2O is a dissolved gas that, like CH_4, can be stripped or outgassed from solution, although N_2O is less readily stripped than CH_4 because of a higher solubility limit. Second, N_2O is already produced, albeit unintended, by conventional denitrification and short-circuit nitrogen removal processes, contributing negatively to the carbon footprint of many WWTPs. Using N_2O as an oxidant in combustion destroys the gas, and maximizing its production increases energy recovery. Finally, converting reactive nitrogen to N_2O, instead of N_2, shortens the treatment steps for denitrification. This results in fewer reducing equivalents consumed, less biomass produced, energy from nitrogen recovered, and possibly shorter SRT. The capture of N_2O during wastewater treatment can be a win-win strategy that offers the possibility of energy generation, cost reductions, and mitigation of climate change and stratospheric ozone depletion.

Figure 3 and Table 3 compares performance metrics for five N treatment processes that are in different development stages (existing, emerging, future). Conventional nitrification-denitrification is the least efficient: the most oxygen and reducing equivalents are consumed, and the greatest quantity of biosolids is produced. Nitritation-denitritation offers a moderate improvement with reductions in oxygen, organics, and biosolids. Nitritation-anammox, as detailed in the previous section, offers the most dramatic improvement with reductions in oxygen demand by 60%, reducing equivalents by 90%, and biosolids by 75%. While various nitritation-anammox based processes are commercially available, concerns related to process stability, robustness, sensitivities to a variety of inhibitors[35,38,78-82], and the slow growth rate of anammox[46] have impeded broader adoption[35,81]. Compared to nitritation-anammox, CANDO is less efficient, but does recover energy from NOD and offers other benefits not associated directly with energy. CANDO selects for heterotrophic bacteria with faster growth rates than anammox. The fast growth rates may improve process stability with short SRT. Also, CANDO may enable phosphorus recovery through alternating anaerobic/anoxic cycling with stored PHB. This operation is similar to conventional Enhanced Biological Phosphorus Removal (EBPR) where anaerobic/aerobic cycling selects for organisms that oxidize stored PHB to drive phosphate uptake. Pilot-scale studies are needed to evaluate these potential benefits. The final process, CANDO autotrophic, represents a future concept that is the most efficient, but has yet to be demonstrated with high conversion to N_2O and over long-term operation. CANDO autotrophic is similar to nitritation-anammox in terms of oxygen, reducing equivalents, and biosolids to nitritation-anammox, but differs because energy is recovered from NOD. It is likely that existing and developing nitritation-anammox based processes, CANDO, and CANDO variants will be complementary, offering a unique treatment process that is ideal for each application.

2.3 Microalgae Cultivation For Joint Energy Production and Nutrient Removal

Microalgae based biofuels, recognized as the "third generation of biomass energy[83]", exhibit many advantages over the first and second generation of biofuels: high-acre productivity; use of non-productive, non-arable land; high lipid content; and low GHG emission and carbon footprint[84, 85]. Life cycle analysis of biofuels production from microalgae based on water footprint and environmental impact has demonstrated that algae cultivation is most economically viable when linked to wastewater treatment[86, 87]. Wastewater is thus a promising substrate for cost-effective and sustainable algae cultivation[88]. Joint wastewater treatment and algal biomass production offers the opportunity for both energy generation and nutrient (N and P) removal. An energy evaluation of coupling nutrient removal from wastewater with algal cultivation showed that biofuel production was energetically favorable for open pond reactors utilizing wastewater[89]. Besides nutrient removal, some heavy metals and other trace elements could also be removed by algae[90, 91]. Despite substantial potential advantages of this process, microalgae-based biofuel production has not yet been used commercially at large-scale because of some remaining technical obstacles. Here, existing problems, current progress and suggested further developments in wastewater algae cultivation are reviewed.

2.3.1 Why not use algal biomass and how can we improve?

Obstacles for algal biomass production from wastewater exist in almost every chain of the process. In contrast to controlled freshwater algae cultivation, the growth rate and algae composition changes with various wastewater influent characteristics. Lipid content and other characteristics to guide the choice of algae species for freshwater cultivation were explained in details by Griffiths and Harrison[92]. But when it comes to use of wastewater as substrate, careful consideration should be made concerning the specific algae species to be cultivated as well as the characteristic of wastewater. Zhu et al.[93] cultivated freshwater Chlorella zofingiensis with six different concentrations of piggery wastewater. Even though nutrients were successfully removed among all the treatments, the specific growth rate and biomass productivity were different, and the lipid content decreased as initial nutrient concentration increased. Abou-Shanab et al.[94] also evaluated joint nutrient removal and biodiesel production ability of monoculture microalgae growing on piggery wastewater, and arrived at similar conclusions. During algae cultivation, the ideal achievement is to obtain high biomass production and high lipid content at the same time. However, biomass productivity and lipid content apparently represent something of a trade-off. Nutrient supplementation, which is common when using wastewater as substrate, would enhance the growth of microalgae but decrease the lipid content. Wastewater-fed algae typically have low lipid contents compared with those grown under nitrogen-limited growth conditions[95]. Several studies have focused on the enhancement of lipid accumulation without sacrificing biomass productivity. Supply of exogenous CO_2 to the cultivation of Auxenochlorella protothecoides was found to increase the lipid content as well as biomass accumulation[96,97]. In addition, the trade-off between lipid content and productivity might be overcome via application of ecological principles to modulate algal diversity. Laboratory experiments have demonstrated that both biomass production and nutrient uptake rates could be enhanced through use of polyculture[98]. Owing to the complex composition of wastewater, polyculture algal bioreactors likely have significant advantages over their monoculture counterparts. It should be noted, however, that biomass productivity is not always correlated with algal species diversity; indeed, declines in productivity in polyculture relative to monocultures have also been noted[99], indicating that selection of (or for) specific algal taxa in polyculture is a key consideration. It is clear that substantial future work is necessary to clarify opportunities for stable lipid and biomass accumulation in wastewater-fed algal polycultures.

Another challenge that restricts the large-scale application of high-rate algae bioprocesses for joint nutrient removal and energy production is the energy-intensive harvesting process. Usually, harvesting requires one or more solid-liquid separation steps to concentrate biomass, and membrane separation has been suggested as a promising technique[100]. A lab scale hollow fiber polyvinylchloride (PVC) ultrafiltration (UF) membrane was tested to concentrate algal suspension 150-fold under a constant pressure of 34.5 kPa, and backwash was conducted every 15 minute[100]. Others suggested that gravity settling enhanced by flocculation could be the lowest-cost approach[85, 101]. Besides the improvement and exploration of improved harvesting methods, immobilized cultivation rather than suspended growth has been suggested as a more effective way to reduce water content of algae. Alginate, with high diffusivity, low production hazards, and low polymer costs, has attracted the most attention for growth of algae in a matrix[102]. Importantly, not all algae can grow well in such a matrix. Liu et al.[103] successfully cultivated immobilized Chlorella sorokiniana GXNN 01 in calcium alginate and observed higher NH_4^+ and phosphate removal rates than with free-living cells. Immobilized cells of Gloeocapsa gelatinosa captured in calcium alginate were also shown to effectively remove NO_3^- and phosphate[104]. Other polymers, such as sodium cellulose sulphate/ploy-dimethydiallyl-ammonium chloride, have also been shown to be effective in immobilized cultivation of certain microalgae[105]. At present, however, large-scale use of polymeric matrix is prohibited by its high cost[106]. Thus, different biofilm systems, including biofilm photobioreactors[107,108] and rotating algal biofilm reactors with spool harvesters[109], are recommended as a potentially effective systems for cultivating high density algae biomass. For practical widespread application of high-rate algal bioprocesses for wastewater treatment and biofuels production, the energy cost of harvesting must be reduced to a reasonable range and the harvesting process needs to be simplified as well.

Following harvesting, algae must be converted to liquid biofuel or biogas through a high efficiency, cost-effective and environmentally friendly pathway. Conventional lipid extraction methods may not be suitable for algae grown in wastewater. Comparison of hydrothermal liquefaction (HTL), oil secretion and alkane secretion has been made by Delrue et al.[110], and secretion of oil or alkane seemed to be better based on energetic and environmental criteria. HTL, however, could be more feasible when treating with algae cultivated from wastewater due to lower lipid contents relative to freshwater monoculture algae cultivation, as mentioned previously. Importantly, HTL does not require drying prior to processing and the resulting bio-crude can be formed not only from the lipid content, but also from the carbohydrate and protein fractions of the algae, thus leading to higher overall yields[85, 111]. Interestingly, pilot-scale tests of HTL of Chlorella and Spirulina under continuous flow by Jazrawi el al.[112] demonstrated bio-crude yields higher than in batch studies. Roberts el al.[113] were the first to demonstrate the feasibility of an integrated wastewater algae-to-biocrude process, and besides 44.5±4.7% ash-free dry weight of bio-crude, the process also formed aqueous co-products and solid biochar. Model compounds such as protein, starch and glucose, triglycerides from sunflower oil, and amino acids have been validated to predict the HTL behavior of microalgae and cyanobacteria[111]. These studies should be helpful to predict potential yields and to instruct the choice of suitable biofuel generation pathways. Recently, several studies have focused on the microbial utilization of aqueous co-products. A microbial side culture in aqueous co-product from Nannochloropsis oculata HTL might have the potential to provide additional biomass[114]. Based on the multiuse of HTL products, Zhou et al.[115] proposed an innovative waste-to-energy system: combined algal wastewater treatment with large-scale bioenergy production via hydrothermal liquefaction, which they called Environment-Enhancing Energy (E^2-Energy). Experiments and mathematical modeling showed that E^2-Energy could effectively utilize nutrients in wastewater and increase biomass and biofuel production by approximately 10 times. In addition to HTL, anaerobic digestion or co-digestion with activated sludge are promising routes for energy recovery from algal biomass regardless of lipid content, which might not important for wastewater-cultivated algae. Wang et al. demonstrated the feasibility of anaerobic digestion of Micracinium nov. and Chlorella sp. grown in mixture of sludge centrate and primary effluent, and both of species also helped to improve volatile solids reduction efficiency of waste activated sludge as well as the biogas yield [116]. Similar results were reported for the co-digestion of Spirulina platensis and Chlorella sp. grown in a mixture of sludge centrate and nitrified wastewater effluent[117]. However, the two different species had an inverse impact on biosolids dewaterability. Performance of both HTL and anaerobic digestion of algal biomass are related to wastewater characteristics and algae species; consequently, it is hard to simply conclude which approach is optimal.

2.3.2 Combined Algal Production, Nutrient Removal & Recovery, and COD ReductionA novel biotechnology, algal-bacterial co-culture, has received significant attention in recent years as well. O_2 produced by algae could reduce aeration requirements of treatment processes, and greenhouse gas emissions are mitigated by the CO_2 consumption during algal photosynthesis[121,122]. In addition, challenges associated with high energy requirements for algal biomass harvesting might be overcome by increased settleability of algal-bacterial biomass. Su et al.[123] demonstrated that an algal-bacterial culture had good COD and nutrient removal efficiency, and was able to settle completely over 20 minutes. They also argued in a follow-up study that algae and sludge inoculation ratios could influence nutrient removal efficiency and settleability, and a ratio of 1:5 (algae/sludge by weight) was shown to have the best settleability[122]. Other groups also claimed that algal-bacterial biofilms exhibited a capacity for higher nutrient removal than bacterial biofilms, but the stability of the system varied with influent wastewater[124]. However, separation of algal biomass from combined algal-bacterial co-cultures (one reactor) for lipid extraction could be a great challenge. Efficient use of oxygen produced in algal systems is also a challenge, especially for open pond algal cultivation. However, the feasibility has been demonstrated recently. Blanc and Leshem built an innovative pilot-scale system utilizing an oxygen-rich algal liquid to supply O_2 to an aerobic biofilm reactor[125]. The system included a moving bed biofilm reactor (MBBR) for aerobic treatment and an algae-growth open pond as a biologically aerated reactor (BAR). Operating for 18 months, the system worked well and produced a high quality effluent with no aeration cost.

In addition to conventional products (biofuels, methane), novel methods may make it possible to manufacture high value products from algae, including protein complements and food additives (aquaculture and animal feed), or products used in agriculture (fertilizers, soil conditioners)[109]. With more NH_4^+-N assimilated into algae biomass, the residual biomass is a sustainable source of nutrients that can be used as a fertilizer[125]. Acetone, butanol and ethanol (ABE) fermentation using wastewater algae biomass have been demonstrated to be feasible[126]. And researchers are trying to optimize two-staged bio-hydrogen production by algae to produce more sustainable sources of energy[127, 128]. A potential combined algae cultivation and wastewater treatment system is illustrated in Figure 4; possible byproducts are also shown here.

As an emerging approach for attaining energy-neutral wastewater treatment with high quality effluent, the application of algae presents both promises and challenges. Since algae need CO_2 for growth, collaboration with other industries or systems (for example, power plants with high CO_2 emissions) could provide additional advantages for this process in terms of overall reduction in carbon footprint. However, algae cultivation requires a large land footprint and might be most suitable to rural areas. Also, slow growth rates will likely limit its usage in temperate regions. The development of more reliable models incorporating the complete algal processing chain (cultivation, harvesting and product generation) would aid practical application of this technique[129, 130].

3. ENERGY POSITIVE BIOPROCESSES FOR COD REMOVAL

In conventional wastewater treatment, removal of COD through aerobic bioprocesses, like conventional N removal, is an energy-intensive processes. Instead of regarding COD as unwanted pollutant, an emerging new paradigm of wastewater treatment views COD as renewable source of energy via “misplaced electrons”[1], as well as a potential source of a diversity of byproducts[131]. It has been estimated that domestic wastewater alone might contain 17.8 kJ/g of COD[132]. By combining innovative N removal processes with effective techniques to recover the inherent energy in COD in the wastewater, it should be feasible to construct zero energy input WWTPs. Till now, two main methods, Anaerobic Digestion (AD) and bioelectrochemical treatment, have been considered as the current trends for future energy saving or generation plants. In this section, we present brief overviews of these two methods for converting waste organic carbon to energy, with an emphasis on efforts and innovations made in recent years.

3.1 Anaerobic Digestion

3.1.1 Historical Development and Application

In the absence of a suitable electron acceptor, a consortia of microorganisms convert organic matter to methane (CH_4) and carbon dioxide (CO_2), which can be used as biogas for either heat or electricity generation. Several life cycle assessments have confirmed that AD is a sustainable waste-to-energy system from the prospects of both energy production and Greenhouse Gas (GHG) emissions[133, 134]. Compared with other techniques for energy recovery, anaerobic digestion is a mature method that is already widely used in WWTPs for recovering energy in the form of methane-rich biogas produced during digestion of primary sludge and biomass generated during conventional aerobic treatment. Efforts have also been made to directly recover energy via AD from municipal wastewater. Previously, high strength wastewater was assumed to be suitable for AD under either mesophilic (28-40°C) or thermophilic (50-57°C) conditions[135]. The existence of psychrophilic methanogenesis provides opportunities for broader application in temperate climates[136]. In recent years, much progress has been made in modification of configuration and process control of AD, especially in anaerobic membrane bioreactors (AnMBR), making application of AD to low strength and low temperature wastewater treatment feasible in temperate areas of the world.

Generally considered as an unfavorable byproduct of wastewater treatment, waste biomass from activated sludge processes can also be thought as a raw material for energy production[137]. AD of activated sludge and other high-strength organic wastes is known as an environmentally friendly and energy saving technology compared with other options like landfilling, incineration, composting, etc[138]. A recent mathematical model[139] suggested that primary and secondary sludge are optimally treated separately, for material recovery and energy recovery respectively. Full-scale data demonstrated that AD of sewage sludge alone allow WWTPs to approach energy self-sufficiency, even for a municipal WWTP with secondary biological treatment located in a moderate climate[140].

Typically, based on the microbial ecology, one-stage and two-stage digesters are used. In a two-stage process, acidogenesis and methanogic processes are separated, preventing the occurrence of acidogenesis in second stage and enhancing sludge properties[141]. Up to the mid-20th century, the use of anaerobic digesters was excluded from wastewater treatment outside waste biomass stabilization because of its slow rate[142]. The introduction of the Upflow Anaerobic Sludge Blanket reactor (UASB; Figure 5A) in the 1970s and diverse advancements of this process, which is now the most widely used anaerobic digestion process by far, triggered widespread use of AD in high-strength industrial wastewater treatment beyond sewage sludge and municipal waste[143].

3.1.2 Recent Advances, and Future Development

Although AD technologies have matured in the past decades, further improvements are still needed to enhance the treatment efficiency, production of biogas, and to evaluate the possibility of mainline utilization. Below, we focus on innovations in AD process implementation and product utilization, and detail key remaining challenges for researchers and practitioners.

3.1.2.1 Co-digestion and Pre-treatment for Yields/Efficiency Improvement

Pre-treatment and co-digestion have been recognized as effective and commercially viable approaches to reduce anaerobic digestion process limitations, improve biogas yields and improve biosolids dewaterability [144, 145,146]. Anaerobic co-digestion provides simultaneous digestion of different solid and liquid wastes by balancing nutrient inputs and diluting toxic substrates, thus leading to higher rates and biogas yields[147-149], and it has higher efficiency in terms of land and equipment utilization by mixing various waste streams in a single facility[150-152]. Unit cost for co-digestion has been shown to be significantly lower due to sharing of facilities and operation[147]. In addition, co-digestion has the potential to reduce the inhibitory effect of accumulating ions, which can cause reactor instabilities and an associated decrease in biogas production[153]. Fat, oil, and grease (FOG), food waste, animal byproducts, and model compounds have been used as co-digestion substrates in lab-scale or pilot-scale experiments[145,147,152,154-161]. In addition several full-scale co-digestion studies have already been applied, as detailed in Table 4. Choice of co-digestion substrate is crucial in sludge treatment: the substrate should be easily obtained without additional transport cost; and experiments should be performed to optimize the mixing ratio between co-substrate and sludge, the organic loading rate and hydraulic loading rate.

In addition to co-digestion, pre-treatment of influent wastes is another common method for performance improvement. Pre-treatment processes are typically focused on releasing intracellular material into the water phase and accelerating hydrolysis, which is the rate limiting process during anaerobic digestion[162,163, 164]. Various methods have been tested and proved to be useful. Hydrothermal, ultrasound, microwave irradiation, mechanical shearing, chemical, and biological (enzymatic) pretreatment alone or in combination are common methods evaluated in research studies, and performance improvements have been demonstrated[162, 165-170]. Since some of the pretreatment methods have drawbacks like high energy demands, high cost, requiring extreme conditions, high toxicity and unrecyclable reagents[165-167, 171], life cycle assessment or other energy and cost analysis are suggested to optimize application.

The main drawback of traditional anaerobic treatment is lower quality effluent generated relative to aerobic treatment processes, especially when operating with low strength wastewater (0.3-0.7 g COD/L) at low temperatures (8-25°C)[172]. Usually, additional post-treatment, physical-chemical, bio-chemical or biological methods are required for further COD polishing as well as N removal prior to final discharge[173, 174,175,176]. Interestingly, Tugtas et al. used bio-electrochemical post-treatment of anaerobically treated landfill leachate, and this lab-scale MFC post-treatment demonstrated substantial promise for additional energy recovery with effective polishing performance[173].

3.1.2.2 Advances in Process Design for Mainline Application

Anaerobic membrane bioreactors (AnMBRs) presented upgraded versions of conventional waste biomass digesters for mainline application. By decoupling SRT from HRT through complete retention of solids and prevention of biomass washout, the reactor volume is substantially reduced, which overcomes the large land requirements for conventional anaerobic digestion[177,178-180]. Kanai et al.[181] reported that an AnMBR volume could be scaled down to approximately 1/3 to 1/5 of a conventional AD. Compared with traditional anaerobic sludge digestion, the addition of coagulant for thickening has been omitted, avoiding extra cost[182]. Energy demand in submerged AnMBRs was lower, ranging from 0.03 to 3.57 kWh/m^3 [172]. Furthermore, the longer SRT enables complete retention of slow-growing methanogenic organisms, increasing the stability of the whole system[183]. With these advantages, the AnMBR is considered a promising option for low strength or low temperature wastewater treatment[184]. The combination of AnMBR and UASB has been most widely applied at lab scale (Figure 5B and 5C). Different membrane configurations—namely, submerged or side-stream—have been under consideration. Immersing a membrane into UASB, Liu et al.[185] observed an enhancement of process performance and stability. The connection of a side-stream membrane filter has also been proved to be a feasible method for treatment of low strength municipal wastewater[177,186]. Different membrane modules designs (e.g. cylindrical, funnel-shaped, U-shaped bundle, and hollow fiber) also impact process performance[187]. Seeding psychrophilic AnMBR with mesophilic inocula was reported to enable stable COD removal and acceptable flux, indicating future potential use of bioaugumentation for AD use in cold and temperate climates[188].

Control of membrane fouling during AnMBR operation is the main obstacle to widespread full-scale implementation of this technology. Fouling contributes to the deterioration of membrane performance and largely determines the energy demand of the process. Lin et al.[179] explored factors that affected sludge cake formation, which is considered the main reason for membrane fouling, and found that cake formation rate was highly dependent on biogas sparing rate and permeate flow rate. Fine particles and a high levels of extracellular polymeric substance (EPS), the adhesive and cohesive matrix of biofilms, were accumulated in the sludge cake layers and likely impact membrane fouling[189,190]. Thus, attempts have been made to control and reduce membrane fouling, combined with minimizing energy and operating cost. Fluidized granular activated carbon, ultrasonication, and enzyme augmentation have proved to be effective in fouling control[178, 191,192]. Novel process control strategies, different membrane modules and SRT optimization, could also act as important drivers of performance improvement[187,193, 194].

3.1.3 Energy Generation, Valuable Product Usage as well as Other Challenges

Biogas utilization and stabilized biosolids usage methods are two significant aspects of AD process performance. Depending largely on substrates characteristics, biogas is composed up of 50-65% CH_4, 30-45% CO_2, moisture and other trace chemicals, including hydrogen sulphide (H_2S) and siloxanes[195]. The impurity of biogas lowers its calorific value and decreases its economical value as a fuel[196]. The removal of water and H_2S to avoid corrosion and further pollution via physical-chemical methods such as scrubbing or biological processes is essential for energy generation, and further CO_2 removal is required for upgrading to a natural gas quality[197]. Flaring is used if purification is not available or economical. The potential of electricity production is lost, but the produced heat can be collected and used.

One promising and increasingly implemented approach to increase energy capture at WWTPs with anaerobic digesters is cogeneration of electricity and usable heat. Such applications, termed Combined Heat and Power (CHP) systems produce two energy outputs (heat and electricity), thus increasing efficiency of energy capture[198]. The U.S. Environmental Protection Agency (US EPA) has encouraged integration of biogas to CHP facilities at WWTPs since 2005[199]. Wastewater treatment CHP systems potentially installed in 1,351 WWTPs contain approximately 411 MW of electric capacity and 37,908 MMBtu (million British thermal unit, 1 MMBtu=293.1 kW)/day of thermal energy[200]. In addition, other high-value byproducts, including hydrogen, useful chemicals (the carboxylate platform, bioplastic), and microbial electrosynthesis are potential future benefits of AD[201-203,204]. The use of biosolids (stabilized sewage sludge from AD) on agricultural lands or in plant nurseries offers the opportunity for nutrient recovery [205,206]. However, due to potential environmental (contaminants, e.g, metals) and health risks, its application has to be thoroughly evaluated[206,207]. In addition to its use as an energy source, specific microbial consortia enable the potential production of bioplastic from biomethane. Particularly promising is the production of (PHB) as a feedstock for bioplastics by certain methanotrophic bacteria fed AD-derived methane[208]. The carbon neutral process could be economically feasible and is being commercialized by Mango Materials[204, 209].

A few remaining issues deserve additional exploration. Although a few studies[210-212] have focused on microbial community analyses under low temperature AD, a more comprehensive understanding of microbial interactions and community dynamics in these novel systems is needed, especially focusing on methanogenesis surviving in cold habitats[213, 214]. Moreover, although the solubility of methane is low, the total amount dissolved in process effluent could still be substantial in high rate mainline AD. Dissolved methane lost in effluent will decrease energy production, increase GHG released into the atmosphere, and effect downstream N removal processes[65, 215]. Thus, enhanced methane extraction efficiency is essential.

3.2 Bioelectrochemical Systems

Bioelectrochemical systems (BESs) are a set of configurations that can convert chemical energy in waste organic matter into electricity or valuable products. Microbial fuel cells (MFCs) have long been the most commonly used type of BESs. MFCs are considered an environmentally friendly energy recovery method for use in wastewater treatment that can operate under ambient and low temperatures, and treat low strength wastewater. Studies have shown that, coupled with power generation, lab-scale MFCs could achieve high COD removal efficiencies from complex wastewater[216]. In addition to direct recovery of electricity from wastewater, microbial electrolysis cells (MECs) allow for energy recovery in the form of valuable chemicals with low input of external energy, usually hydrogen gas or methane[218, 219, 220]. In Figure 6, simplified schematics for these two bioelectrochemical systems are illustrated.

We focus here on energy recovery from carbon sources via MFCs and MECs, but it is important to note that routes for nutrient (N) removal and recovery constitute an important and rapidly development area of research. High levels of N_2O emissions from MFCs for nitrogen removal have been demonstrated [221], and the accumulation of N_2O could be an opportunity to recover energy via the CANDO process. In addition, nitrogen recovery could be achieved via ammonia migration and deprotonation at the cathode due to high pH[222].

3.2.1 Electricity Generation: MFCs

A MFC is a system that uses microorganisms as a biocatalyst to convert chemical energy to electrical energy[223]. In addition to COD removal, autotrophic denitrification has been characterized on MFC cathodes[224, 225], but performance is influenced by carbon source and C/N ration, which means the actual performance will be dependent on application[226, 227]. Incomplete reduction of NO_3^- to N_2O has been observed during cathodic denitrification[228]. This should be emphasized since N_2O is a potent greenhouse gas that should be controlled.

The performance of MFCs is affected by several factors: rate of substrate degradation, microorganism activity, proton mass transfer in the liquid, electrode material and construction, and operational parameters (e.g., pH, buffer availability, temperature)[229-231], among which the expensive electrode material is usually an important limiting factor[232]. At present, carbon-based materials are most commonly used in MFCs[233, 234]. The current trend of electrode material exploration is to apply more cost-effective and biocompatible materials with higher electrical conductivity[235-238]. Nanomaterials (nanosheet, nanotube or nanofiber), open macroscale porous materials, and other modifications of conventional materials are attracting significant attention, and reported power densities have increased by as much as fivefold compared with traditional materials[235, 236, 239-244]. In addition to improvement of electrode materials, progress towards cost-effective, low resistance separators such as exchange membranes or filters is required[245].

To date, large-scale utilization of MFCs is still constrained by low power output and high cost, which makes the system not as energy effective as once thought[246]. The maximum area power density of MFCs has reached 6860 mW/m^2 in lab-scale[247], and the volumetric power density has increased up to 2.87 kW/m^3 [248]. Based on these lab-scale data, scaling up of MFCs appears promising. However, practical demonstrations of pilot-scale MFCs have not yielded equivalent area or volumetric power densities. Indeed, several experiments have demonstrated performance deterioration of 10-fold or more during scaling up, and power density in MFCs was found to be inversely proportional to the logarithm of the anode surface area[249]. Usually, increasing the volume of each cell and connecting several MFC stacks are the two main approaches used for scaling up[250-252]. However, the increase in the anode resistance, specifically within the leading-out terminal of anode, leads to power loss in MFCs[248, 249,246]. Several novel configurations and operational controls have been introduced recently, and more progress is expected. Single-chamber, air-cathode MFCs are suggested to be most promising because the configuration avoids the need of separators, and passive oxygen transfer is used for electron acceptor supply[253]. Multi-anode single-cathode MFCs could help to reduce voltages loss among multi anode/cathode systems[254, 255]. Other researchers are targeting energy harvesting systems, and are trying to enhance output by improving the converter efficiency[256]. Electron transfer from microbes to electrodes is also critical for electricity production. Till now, two mechanisms have been recognized for electron transfer: direct electron transfer by outer membrane cytochromes or nanowires, and indirect transfer through electron shuttles[257, 258]. Genetic manipulation of the electron transfer pathway has been demonstrated as an efficient approach for increasing energy output[259,260]. Recently, several models have been developed by integrating bio-electrochemical kinetics, mass and charge balances within MFCs of different types, which is similar to chemical fuel cells[261-263]. Although there is much room for technology improvement, development of more mature MFC models is also needed to facilitate scale-up of more efficient MFCs.

The application of MFCs could also combine energy recovery from COD and NOD. The growth of algae consumes CO_2 and produces O_2. By taking advantage of these metabolic activities, the combination of algae cultivation and Microbial Fuel Cells (MFCs) or aerobic activated sludge for COD reduction has been proposed as a promising sustainable and energy-positive system. Photosynthetic Algal Microbial Fuel Cells (PAMFCs) or Microbial Carbon Capture Cells (MCCs) with algae growth have been designed to simultaneously accomplish wastewater treatment, electricity generation and biomass production. In these applications, microalgae or cyanobacteria are grown in a photocathode, using CO_2 from the anode chamber as the carbon source for biomass accumulation and reducing the carbon footprint. Pandit et al.[118] demonstrated that MCCs generated a higher power density with cyanobacteria Anabaena culture sparged with a CO_2-air mixture (57.8 mW/m^2) than a conventional cathode sparged with air only (19.6 mW/m^2). The first introduction of immobilized microalgae (Chlorella vulgaris) into MCCs was reported by Zhou et al.[119], and the process achieved 84.8% COD removal and 2485.35 mW/m^3 maximum volumetric power density. A slightly higher COD removal efficiency (92.1%) and similar power density (2572.8 mW/m^3) were obtained by the introduction of immobilized Chlorella vulgaris into a PAMFC[120].

Recently, several other innovative modified bioelectrochemical systems have been reported. For example, a Microbial battery (MB), was introduced by Xie et al.[217]. Unlike MFCs that use air-cathodes, the MB contains a solid-state cathode that can be "recharged" periodically. In addition, Cusick and colleagues proposed a novel Microbial Reverse-Electrodialysis Cell (MRC) that relies on waste heat and salinity gradients for energy capture[265]. These novel approaches are based on lab-scale experiments, and additional work is needed to clarify their potential for practical large-scale applications.

On average, modern methanogenic digesters have the potential to generate ~380-960 W/m^3 electricity[233]. To be comparable to AD, the power density of MFCs still needs to increase by a factor of approximately 3.5 (the typical area power density for MFCs is ~1000mW/m^2)[241], making the current generation of MFCs un-competitive. In addition, in WWTPs, the removal of contaminants is the primary goal, and power production comes second[264]. Despite these challenges, the high-energy generation potential and positive carbon footprint make MFCs still one of most promising methods for achieving energy positive wastewater treatment.

3.1.2 High Value Byproduct Formation: MECs

Unlike MFCs and MB that produce electricity, microbial electrolysis cells (MECs) consume electricity and harness the energy in the form of hydrogen or other energy sources. A LCA (Life Cycle Assessment) indicates that high value products from well-designed MECs provide significant environmental benefits[266]. On the anode surface of MECs, electrochemically active bacteria oxidize organic matter and produce electrons and protons. Then on the cathode with the presence of suitable catalyst, hydrogen is produced by protons and oxygen via extra voltage[267]. The applied voltages should be considered carefully for reasonable energy efficiencies (the energy in the hydrogen gas produced relative to the electrical energy input) and COD removal rate[268, 269]. A recent study demonstrated that the energy efficiency ranged between 406±6% and 194±2% when applied voltages rose from 0.3V to 0.8V[268]. As a modification of MFCs, both single-chamber and two-chamber cells could be used. But usually, a two-chamber MEC divided by membrane is suggested so that the effect of hydrogenotrophic methanogenesis would be minimized[270].

Similar to other bioelectrochemical processes, anode and cathode properties are extremely important for MEC performance. Studies showed that the interaction between microbial metabolism and electrodes could affect the performance of the fuel cell[271]. Bioelectrical reactions cause pH to decrease in the anode chamber and increase in the cathode chamber. As the solution chemistry (pH, conductivity) is so important, choice of catholyte acts as a key factor regulating hydrogen production[220, 270]. Similar to MFCs, process scale-up is challenging. Large effective cathode surface area and the elimination of methanogens are both thought to be key considerations for bioelectrochemical system scale up[274]. To demonstrate that MECs are suitable for practical usage, scaled up processes have been installed in several studies, as detailed in Table 5.

Besides the main product (hydrogen), it is possible to obtain other valuable products from MECs to further recover energy or nutrients. This approach is termed microbial electrosynthesis.

Some H_2-driven reactions could produce storage polymers such as PHB for bioplastic production[275], or produce acetate by homoacetogens[276]. Methane could be produced either by acetoclastic methanogenesis and hydrogenotrophic methanogensis (mostly from hydrogen)[277] or by direct electron transfer to methanogens rather than from hydrogen or acetate[278]. Thus, a methane-producing MEC combined with AD has been proposed as a promising polishing post-treatment for AD[279-281]. Ethanol and butanol formation are also observed on the cathode[282]. Cusick and Logan[283] also introduced a Microbial Electrolysis Struvite-precipitation Cell (MESC) for concurrent recovery of phosphate and hydrogen.

4. OUTLOOK FOR ENERGY POSITIVE WASTEWATER TREATMENT

While several technologies have been reviewed separately here, it is unlikely that our goal of energy neutral or positive wastewater treatment can be attained with single technology. The combination of various technologies, deliberate arrangement of pre-treatment, core treatment and post-treatment methods, and a combination of sidestream and mainline treatment are the key to energy positive operation and resource recovery from wastewater treatment. On the one hand, we are trying to combine contaminant removal, energy generation and resource recovery using diverse processes and effective control systems. On the other hand, efforts should be made to simplify configurations since complex configurations and processes likely would require high capital investments as well as operational and maintenance costs. In addition, since wastewater treatment processes are highly environment dependent, it is unlikely that a single universal process will be optimal for all wastewaters. This is especially true for the biological treatment processes that are the focus of this review, due to their often strong dependence on temperature and influent composition. Furthermore, while focusing on energy neutral strategies, it is critically important to retain public health and environmental protection as our primary goals in wastewater treatment processes, via production of clean water without health risks from pathogens, heavy metals and trace organics[284].

4.1 Future Directions

Compared with conventional activated sludge systems, advanced wastewater treatment plants are now making significant progress towards energy neutrality through installation of, among others, AD and nitritation-anammox processes. Despite extraordinary recent advances in the laboratory and in practice, much remains to be done to realize the full potential for energy savings or recovery from wastewater. We highlight selected routes for future investigations below.

Microbial ecology and metabolic mechanisms. Even though suspended and attached growth bioprocesses have been widely applied in wastewater treatment for over a hundred years, we have only a surficial understanding of microbial community structure, dynamics, interactions, and structure-function relationships in these engineered systems. Future research efforts in this realm will doubtless spur advances in process development and operation. Among each of the methods reviewed, numerous open questions related to microbial ecology remain. These include identification of functional groups relevant to bioelectrochemical systems; the impact and importance of spatial relationships among AOB, NOB and anammox on performance and stability in nitritation-anammox processes; and the importance of and controls on diverse metabolic pathways for N_2O production in the CANDO process. Moreover, efforts are warranted towards inclusion of molecular microbial ecological analyses into predictive models for process performance (function) and for improved process control strategies[285, 286]. For example, metrics of microbial community structure could potentially be used as a predictor of contaminant removal rates, along the lines of recent efforts by Seshan et al. and Helbling et al[287]. In addition, detection of low levels of unwanted taxa via molecular methods, such as NOB in nitritation-anammox processes, might be an early warning signal of process deterioration.

Process stability and efficiency of energy capture. Fluctuations in process stability are a common challenge in wastewater treatment processes, especially for refractory wastewater and low temperature environments. In practice, the deterioration of treatment performance and consequent reduction of energy production in the bioprocesses reviewed hereneeds to be prevented. Advances in instrumentation and sensor technology will doubtless aid in development of improved monitoring and control strategies for prevention of process upsets, but large design safety factors or inclusion of redundant backup units may also be warranted at full-scale, at least initially, to offset uncertainties in process stability. In addition, opportunities for improvement remain in terms of energy capture efficiency. Typically only 50% of the BOD input is digested in AD, and the production of electricity via combustion results in losses as large as 65% energy[1, 288], which means that most of the energy captured has lost. Even though bioelectrochemical systems have higher efficiencies[289], there is still much work to be done to maximize this important parameter.

Combined energy and nutrient or material recovery. In this review, we emphasize energy savings or recovery during nutrient and organic matter removal. In same cases, however, material recovery, particular nutrient recovery, may be a better choice. For example, instead of N removal from wastewater, direct recovery of NH_4^+ as a fertilizer is a conceptually extremely attractive option, as highlighted above. As these innovative technologies for energy and nutrient recovery mature, economic and technical feasibility analyses will be needed to optimize use of these approaches. We wish to emphasize that this need not be an “either/or” proposition; in all probability, a combination of energy and N (and other material) recovery technologies will prove most beneficial, and this combination will likely differ on a case-by-case basis.

Model development. Simulations for organic matter, nutrient and microbial transport in bioreactors, as well as quantitative evaluation of the impacts of difference environmental factors on microbial growth, metabolic reactions, and pathways are trends for further WWTP research and design. As mentioned before, models for COD removal are well-developed. By comparison, much work remains for model development for emerging N removal processes. Modeling activity for these processes has largely focused thus far on sidestream nitritation-anammox systems. Experimental work has shown that the nitritation and anammox activity balance in such systems could be affected by aggregate size distribution[54]. The impact of this relatively easily measured parameter has been corroborated by recent modeling efforts[290], and aggregate physical characteristics (balance between floccular and granular biomass) has also been shown via modeling to be a likely influential driver of nitritation-anammox process performance and activity segregation [291]. We suggest that additional modeling efforts along these lines are warranted to predict process performance characteristics under dynamic, fluctuating conditions, and to aid in development of effective control schemes for sidestream and mainline nitritation-anammox, CANDO, and microalgal processes.

LCA analysis. Cradle-to-Gate LCA is a useful tool for evaluation and comparison of different methods by considering both downstream and upstream processes and impacts. Several studies describing LCA application to mature processes like AD are available in the primary literature[133, 134, 292-294]. The application of LCA to lab or pilot scale techniques, e.g. mainline anammox and CANDO, would not be easy since little reliable input or output data could be obtained. Variability in boundary setting, inventory input and interpretation of results are key challenges to the application of LCA. Development of standardized guidelines has thus been suggested to normalize use of the LCA methodology[295]. However, it is still a strong tool for methods comparison and could be used as supplemental criteria for methods selection or to direct future research strategies. As data emerges from full-scale trials of the technologies highlighted here, LCA will become an important decision-making tool for practitioners, and should be the focus of future efforts.

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Table 1. Studies focusing on application of anammox processes under moderate or low temperature

Configuration		Volume (L)	Operation Conditions: Influent nitrogen concentration	T (℃)	HRT (day)	Major Conclusions	Reference
Granular Sequencing Batch Reactor (SBR)	Two units	1.0	400-700 mg/L NH_4-N with different dilution rates	20	0.25+1	The single-unit seems to be more stable than two-stage unit at moderate temperature; DO concentration could be used as the control parameter adapting to the changes of the operational conditions	25, 296
	One unit	1.5+1.0			0.25		
A lab-scale anammox UASB		4.5	69±5 mg N/L	20	0.22	Nitrogen removal rate reached 0.26 g N/(Ld); A low effluent concentration: 0.03-0.17 mg (NH_4^++NO_2^-)/L; Anammox biomass was retained as granules and as a biofilm on the reactor walls, and both contributed to nitrogen removal	297
An anammox UASB		8.0	16.87+2.09 mg/L NH_4^+-N, 20.57±2.31 mg/L NO_2^--N, 13.97±3.99 mg/L NO_3^-—N	30-16	0.12-0.26hr	Nitrogen removal rate reached 5.72 gN/(Ld) at 30°C, and 2.28 gN/(Ld) at 16 °C; Anammox granular sludge was formed at 30 °C and could maintain at lower temperature	298
An anammox UASB with low-intensity ultrasound irradiation		1.0	N/A	15	N/A	It was possible to increase the stability of Anammox by ultrasound irradiation under moderate temperature	299
A one-stage nitritation-anammox SBR		5	70 mg NH_4^+-N/L	12	0.5	90% of the supplied nitrogen was removed at low temperature; NOB activities was not detected under oxygen limitation; The decreasing of activities due to low temperature was reversible so that biomass could adjust seasonal changes	300

A one-stage nitritation-anammox Rotating Biological Contactor (RBC)	2.5	60 mg NH_4^+-N/L	15	1.09-1.57hr	The total nitrogen removal rates can be maintained at 0.5 gN/(Ld) when temperature was decreased from 29 °C to 15 °C with low nitrogen loading and moderate COD levels; The accumulation of nitrite and nitrate was observed, and authors noted the need for future improvement	47
A pilot scale MBBR nitritation-anammox	200	715-837 mg/L NH_4^+-N	10-19	1.7-4.1	The system had stable nitrogen removal when decreasing temperature from 19 °C to 13 °C, and became unstable at 10 °C; Anammox bacteria were dominant despite of temperature changes	301

Table 2. Mainline nitritation-anammox demonstrations and NOB suppression strategies

Configuration	Facility & Location	NOB Suppression strategy	Major outcome	Reference
A lab-scale single-stage nitrogen-removal biological filter (NRBF) and an external aeration cell	Inha University, Republic of Korea	HRT adjustment Oxygen supply control	The nitrogen removal rate as well as nitrogen loading rate increased with a decrease in HRT ,and efficient nitrogen removal was obtained with 1h HRT Over 90% total N removal by controlling oxygen supply to 0.75 mol O_2/mol NH_3 added	59
A lab-scale membrane bioreactor (MBR)	Beijing University of Technology, Beijing	HRT adjustment Oxygen supply control	The nitrogen removal rate reached 0.97 kg/m^3d Sufficient oxygen supply suppressed NOB	302
A lab-scale rotating biological contactor	LabMET, Ghent University, Belgium	High DO Transient anoxia Residual ammonium	RBCs demonstrated to be a reliable configuration to ensure anammox retention at short HRT operation; Rapid transient anoxia, high DO exposures due to atmospheric contact contributed to high AerAOB rates	303
A pilot scale A/B process: A-stage: COD removal; B-stage: CSTR and MBBR	Chesapeake-Elizabeth WWTP, the Hampton Roads Sanitation District (HRSD), Virginia	Residual ammonia Novel AVN aeration controller[a] Transient anoxia Controlled COD input Limiting aerobic SRT	The mainstream deammonification at ambient temperature removed up to 95% total influent nitrogen The major NOB suppression mechanism was DO control CSTR biomass has poor settling characteristics and challenges for SRT control	53, 304
A 4m^3 pilot-scale plug flow reactor	Dokhaven-Sluisjesdijk WWTP, Rotterdam, The Netherlands	High DO; Granular anammox biomass inoculation; Controlled COD input; SRT adjustment	Oxygen competition plays key role in NOB out-selection; Granular sludge has ability to resist harsh environments	305

A 10L pilot scale bench-scale sequencing batch reactor (SBR)	Blue Plains WWTP, Washington, DC	Transient anoxia; Sieve/fine screen based technologies for bioaugmumentation from sidestream; Cyclones on mainstream to retain anammox	Higher DO (1.5 mg/L) is effective for NOB suppression; Transient anoxia seems to be the crucial process	5, 57
A full scale A/B mainstream process with sidestream DEMON process	Strass WWTP, Austria	Cyclones for bioaugumentation from sidestream system	With mainline and sidestream Anammox, Strass WWTP is a net energy positive plant	5, 57
A full scale step feed activated sludge (SFAS) process	Changi Water Reclamation Plant (WRP), Singapore	Short SRT under the high operating temperature; Alternating aerobic and anoxic conditions	Lower ammonium concentration and higher COD/NH_4 result in a suspended/floc or free anammox growth; the utilization of COD by PAO (phosphate accumulate organisms) could cause the out-selection of denitrifiers	60

a. AVN aeration control strategy is to control aerobic duration based on the comparison between NH_4-N and NOx-N.

Table 3. Comparison of processes for complete N removal in terms of oxygen and reducing equivalents from organics consumed, biosolids produced, and energy recovered per mole ammonia. All calculations based on reported biomass yield and typical solids residence time for each unit operation (Rittmann and McCarty, 2001)[306].

\	Nitrification-Denitrification	Nitritation-Denitritation	Nitritation-Anammox	CANDO	CANDO (autotrophic)[b]
O_2 (mole)	1.8	1.3	0.7	1.3	0.7
Reducing Equivalents from Organics (e^-)	9	5.5	1	3.5	0
Biosolids Produced (g VSS)[a]	28	18	7	12	8
Energy Recovery from NOD (kJ)	0	0	0	41	41

[a]Value includes biosolids produced from ammonia oxidation and nitrite, or nitrate, reduction

[b] Theoretical values from aerobic ammonia oxidation coupled to nitrifier-denitrification

Table 4. Summary of full-scale co-digestion applications

Co-digestion Substrate	Full-scale Application	Reference
Domestic solid waste	Velenje, Slovenia Viareggio and Treviso, Italy	[307, 308]
Food waste	British Columbia, Canada EBMUD[a], CA, USA	[309, 310]
Manure and food waste	Marcon-Venice, Italy	[311]
Slaughterhouse waste	LinkÖping AB, Sweden	[312]

a. EBMUD: the East Bay Municipal Utility District

Table 5. Examples of scale-up demonstrations for MECs

Anode	Cathode	Configuration	Inoculation	Hydrogen Production Rate	Reference
Two layers of carbon felt	Carbon paper with electrodeposited nickel particles	A continuous-flow single-chamber 20L MEC (two modules in serious)	Other existing MEC effluent	0.2 and 0.9 mol H_2 mol/COD for two reactors	[313]
One layer of carbon felt	Carbon paper with electrodeposited nickel particles	A continuous-flow single-chamber 10L MEC (two modules in serious)	Homogenized anaerobic mesophilic sludge	0.12-0.36 mol H_2 mol/COD	[314]
A sheet of carbon felt	Stainless steel wire wool (grade 1)	120L MEC	N/A	H_2 production: 0.015 L/Ld	[315]
Graphite fiber brushes	SS 304 (mesh #60, W=7.6cm, L=66cm, McMaster-Carr, OH, USA)	1000L continuous flow MEC	Various inoculation and feed adjustment (Geobacteraceae as dominant species)	Gas production: 0.19±0.04L/Ld (with 86±6% of methane)	[316]

Figure 1. Nitrogen flow for nitrification-denitrification, nitritation-anammox and nitritation-denitritation

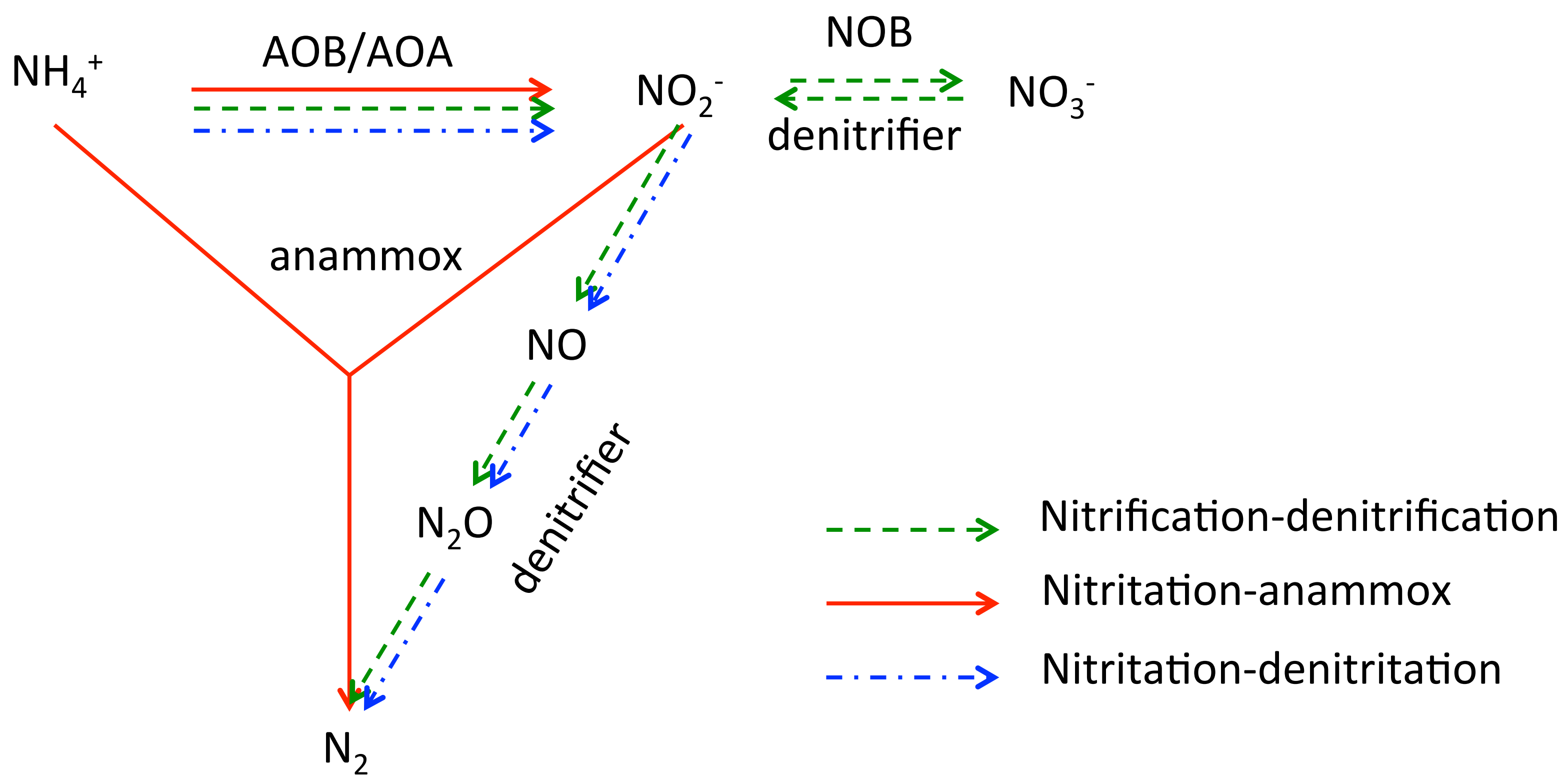
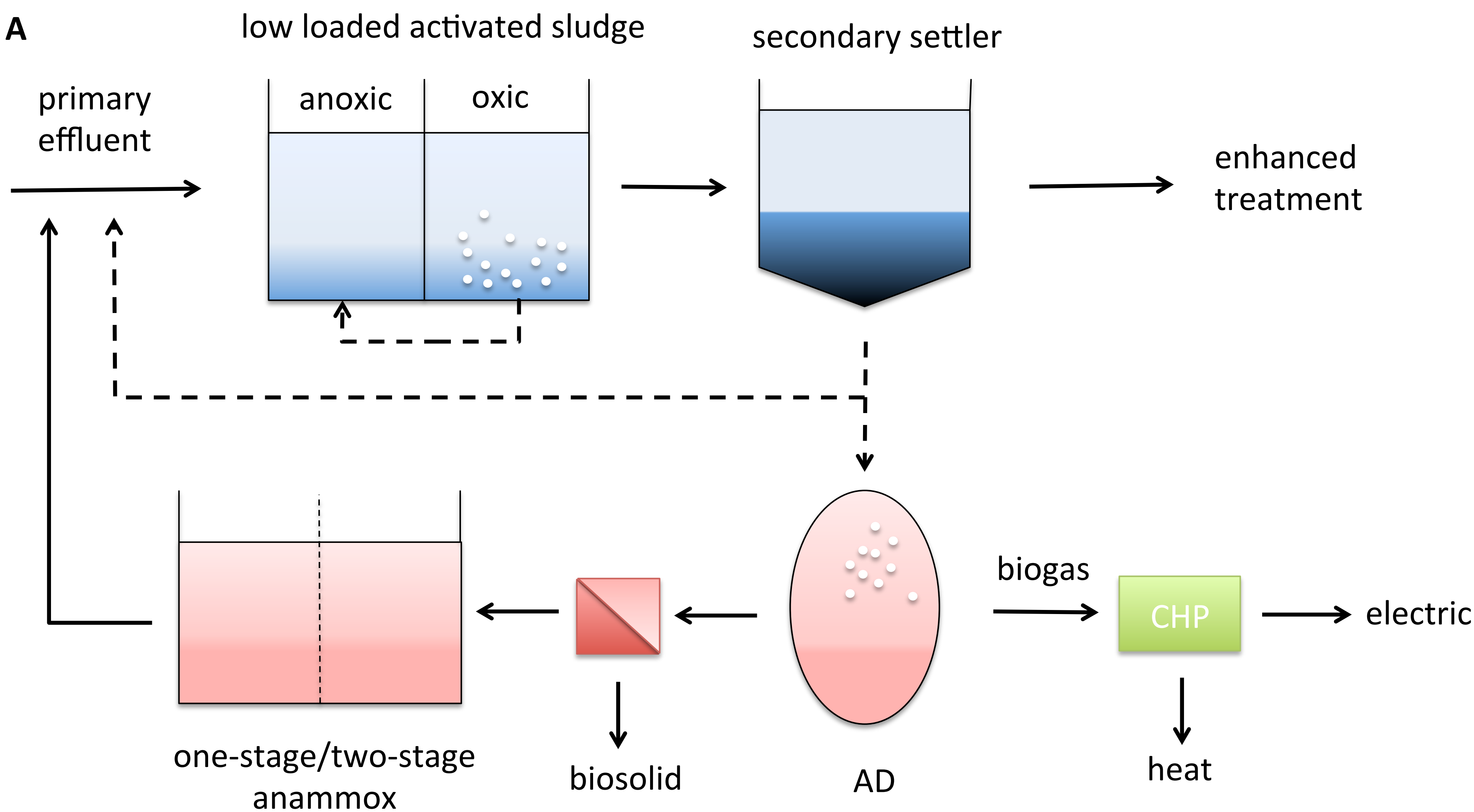
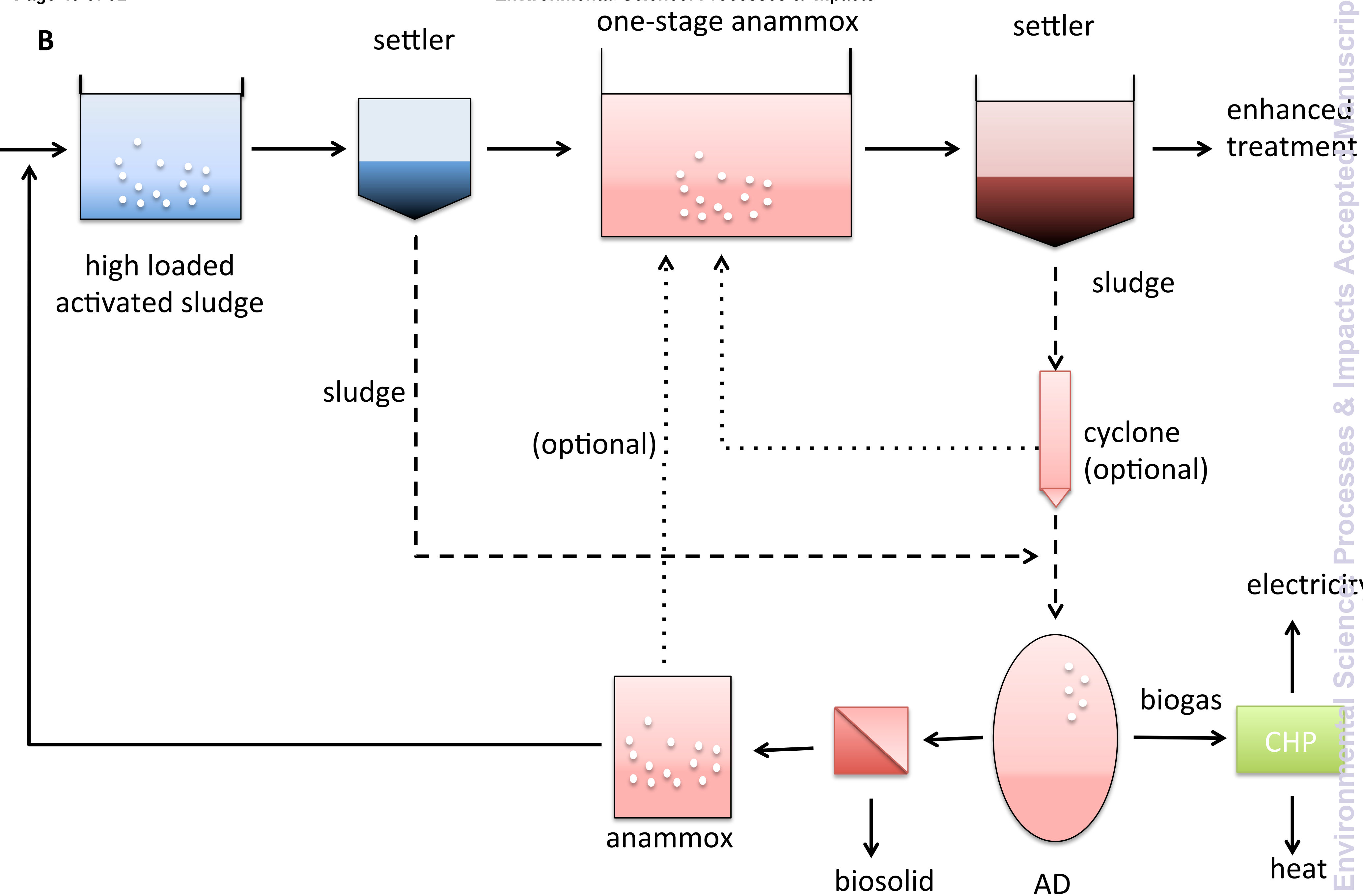


Figure 2. Schematic overview of nitritation-anammox based wastewater treatment processes in the (A) sidestream and (B and C) mainstream. AD: anaerobic digestion; CHP: combined heat and power; AnMBR: anaerobic membrane reactor. (After De Clippeleir et al. (2013), Ref. 303)




B
settler
one-stage anammox
settler
enhanced
treatment
high loaded
activated sludge
sludge
sludge
(optional)
cyclone
(optional)
electricity
biogas
CHP
anammox
biosolid
AD
heat

c

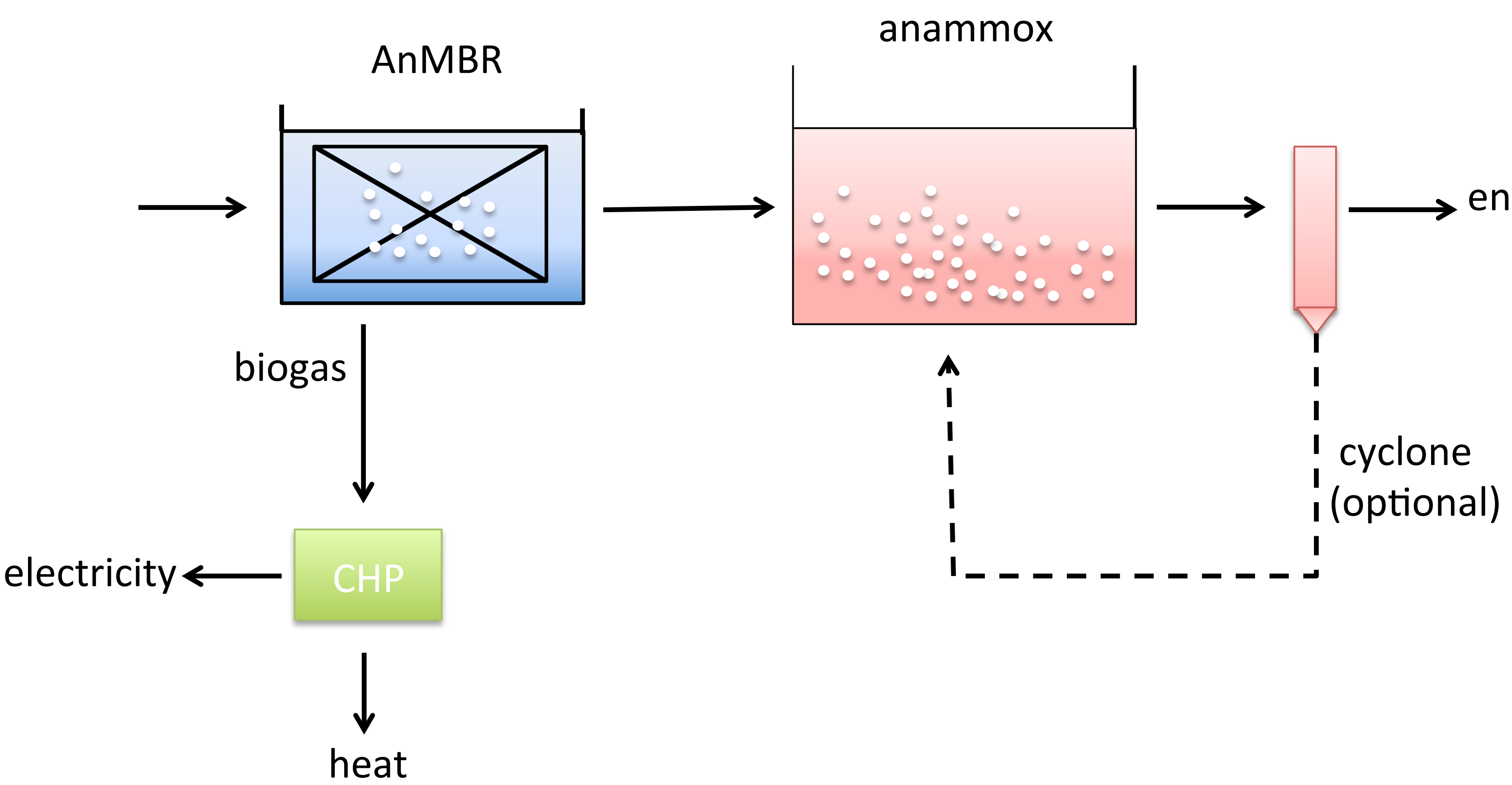
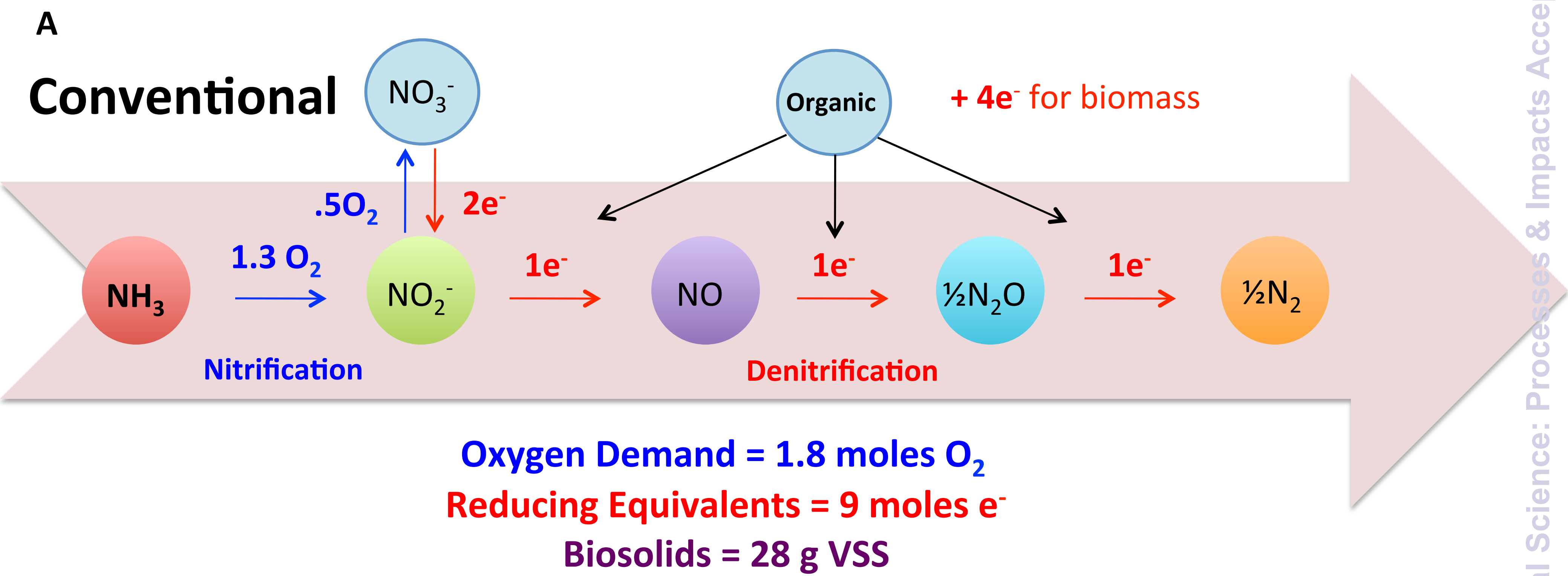
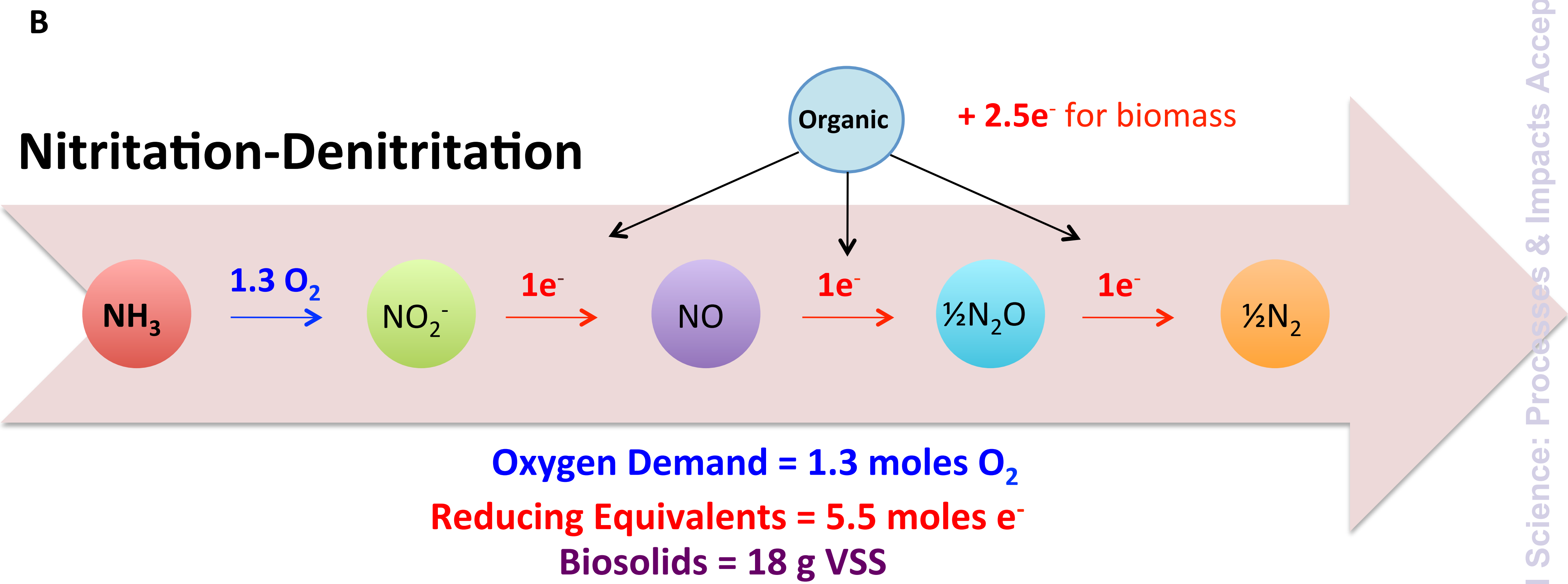
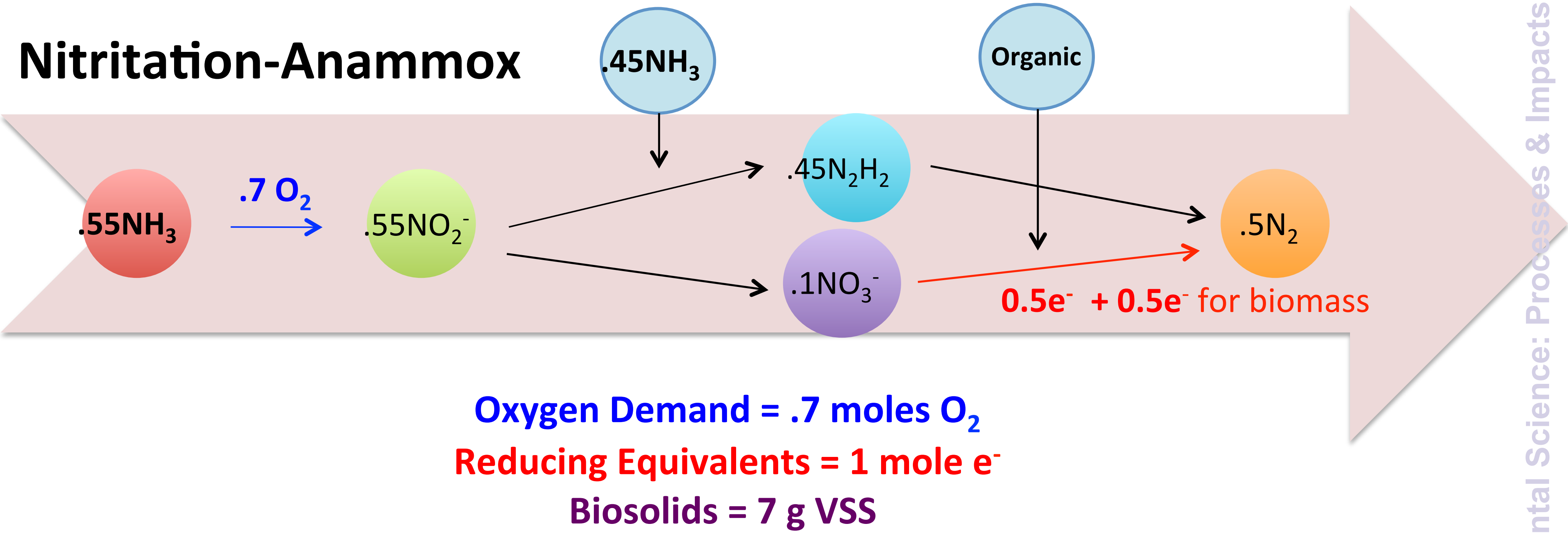

AnMBR
anammox
enhanced treatment
biogas
cyclone
(optional)
electricity
CHP
heat

Figure 3. Comparison of four processes for nitrogen removal in terms of oxygen and reducing equivalents from organics consumed, biosolids produced, and energy recovered: (A) Conventional Nitrification-Denitrification, (B) Nitritation-Denitritation, (C) Nitritation-Anammox, (D) CANDO, and (E) a possible future variation of CANDO, here termed CANDO autotrophic. All calculations based on reported biomass yield and typical solids residence time for each unit operation (Rittmann and McCarty, 2001, Ref. 306).

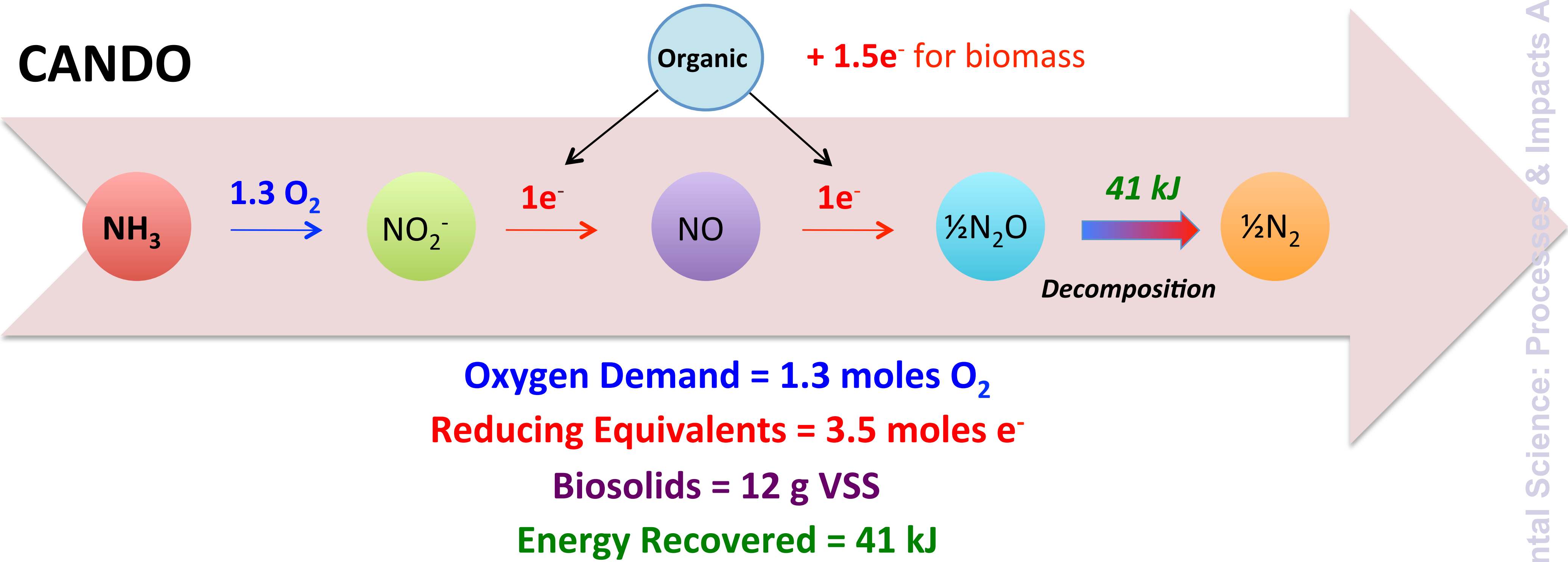



B
Nitritation-Denitritation
Organic
+ 2.5e- for biomass
NH3
1.3 O2
NO2-
1e-
NO
1e-
½N2O
1e-
½N2
Oxygen Demand = 1.3 moles O2
Reducing Equivalents = 5.5 moles e-
Biosolids = 18 g VSS

C


Nitritation-Anammox
.45NH3
Organic
.55NH3
.7 O2
.55NO2-
.45N2H2
.1NO3-
.5N2
0.5e- + 0.5e- for biomass
Oxygen Demand = .7 moles O2
Reducing Equivalents = 1 mole e-
Biosolids = 7 g VSS

D


CANDO
Organic
+ 1.5e- for biomass
NH3
1.3 O2
NO2-
1e-
NO
1e-
½N2O
41 kJ
½N2
Decomposition
Oxygen Demand = 1.3 moles O2
Reducing Equivalents = 3.5 moles e-
Biosolids = 12 g VSS
Energy Recovered = 41 kJ

E

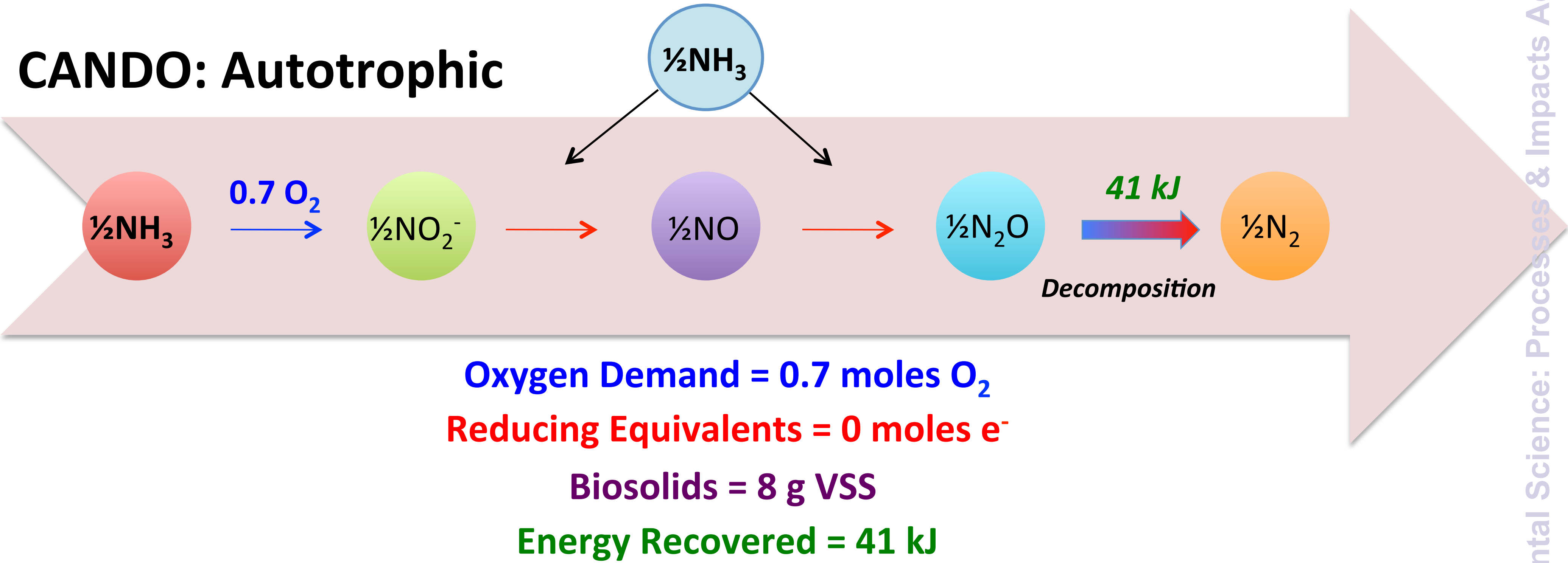

CANDO: Autotrophic
½NH3
½NH3
0.7 O2
½NO2-
½NO
½N2O
41 kJ
Decomposition
½N2
Oxygen Demand = 0.7 moles O2
Reducing Equivalents = 0 moles e-
Biosolids = 8 g VSS
Energy Recovered = 41 kJ

Figure 4. A portrait of algae cultivation combining with effluent polishing, energy generation, and multi-byproducts utilization

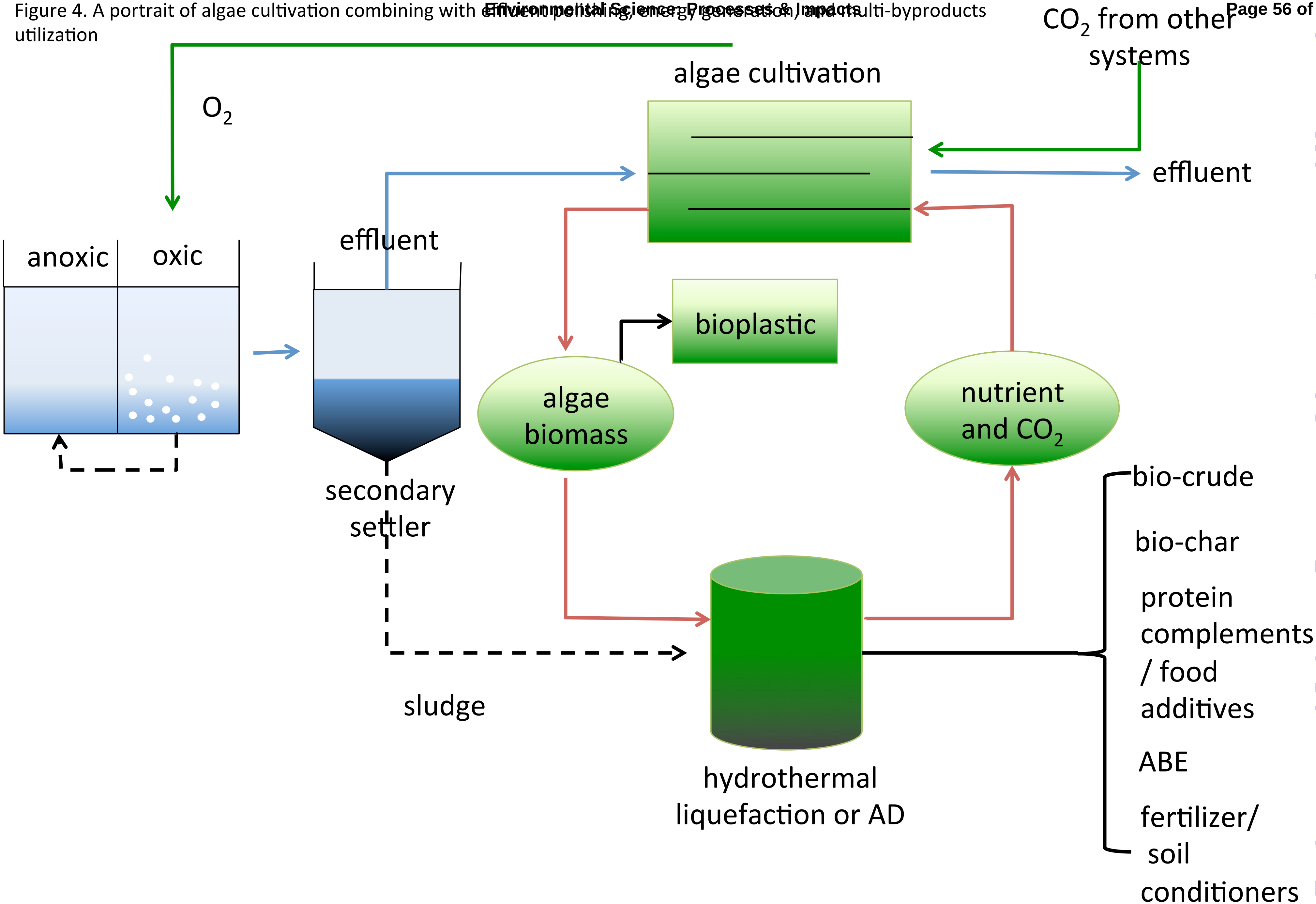
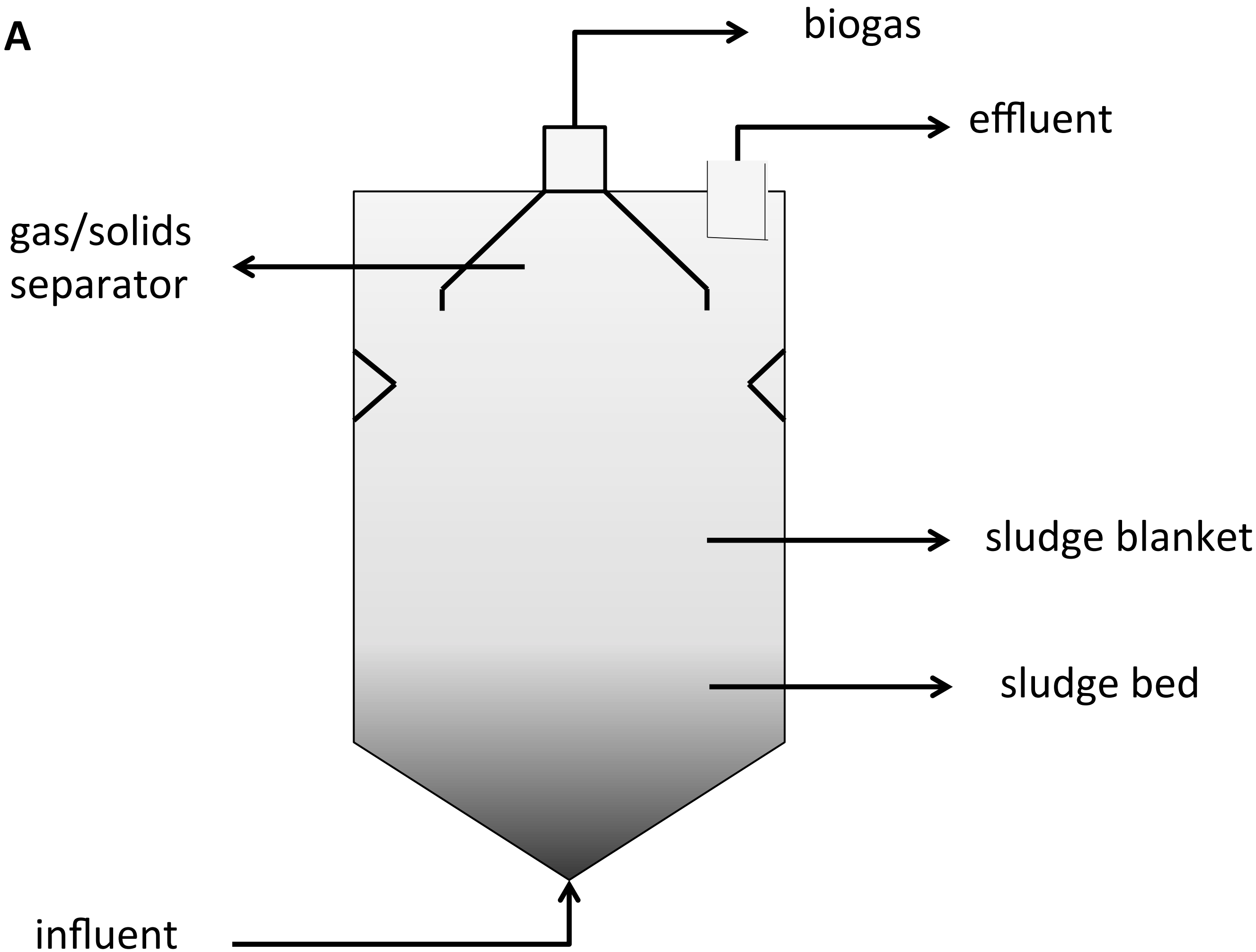
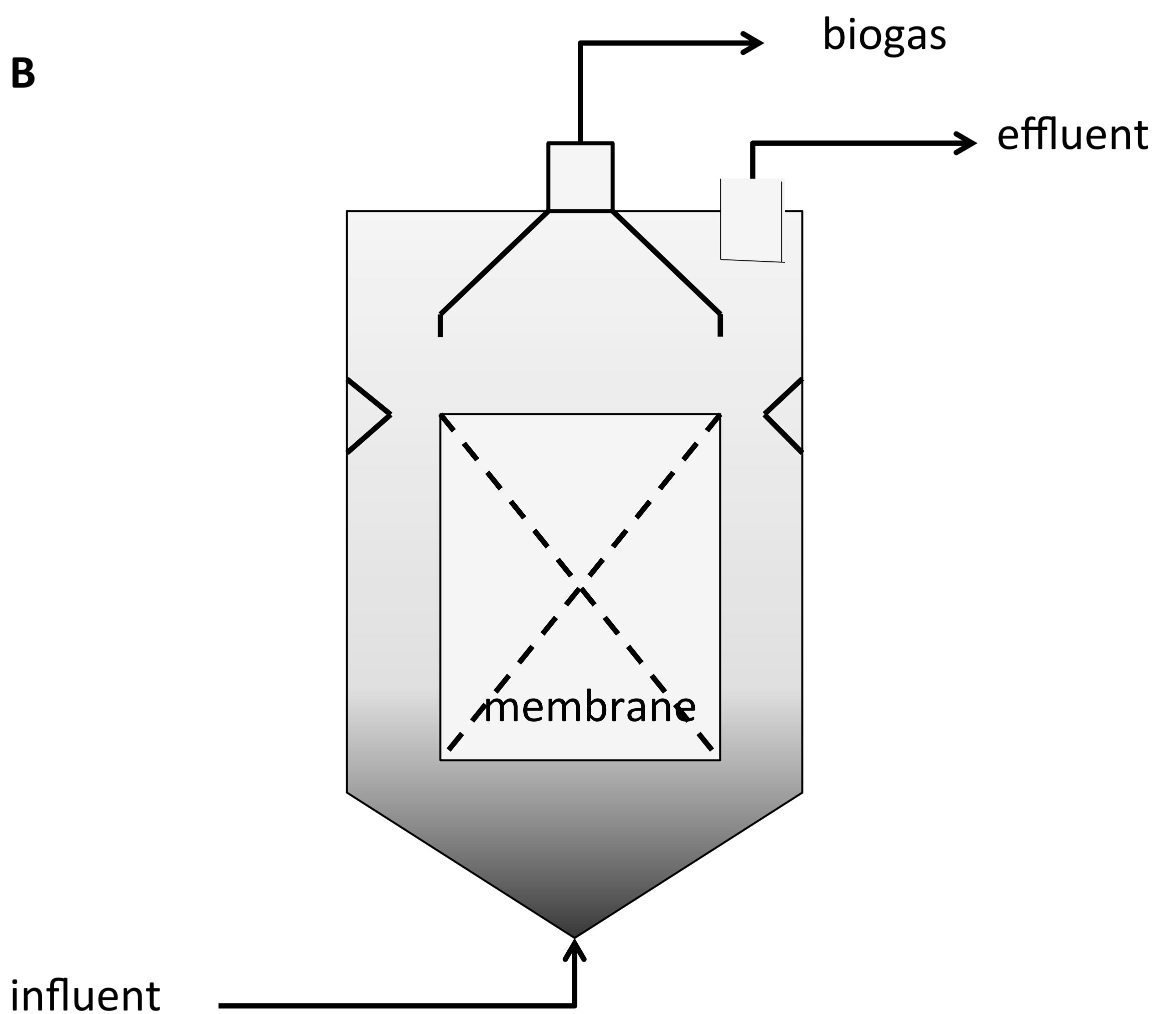


Figure 5. Schematic configuration of a (A) UASB and two kinds of AnMBR: (B) submerged and (C) sidestream

A



B



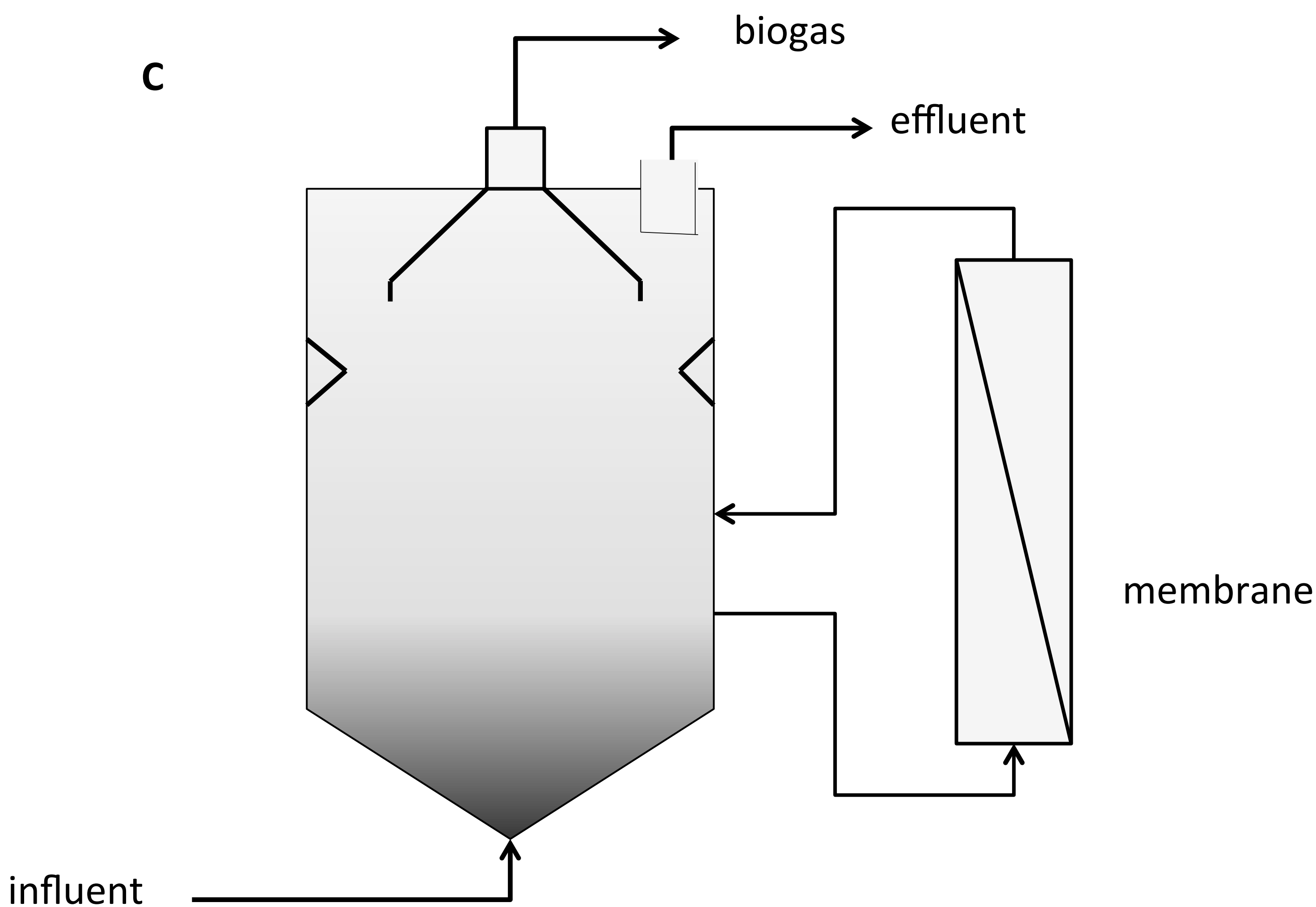
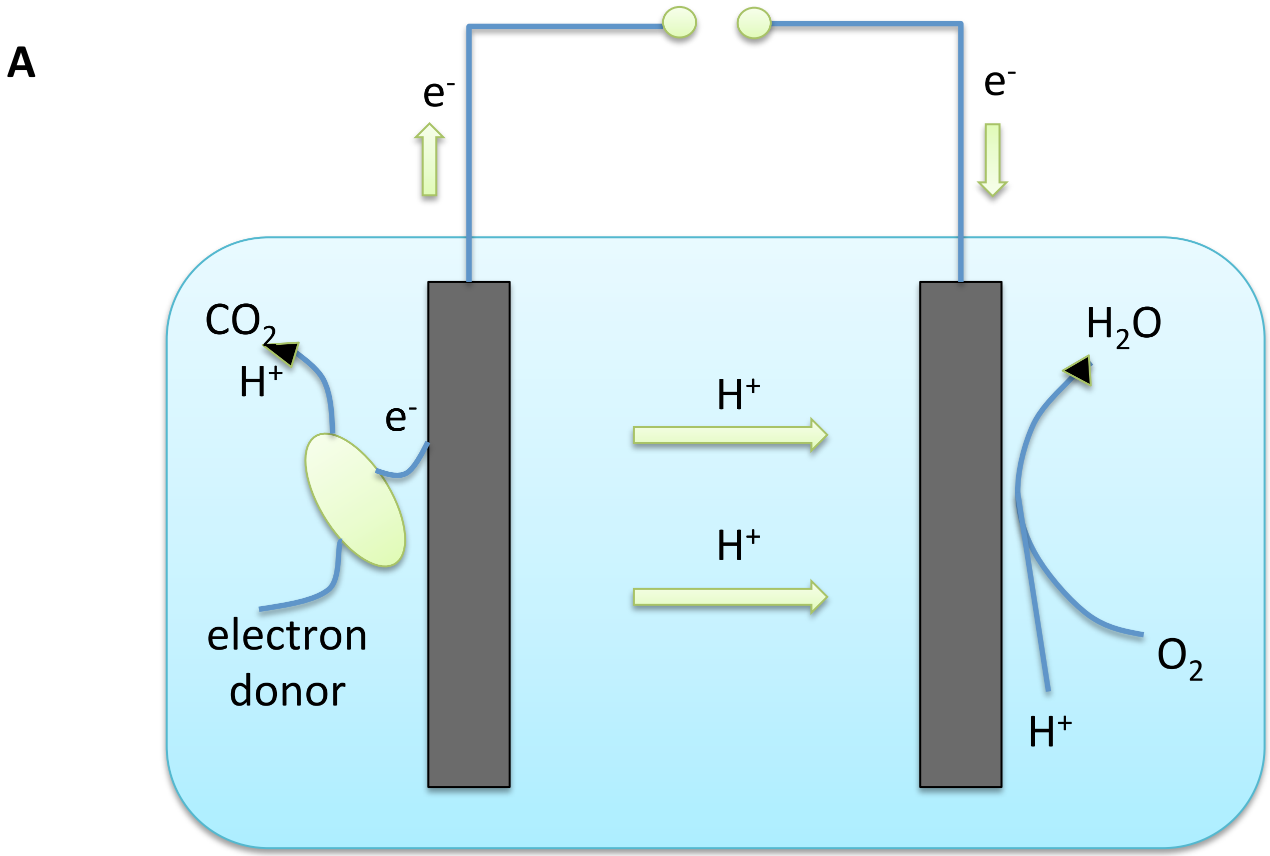

c
biogas
effluent
membrane
influent

Figure 6. Schematic illustration of energy generation or byproduct formation using (A) MFC and (B) MEC



B