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The use of ammonia recovered from wastewater as a zero-carbon energy vector to decarbonise heat, power and transport – A review

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ABSTRACT

Ammonia (NH_3) is an energy vector with an emerging role in decarbonising heat, power and transport through its direct use as a fuel, or indirectly as a hydrogen carrier. Global ammonia production is having to grow to enable the exploitation of NH_3 for energy decarbonisation, which it is projected will consume >50 % of manufacturing capacity by 2050. Ammonia recovered from wastewater can be directly exploited as a sustainable source of ammonia, to reduce the demand for ammonia produced through the energy intensive Haber-Bosch process, while fostering a triple carbon benefit to the water sector, by: (i) avoiding the energy required for aeration of biological processes; (ii) reducing nitrous oxide emissions associated with ammonia oxidation, which is a potent greenhouse gas; and (iii) producing a zero-carbon energy source that can decarbonise energy use. While previous reviews have described technologies relevant for ammonia recovery, to produce ammonia as a zero-carbon fuel or hydrogen carrier, wastewater ammonia must be transformed into the relevant concentration, phase and achieve the product quality demanded for zero carbon heat, power and transport applications, which are distinct from those demanded for more conventional exploitation routes (e.g. agricultural). This review therefore presents a synthesis of established and emerging technologies for the extraction and concentration of ammonia from wastewater, with specific emphasis on enabling the production of ammonia in a form that can be directly exploited for zero carbon energy generation. A précis of technologies for the valorisation of ammonia as a clean energy or hydrogen resource is also introduced, together with discussion of their relevancy and applicability to the water sector including implications to energy, carbon emissions and financial return. The exploitation of ammonia recovered from wastewater as a zero carbon energy source is shown to offer a critical contemporary response for the water sector that seeks to rapidly decarbonise existing infrastructure, while responding to ever stricter nitrogen discharge limits.

1. Introduction

Ammoniacal nitrogen exists within municipal wastewaters, industrial effluent and chemical manufacturing, and slurries from food waste and livestock management (Kang et al., 2017; Maharaja et al., 2023; Mondor et al., 2008; Ndam, 2017). The discharge of ammoniacal nitrogen into waterways is harmful for human health and the environment. Municipal wastewater treatment therefore uses activated sludge processes to breakdown ammoniacal nitrogen through oxidation using forced aeration to supply the required oxygen, but this requires 3.0–5.0 kWh kg_N^{-1} (Table 1) (Garrido et al., 2013; Ramalingam et al., 2017; Davey et al. 2022). To further improve environmental standards and public health, nitrogen limits for treated wastewater are reducing to 10 mg L^{-1} (>0.1 million P.E.) within the Urban Wastewater Treatment Directive (91/271/EEC) which is likely to stimulate expansion of activated sludge-based processes. The treatment of primary and secondary sludge produces concentrated ammoniacal 'sidestreams' (e.g. sludge liquor) which represents approximately one-third of the total ammonia load within just 1 % of the wastewater flow (Fig. 1) (Johnson, 2011; Mackinnon et al., 2003). Advanced activated sludge processes have therefore been developed to intensify sidestream ammonia removal utilising partial oxidation to reduce aeration energy by 30–80 % (Jardin and Hennerkes, 2012; Peng et al., 2019; van Dongen et al., 2001). However, activated sludge processes are associated with almost half of greenhouse gas emissions (GHG) in wastewater treatment, largely due to the release of nitrous oxide (N_2O) which is formed as a by-product of ammonia oxidation. Nitrous oxide is a greenhouse gas that is 310 times more potent than CO_2 over a 100 year period (Winter et al., 2012).

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Table 1
Conventional and advanced activated sludge process comparison.

Biological nitrogen removal	Nitrogen removal rate $kg_N\ m^{-3}\ d^{-1}$	Aeration energy demand kWh kg_N^{-1}	N2O emission factor $kg_{N2O}\ kg_N^{-1}$
Conventional activated sludge process	<0.1[a]	3.0 - 5.0 [a-c]	0.011–0.016[d,e]
Sidestream nitrification	0.2–1.2[a,f,g]	1.0 – 2.0[a,c,h]	

[a] Ramalingam et al. (2017)
[b] Garrido et al. (2013)
[c] Maurer et al. (2003)
[d] de Haas and Andrews (2022)
[e] IPCC, 2019
[f] Jardin and Hennerkes (2012)
[g] van Dongen et al., 2001
[h] Lackner et al. (2014)

To address the energy and emission challenges related to the biological treatment of ammonia, many researchers have proposed a shift from nitrogen removal to resource recovery to align with contemporary visions for the 'water-energy-food' nexus (Robles et al., 2020; Ye et al., 2020). This is consistent with the development of low-energy anaerobic processes for mainstream wastewater treatment which do not incorporate nitrogen removal, thus providing unfettered access to the ammonia audit (Shahid et al., 2020). Ammonia is commercially synthesised using the energy intensive Haber-Bosch process (19 kWh kg_N^{-1}) which is typically fuelled with natural gas and uses a fossil derived hydrogen feedstock for ammonia synthesis (Nayak-Luke et al., 2018; Smil, 2017). Approximately 183 Mtonnes y^{-1} ammonia is produced globally (IRENA and AEA, 2022) and is associated with up to 7 % of global natural gas consumption and 1 % of global CO_2 emissions (Nayak-Luke et al., 2018; Smil, 2017). Sustainable ammonia recovery from wastewater therefore presents an opportunity to reduce energy and emissions during

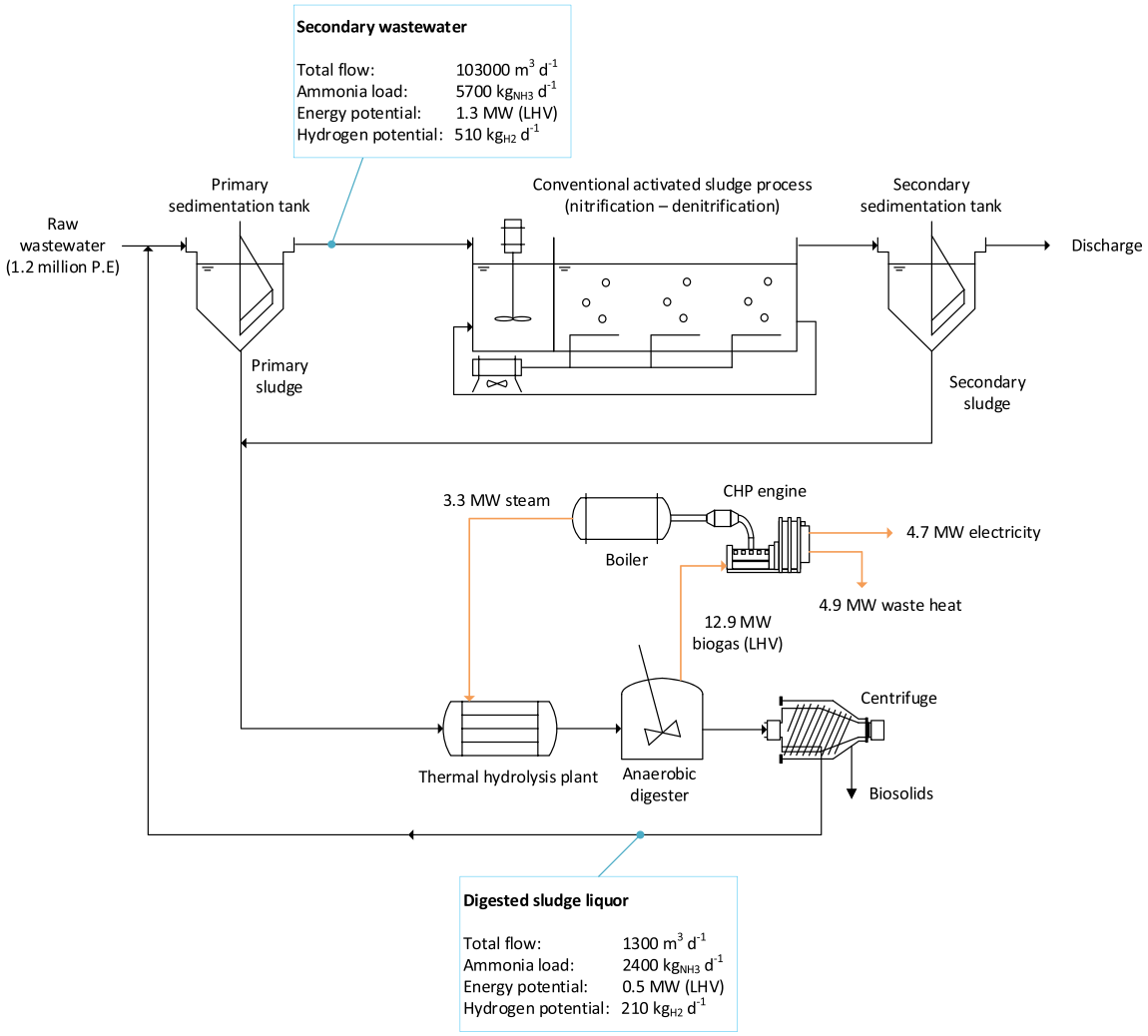


Fig. 1. Example wastewater treatment works with 1.2 million P.E. design capacity treating influent from domestic and industrial sources (Moore and Auty, 2013; Ndam, 2017).

biological ammonia oxidation which is complimentary to the water sectors pursuit of energy and carbon neutrality and the industrial decarbonisation of ammonia production (Water Europe, 2021; Water UK, 2020). The primary use of ammonia is currently within agricultural fertilisers (70 %) and the remainder is applied as an industrial feedstock (International Energy Association, 2023). Ammonia recovery has principally focused on the production of struvite and ammonium sulphate as possible sustainable fertilisers (Jamaludin et al., 2018; Vaneeckhaute et al., 2017) that could help to close the nutrient cycle. However, key supply chain and legislative barriers exist, such as the classification of these materials as wastes under European law (Directive 2008/98/EC, 2008). This creates challenges for entry and acceptance of these products in the market versus virgin materials, which has disincentivised investment in ammonia recovery (Sfetsas et al., 2022; Vaneeckhaute et al., 2017).

Ammonia also has an emerging role in decarbonising transport, heat and power generation either by using ammonia directly as the fuel, or indirectly where ammonia can behave as a hydrogen carrier (Lan and Tao, 2014; The Royal Society, 2020; Zamfirescu and Dincer, 2008). By 2050, more ammonia will be used for these emerging energy applications than is currently used for fertiliser; over 50 % of ammonia production capacity is therefore expected to be for zero carbon energy applications (IRENA and AEA, 2022). Consequently, large investments are being undertaken in expanding the production of 'green' and 'blue' ammonia to decarbonise production and accelerate the energy transition to net zero. The use of ammonia recovered from wastewater as a fuel can aid in decarbonising ammonia production. Transformation of wastewater ammonia to an energy product may also lower barriers to adoption by the supply chain, where risks to product formulations or human health are mitigated, and the intrinsic energy may be used internally by the water utility to produce clean energy therefore providing value to the operator and avoiding the dependency on the downstream supply chain.

Ammonia can be decomposed to generate hydrogen (Jackson et al., 2015). Hydrogen requires cooling below -253 °C to liquefy it for storage and transportation whilst ammonia can be liquefied at ambient conditions under 10 bar pressure (Table 2). Since liquid ammonia has a hydrogen density which is 1.7-times higher than liquid hydrogen, its use as a carrier within the 'hydrogen economy' could reduce energy storage and transportation costs by an order of magnitude (Kojima, 2013; Valera-Medina et al., 2018; Kobayashi et al., 2019; Lamb, Dolan and Kennedy, 2019). The generation of hydrogen from ammonia could complement planned investments within the water sector for the electrolysis of treated wastewater for hydrogen production which attract incentives under the EU Renewable Transport Fuel Obligation (Anglian Water, 2021; Jacobs, 2022). Clean water demands of 0.1–0.3 L kWh_{H2}^{-1} and 0.5 L kWh_{H2}^{-1} are required for the production of natural gas steam reforming and water electrolysis respectively, and so the delivery of large-scale renewable hydrogen production (312–700 TWh_{H2} y^{-1}) could be equivalent to an increase in national water demand between 85,000 and 960,000 m^3 d^{-1} (Water Resources East, 2020). Capital investments required to increase water supply capacity to meet the demand of hydrogen production could therefore be offset by the production of carbon-free hydrogen from ammonia. Alternatively, strategies for energy generation from ammonia would complement ongoing investments taken by the water industry for renewable energy generation and biomethane production where incentives offered under legislation such as the EU Renewable Energy Directive II (European Parliament Council of the European Union, 2018) aim to increase production of renewable energy to at least 32 % by 2030. Ammonia has a lower heating value (LHV) of 5.3 kWh kg^{-1} similar to biogas (6.1 kWh kg^{-1}) and could co-fuel existing biogas and biomethane turbines for combined heat and power generation or be exploited for high efficiency electricity production in emerging electrochemical fuel cells (Lan and Tao, 2014; Okafor et al., 2019; Uchida et al., 2019). To contextualise this opportunity, the chemical potential of ammonia in UK municipal wastewater is approximately 1.0 TWh $year^{-1}$, which is equivalent to approximately 40 % of the total energy required for wastewater treatment nationally (2.3 TWh $year^{-1}$) and is greater than the total renewable energy presently produced by the sector (0.5 TWh $year^{-1}$) (Davey et al., 2022; The Parliamentary Office of Science and Technology, 2007). However, to realise ammonia as a zero-carbon fuel and hydrogen carrier, ammonia must be recovered from wastewater at the relevant concentration, phase and product quality requirements demanded by the methods of energy generation, which is distinct from those demanded for agricultural purpose. This review presents a synthesis of established and emerging technologies for the extraction and concentration of ammonia from wastewater, critically evaluating process scale, complexity and implementability, reflecting on the energy requirements for conversion to an ammonia product to meet the quality specification demanded for fuels. This is complemented by a précis of technological routes for the valorisation of ammonia as a clean energy or hydrogen resource, together with an appraisal of various implementation strategies that may be used to integrate ammonia to energy into the existing asset base to emphasise how the various exploitation routes can benefit operators based on energy, carbon emissions and financial return.

2. Ammonia concentration and recovery from wastewater

Approximately one-third of the ammonia load is concentrated within the centrate (return liquor) produced from anaerobic digestion (AD) digestate. Centrate ammonia concentration (1 to 2 kg m^{-3}) is 20 to 40 times richer than crude wastewater depending on whether the site is equipped with conventional AD or advanced AD (AAD) (Lubensky et al., 2019; Ndam, 2017; Davey et al., 2022). The high ammonia concentration of the centrate will benefit mass transfer to enable more efficient and smaller footprint separation technologies to be realised. This is analogous to ammonia separation from industrial and agricultural slurries arising from livestock and industrial applications which can exceed ammonia concentrations of 5.5 kg m^{-3} (Table 3) and are more commonly treated by stripping technologies at full-scale for the selective recovery of ammonia (Bavarella et al., 2020; Bonmatı and Flotats, 2003; Ukwuani and Tao, 2016; Zeng et al., 2006; Kang et al., 2017; Mondor et al., 2009). Ammonia stripping exceeding 90 % removal has been

Table 2
Thermo-physical properties of ammonia and conventional fuels.

		Ammonia	Biogas[a]	Biomethane	Propane	Hydrogen
Energy density (LHV)	kWh kg^{-1}	5.3	6.1[a]	11.7	12.8	33.3
Laminar flame velocity at 1 bar/20°C	m s^{-1}	0.1[b]	0.3[c]	0.4[b]	0.4	2.9[b]
Gravimetric hydrogen density	%wt	17.5 %	9 %[a]	25 %	18 %	100 %
Liquifaction temperature at 1 bar	°C	-33.4	-	-161	-42	-253
Liquifaction pressure at 25°C	bar	10	-	-	10	-
H_2 density in liquified state[d]	kg_{H2} m^{-3}	121	-	113	101	71

[a] Biogas based on 60 % CH_4 (Moore and Auty, 2013)
[b] Kobayashi et al. (2019)
[c] Hinton and Stone (2014)
[d] Liquified at 1 bar, (Lamb et al., 2019)

Table 3
Characterisation of wastewaters present across municipal wastewater treatment.

Type	Feed NH_3 kg m^{-3}	pH -	Alkalinity g L^{-1}	Refs.
Municipal wastewater treatment				
Raw and secondary wastewater	<0.05	<7.5	0.1	Henze and Comeau (2008), Ndam (2017), Saddoud et al. (2007)
AnMBR / UASB effluent	<0.05	7.2 - 8.1	-	Deng et al. (2014), Martin Garcia et al. (2013), McAdam et al. (2011)
Centrate from anaerobic digestion	0.4 - 1.1	7.6 - 8.3	1	Lubensky et al. (2019), Ramalingam et al. (2017)
Centrate from advanced anaerobic digestion	1.5 - 2.0	8.2 - 8.4	7	Bavarella et al. (2020), Davey et al. (2022), Ndam (2017)
Other sources				
Digested food waste	2.8 - 3.6	7.9 - 8.5	11	Kang et al. (2017), Waeger et al. (2010)
Landfill leachate	0.4 – 4.0	7.5 - 8.5	3	Brennan et al. (2016), Waeger et al. (2010), Zhang et al. (2020a)
Livestock slurry (swine, cattle, poultry)	2.8 - 5.5	7.4 - 8.4	18	Chantigny et al. (2009), Frost et al. (1990), Luo et al. (2022), Mondor et al. (2008)
Pharmaceutical effluent	0.6 - 6.3	3.0 - 8.0	-	Maharaja et al. (2023), Zhang et al. (2022), Zuo et al. (2020)

AnMBR – anaerobic membrane bioreactor; UASB – upflow anaerobic sludge blanket; AAD – advanced anaerobic digestion.

demonstrated down to crude wastewater concentrations but only at laboratory scale (Zangeneh, 2021). Crude wastewater represents around two thirds of the ammonia load present within the mainstream flow, where ammonia concentrations for municipal wastewater range 0.01–0.05 kg m^{-3} (Fig. 1) (Guida et al., 2022; Henze and Comeau, 2008). 'Extractive technologies' have been investigated that enable the selective physical separation of ammonia from this comparatively dilute wastewater stream to meet discharge limits. These are unlike the biological processes that breakdown ammonia because each extractive technology produces a semi-concentrated ammonia solution (i.e., ion-exchange brine) that conventionally requires further treatment or costly disposal (Canellas-Garriga, 2018). A synergy therefore exists between these extractive technologies that can access the more dilute ammonia fraction in wastewater, which produce semi-concentrated solutions, and the stripping technologies advocated for the treatment of concentrated wastewaters. By applying both strategies collectively up to 100 % of the wastewater ammonia load can be recovered. Then the stripping technology can transform the ammonia from within the concentrates produced from extractive technologies into a form that can be readily exploited for energy generation (Guida et al., 2022). This is particularly emphasised within contemporary anaerobic wastewater flowsheets which aim to replace activated sludge with mainstream anaerobic processes (e.g. anaerobic membrane bioreactors) therefore enabling access to the full ammonia load in treated, particle free wastewater (Aquatech, 2021; Martin Garcia et al., 2013). In this section, the adaptation of current and future stripping technologies to produce ammonia fuels from concentrated wastewaters is described, including the practical challenges associated with implementation in sludge liquors comprising high suspended solids, and the development of extractive technologies for application to mainstream wastewater treatment (Table 3).

2.1. Air, steam and vacuum stripping for concentrated wastewaters

Air and steam stripping are commercially established processes for ammonia removal and recovery from concentrated municipal, food and industrial sources (Organics Group, 2020; RVT, 2015). Ammoniacal feeds are treated with a counter-current air or steam flow in gas-liquid contacting columns (Fig. 2). The sweep gas is used to continuously renew vapour pressure exerted by ammonia which reduces its equilibrium concentration in the liquid-phase and drives mass transfer into the gas-phase. Therefore, the separation is controlled in the gas-phase and due to the solubility of ammonia in water, high gas-liquid (G/L, m^3_{gas} m^{-3}_{liquid}) ratios are needed. It is also necessary to increase the fraction of free ammonia in the liquid-phase during stripping by adding an alkali and/or operating at raised temperatures. Concentrated wastewaters are typically pH 7.5–8.5 (Table 3) and under these conditions, dissolved ammonia will largely dissociate into non-volatile ammonium which will reduce the driving force for mass transfer (Fig. 3) (Bavarella et al., 2020; Lubensky et al., 2019; Bates and Pinching, 1949). Amendment up to pH 10–12 is typical for air stripping processes (Boardman and McVeigh, 1998; Guštin and Marinšek-Logar, 2011), whilst steam stripping can facilitate efficient ammonia removal at pH 7–8 (Table 4) (Teichgraber and Stein, 1994; Zeng et al., 2006). Ammonia vapour pressure is also increased substantially by raising feed temperature and has led to the development of hot air stripping (Fig. 4).

The driving force for mass transfer is enhanced by reducing the equilibrium concentration while raising the free ammonia fraction in the liquid-phase. The transport of ammonia into the gas phase can be described by the two-film model, which assumes that mass transfer is dominated by diffusion across the interfacial liquid and gas films (Eq. (1)) (Heile et al., 2017; Tao and Ukwuani, 2015).

$$J_{NH3} = -k_L\ a\ (C - C^*) \tag{1}$$

where J_{NH3} is the volumetric rate of ammonia transfer (kg m^{-3} h^{-1}); k_L is the liquid-phase mass transfer coefficient for ammonia (m h^{-1}); a is the volumetric interfacial area (m^2 m^{-3}); C is free ammonia in the liquid-phase (kg m^{-3}); and C* is the equilibrium concentration for ammonia in the liquid phase (kg m^{-3}). Higher temperatures result in a greater rate of ammonia mass transfer as evidenced by liquid-phase volumetric mass transfer coefficients of 1.3, 4.5 and 11.0 h^{-1} when stripping with air at 25 °C and 50 °C or with steam at 100 °C, respectively (Boardman and McVeigh, 1998; Guštin and Marinšek-Logar, 2011; Zeng et al., 2006). The G/L ratio will decline when the stripping temperature is increased because the driving force is maintained with the reduction in equilibrium concentration, whilst the free ammonia fraction rises (Eq. (1)). An 'ideal' G/L stripping ratio (S) can be derived for a steady state process at 100 % ammonia removal (Eq. (2)) (Huang and Shang, 2006). In practice, operating at a stripping ratio of $S = 3$ is recommended to account for non-ideality (Huang and Shang, 2006):

$$S = \frac{G}{L}\frac{\frac{M_G}{\rho_G}}{\frac{M_L}{\rho_L}} = \frac{x_{NH3}}{y_{NH3}} \tag{2}$$

where S is the stripping ratio (m^3_{gas} m^{-3}_{liquid}); G is the gas flow rate (mol h^{-1}); L is liquid flow rate (mol h^{-1}); M is molar mass (kg mol^{-1}); ρ is density (kg m^{-3}); x_{NH3} is mole fraction of ammonia in the liquid-phase (-); y_{NH3} is mole fraction of ammonia in the gas-phase in equilibrium with x_{NH3} at the operating temperature as predicted by Henry's Law (Fig. 4); G and L subscripts refer to the gas and liquid respectively. At $S = 3$, air stripping at 20 °C requires 5300 m^3_{gas} m^{-3}_{liquid}, compared to 1500 m^3_{gas} m^{-3}_{liquid} for air stripping at 50°C, and 300 m^3_{gas} m^{-3}_{liquid} for steam stripping at 100°C (Fig. 5a). This temperature dependence is reflected in published operating data for ammonia stripping. Stripping at increased temperatures and lower G/L ratios will also increase the concentration of ammonia in the off-gas (Fig. 5b), which is of critical importance for the recovery of ammonia in a form that can be exploited as a zero-carbon energy vector.

Vacuum thermal stripping is an emerging technology for ammonia recovery from wastewater that has been demonstrated so far at lab-scale in batch configuration (Fig. 6) (Bavarella et al., 2020; Han et al., 2022).

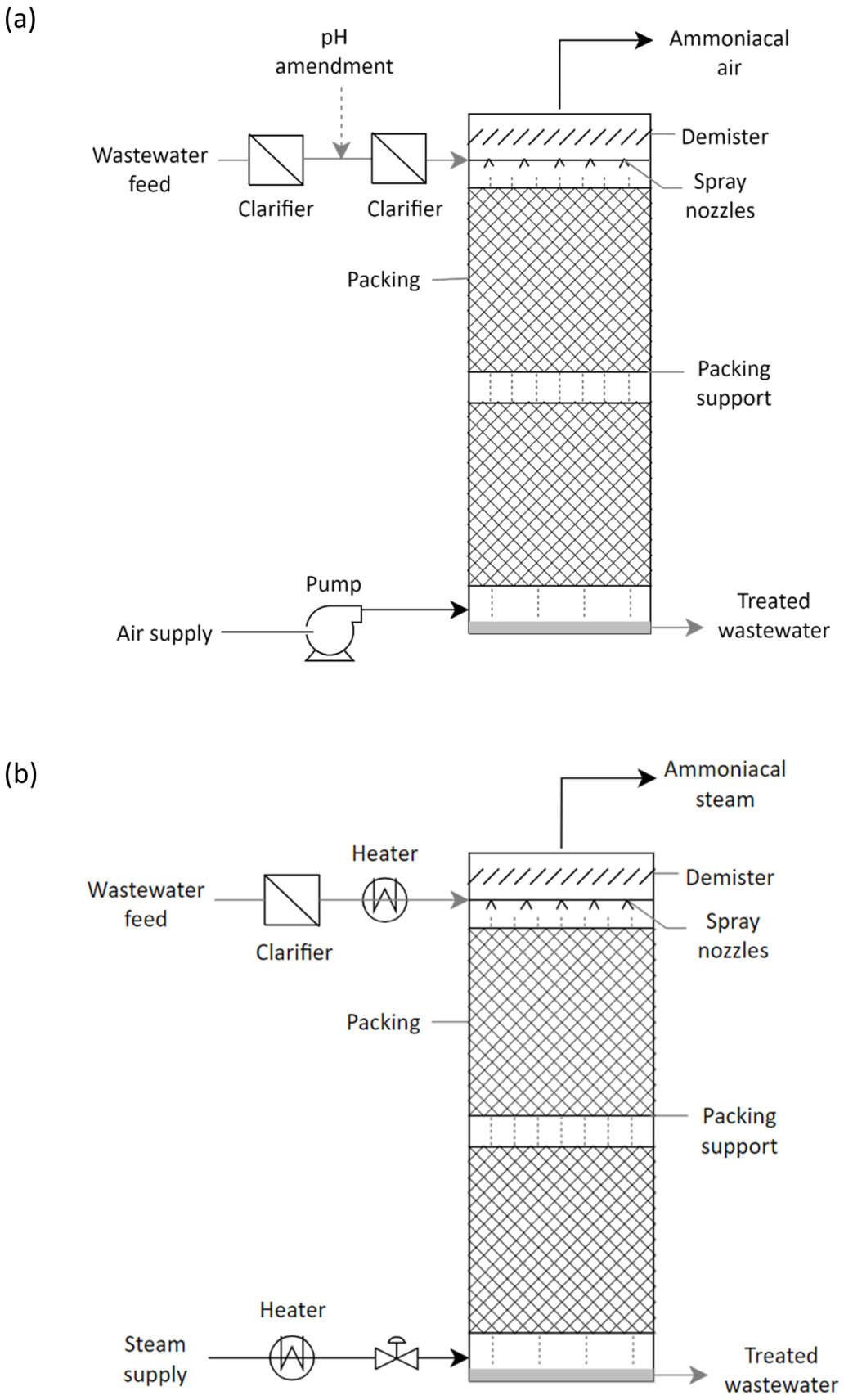


Fig. 2. Simplified flowsheets for continuous ammonia removal by (a) air stripping and (b) steam stripping in packed columns.

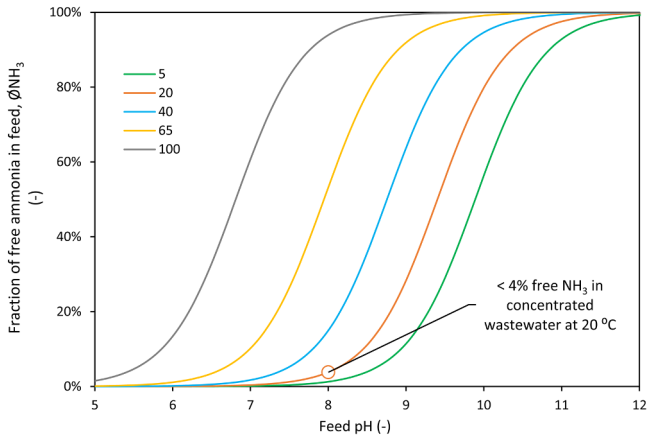


Fig. 3. Influence of temperature and pH on free ammonia fraction in feed. Derived from ammonia-ammonium equilibrium data (Bates and Pinching, 1949).

Wastewater is boiled under vacuum conditions (i.e., ~65ºC at 0.25 bar (a)) to generate an ammonia-rich vapour at the interface, which occurs since ammonia is more volatile than water (Ukwuani and Tao, 2016; Tao and Ukwuani, 2015). Similar to the function of sweep gas, the vacuum continuously renews vapour pressure exerted by ammonia by recovering gas-phase ammonia thereby reducing its equilibrium concentration in the liquid-phase and sustaining the driving force for mass transfer (Ukwuani and Tao, 2016). By operating at greater temperatures, the ammonia vapour pressure and free ammonia fraction rise which further enhances this driving force (Eq. (1)). This enables efficient stripping at pH 9–10 (Table 4) (Anwar and Tao, 2016; Bavarella et al., 2020). For example, by increasing the temperature of thermal vacuum stripping from 60 to 70 °C, whilst keeping pressure, pH (9) and time in batch stripper identical, ammonia removal increased from 75 to 88 % (Reza and Chen, 2022).

Determining conditions most optimal for enhancing mass transfer and thereby ammonia removal is generally prioritised over characterising ammonia-water vacuum thermal stripping energy demand and quality of product recovered (Reza and Chen, 2022). While the quality and 'state' of the final product is more critical to energy applications, product quality is also directly attributed to the cost of heat and power for separation. Thermal stripping is a distillation process that exploits the difference in volatility between ammonia and water. Consequently, the vapour-liquid equilibrium (VLE) can be used to describe the separation of the binary ammonia-water mixture based on the distribution of chemical species across liquid and vapour phases (Richardson and Harker, 2002). Historically, the binary ammonia-water VLE has only been characterised for refrigeration mixtures that have much greater

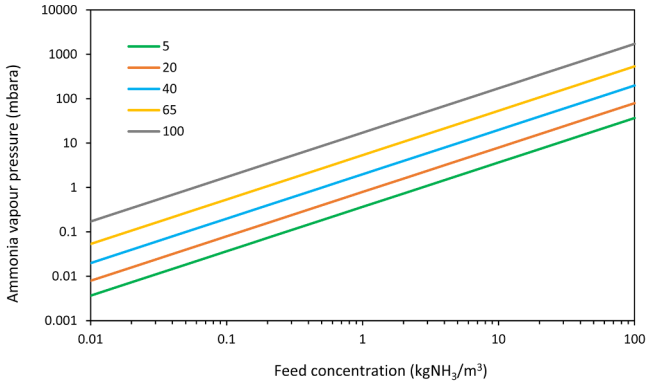


Fig. 4. Influence of temperature and concentration on ammonia vapour pressure exerted by feed. Derived from Henry's law data for ammonia (National Institute of Standards and Technology, 2024).

Table 4
Air, steam and vacuum stripping process data.

Process/ feed	Plant/ mode	Feed NH_3 kg m^{-3}	NH_3 removal %	pH	T ºC	G/L ratio m^3 m^{-3}	HRT h	Hydraulic loading m^3 m^{-2} h^{-1}	k_La h^{-1}	Product	Refs.
Ambient air stripping/ seafood wastewater	Packed column/ continuous	0.1	50 %	12	9–19	2230 [a]	0.7[a]	2.5	1.3	-	(Boardman and McVeigh, 1998)
Ambient air stripping/ dairy wastewater		0.4	29 %	10	25	2125 [a]	0.2[a]	3.1[a]	1.4[b]	$(NH_4)_2SO_4$ (aq)[c]	(Jiang et al., 2010)
Thermal air stripping/ dairy wastewater		0.4	54 %	10	40	2125 [a]	0.2[a]	3.1[a]	3.2[b]	$(NH_4)_2SO_4$ (aq)[c]	(Jiang et al., 2010)
Thermal air stripping/ digested sludge liquor		2.2	93 %	11	50	1875	0.6[a]	2.7[a]	4.5[b]	$(NH_4)_2SO_4$ (aq)[c]	(Guštin and Marinšek-Logar, 2011)
Steam stripping/ digested sludge liquor		0.9	91 %	8	~100	70–86	0.2[a]	5.3[a]	11[b]	8 kg m^{-3} NH_3 (aq)	(Zeng et al., 2006)
Steam stripping/ digested sludge liquor		1.3	91 %	8	~100	100–200	-	6.0	-	130 kg m^{-3} NH_3 (aq)	(Teichgraber and Stein, 1994)
Vacuum thermal stripping[d]/ dairy-municipal co-digestate	Stirred vessel/ batch	2.1	95 %	9.5	65	N/A	6.0	2×10^{-2}	0.5	$(NH_4)_2SO_4$ (aq)[c]	(Han et al., 2022)
Vacuum thermal stripping[d]/ digested sludge liquor		2.0	91 %	11	65	N/A	1.5	3×10^{-3}	1.5	17 kg m^{-3} NH_3 (aq)	(Davey et al., 2022)
Vacuum thermal stripping[e]/ synthetic wastewater		8.5	50	12	80	N/A	0.8	3×10^{-2}	0.9	99 kg m^{-3} NH_3 (aq)	(Bavarella et al., 2020)

G/L – Gas-liquid ratio; HRT – hydraulic residence time; T – stripping temperature; IEX – ion exchange; $(NH_4)_2SO_4$ (aq) – ammonium sulphate solution; NH_3 (aq) – aqueous ammonia

[a] Calculated value
[b] k_La estimated from experimental data
[c] Unspecified concentration
[d] Stripping pressure: 0.25–0.27 bar
[d] Stripping pressure: 0.42 bar

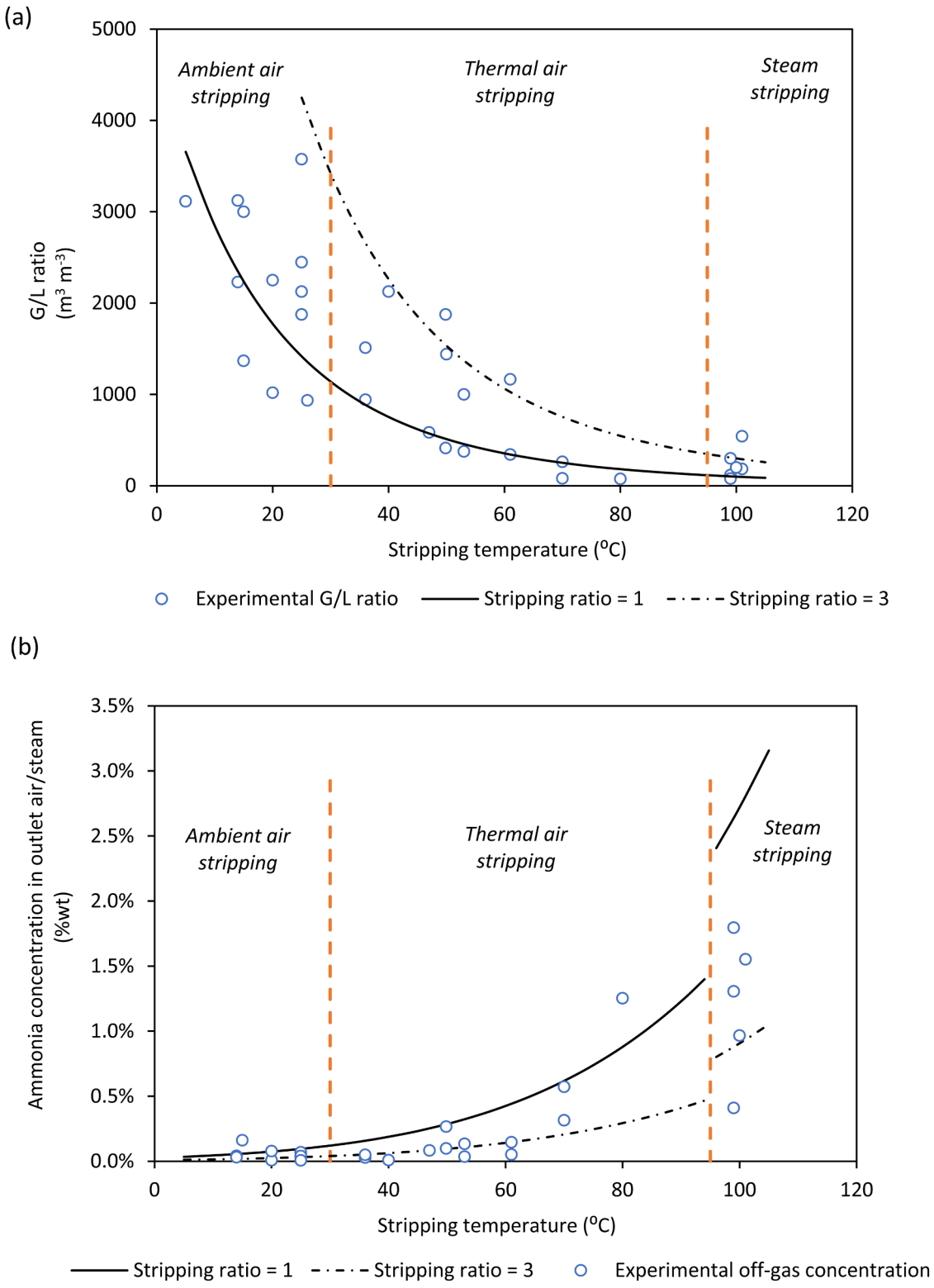


Fig. 5. Influence of temperature on (a) G/L ratio and (b) ammonia concentration in outlet gases for air and steam strippers (Quan et al., 2014; Değermenci et al., 2012; Bonmatı and Flotats, 2003; Liu et al., 2015; Ferraz et al., 2013; Melgaço et al., 2020; Kim et al., 2021; Zeng et al., 2006; Serna-Maza et al., 2014; Quan et al., 2009; Katehis et al., 1998; Alitalo et al., 2012; Gopalakrisnan et al., 2000; EPA, 1992; Teichgraber and Stein, 1994; Boardman and McVeigh, 1998; Guštin and Marinšek-Logar, 2011; Jiang et al., 2010).

ammonia concentrations (>50wt %) compared to wastewater (Raghuvanshi and Maheshwari, 2011). More recently, Luqmani et al. (2024) used an aqueous ammonia feed (1.5 $kgNH_3$ m^{-3}) in a batch thermal stripper (Fig. 6) under vacuum pressure to experimentally characterise the region of the VLE relevant for wastewater (Luqmani, et al., 2024; Patek and Klomfar, 1995). By lowering temperature during vacuum stripping from 65 to 61 °C at an equivalent pressure (0.25 bar (a)), vacuum operation entered a two-phase region of the VLE which

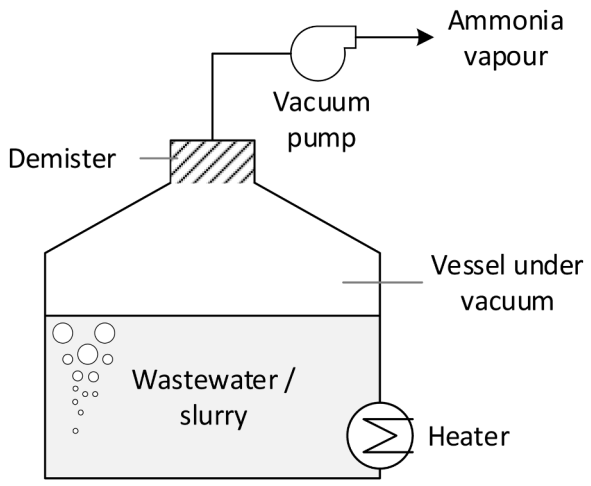


Fig. 6. Lab-scale setup for batch removal of ammonia from wastewater by vacuum thermal stripping.

greatly reduced vaporisation of water relative to ammonia which increased selectivity. Consequently, at the temperature corresponding to the apparent 'bubble' point of solution (saturated liquid), the ammonia concentration in the vapour increased to 43–64 mol % whilst thermal demand for stripping largely reduced due to the lower latent heat loss. Importantly, this study emphasises conditions through which economic thermal stripping can be realised for municipal wastewater treatment. Further characterisation across a wide range of operating conditions and feed concentrations is needed to inform the trade-off between thermal stripping separation energy and ammonia product recovery.

2.2. Energy consumption, product quality and recoverability

This trade-off between energy consumption and recovered product quality can be directly related to stripping technology design. Ambient air stripping requires no thermal input and has a low electricity demand related to air compression (<3 kWh kg_N^{-1}) which is competitive with biological ammonia oxidation processes (Grasham et al., 2019). However, high G/L ratios are required due to the low operating temperatures which results in gas-phase ammonia being highly diluted in the stripping exhaust (~0.01 %wt) (Fig. 5). The subsequent stages required to upcycle this dilute ammonia/air mixture presents an energetic challenge for ammonia recovery as a fuel. This route is therefore favoured for ammonia abatement, where oxidation of the stripped ammonia to nitrogen gas (Eq. (3)) over a transition metal oxide catalyst between 250 and 450 °C permits compliance with emission regulations (Kobayashi et al., 2019; Wang et al., 2021).

$$2NH_3 + 1.5O_2 \rightarrow N_2 + 3H_2O \ \Delta H = -634\ kJ \quad (3)$$

Without intervention, the ammonia exhaust gas is >5000 times more concentrated than the regulatory threshold of 20 μg m^{-3} which has been instigated due to critical role ammonia can play in the formation of harmful $PM_{2.5}$ particles (Defra, 2023). Alternatively, acid scrubbers can be installed to recover gas-phase ammonia in the form of ammonium-based fertilisers. Sulphuric acid is widely applied as a scrubbing agent due to the market demand for ammonium sulphate (Table 5). High acid usage will increase the cost of ammonia recovery and present safety and environmental challenges related to its storage and handling (Jamaludin et al., 2018). Organic acids (citric and acetic) have been proposed as environmentally sustainable alternatives but demonstrate lower ammonia absorption capacities and higher unit cost (Jamaludin et al., 2018). For most agricultural applications, solid ammonium salts are preferred which necessitate a downstream

Table 5
Characterisation of air, steam and vacuum thermal stripping systems for ammonia recovery.

	Ambient air stripping	Thermal air stripping	Steam stripping	Vacuum thermal stripping
Scale tested Reactor Gas-phase ammonia removal / recovery	Commercial scale Packed column Thermal oxidation / acid scrubbing	Commercial scale Packed column Acid scrubbing / water-scrubbing and distillation	Commercial scale Packed column Condensation / water scrubbing and distillation	Lab-scale Boiling reactor Acid scrubbing / condensation / water scrubbing and distillation
Advantages	• Zero thermal demand, energetically competitive with biological removal (<5 kWh kg_N^{-1})	• Reduced/ or no chemical demand for pH adjustment • Moderate rates of ammonia mass transfer (~k_La 1–5 h^{-1}) to reduce process footprint • Thermal demand mostly for sensible heat, which is more easily recovered • Lower G/L demand due to reduced solubility of ammonia at raised temperatures • Can utilise low-cost waste heat on site	• No chemical demand for pH adjustment • High rates of ammonia mass transfer (~k_La 5–11) to reduce process footprint • Ammonia in steam produced at moderate concentrations and readily captured by condensation	• Simple design • Low scaling potential by carbonates formation as sweep gas is not required (which introduces CO_2) • No chemical demand for pH adjustment, provided temperatures >~60°C are used • Absence of sweep gas can facilitate highly concentrated ammonia product • Low boiling temperatures permit incorporation of low-grade waste heat; temperature required for sensible heat can be reduced with vacuum
Disadvantages	• High chemical demand for stripping (pH ~11–12) • Dilute ammonia product in air stream due to high G/L ratio which limits use and recovery options • High G/L ratio demands greater power to generate strip gas • Vulnerable to clogging from high fouling feeds • Maybe vulnerable to biological fouling due to the use of air • Vulnerable to scaling due to high pH and high G/L ratios (CO_2 in air)	• Moderate thermal demand for pre-heating wastewater feed • Vulnerable to clogging from high fouling feeds • Concentration of dilute ammonia in off-gas is required; generally proposed by distillation which demands high latent heat	• High thermal demand due to raising steam (1.33 MJ m_{steam}^{-3}) • Onsite steam generation increase upfront investment cost • Vulnerable to clogging from high fouling feeds • Feed decarbonisation required to prevent inorganic scaling at high temperatures	• Unless optimised for selective NH_3 separation, latent heat loss can introduce a high thermal energy penalty • Only reactors with low interfacial surface area (<40 m^2 m^{-3}) demonstrated. Requires investigation into scalability of reactor design for full-scale use, including the roles of hydraulics in design • Only low hydraulic loading illustrated to date; translation to continuous mode required for high-volume treatment

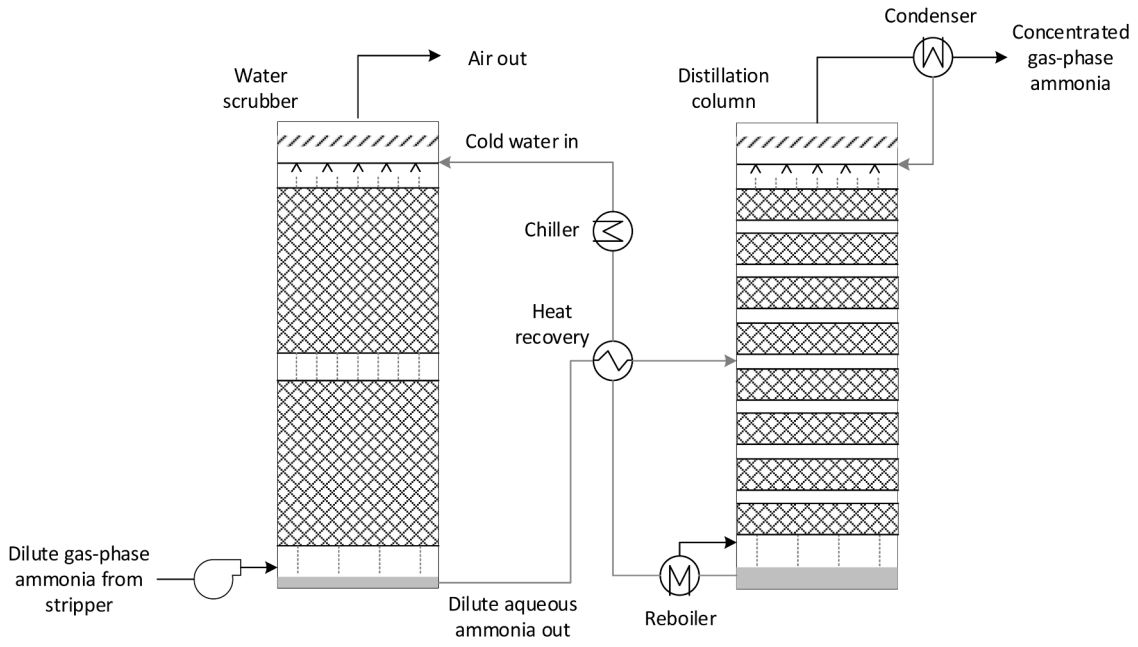


Fig. 7. Water scrubbing and distillation recovery flowsheet for dilute gas-phase ammonia concentration.

crystallisation stage and adds further cost and operational complexity for ammonia recovery (Chen et al., 2021; Davey et al., 2020).

Thermal air stripping will introduce sensible heating requirements for the feed and air supply (~5–20 kWh kg_N^{-1}) yet generate a higher ammonia concentration in the off-gas (~0.1–1.0 %wt NH_3) because of the lower strip gas rate required (Fig. 5). Gas-phase ammonia from thermal air stripping can be captured and concentrated by cold water scrubbing, followed by thermal separation of the ammonia from the absorption fluid using distillation to increase the product quality to achieve a concentrated gas-phase or anhydrous ammonia product (Grasham et al., 2019, 2020; Organics Group, 2020) (Fig. 7). Upgrading the product quality will be energy intensive due to the low gas-phase concentration leaving the stripper. Grasham et al. (2019) considered a scheme to recover ammonia from digested sludge liquor by thermal stripping at 75 ºC to produce dilute gas-phase ammonia, followed by absorption in a water scrubbing tower and flash distillation to increase the final gas-phase ammonia concentration to 3.9 %wt. Whilst the heat demand was not specificied, a substantial amount of energy would be necessary to vaporise the water during distillation due to the latent heat of water (ΔH_{vap} 0.7 kWh kg^{-1}).

Steam stripping is associated with the highest thermal demand (35–160 kWh kg_N^{-1}) and requires infrastructure for steam generation (EPA, 1992; Teichgraber and Stein, 1994). However, on sites where gas-turbines are operated for combined heat and power generation, the water used to raise steam can be partially pre-heated thereby reducing steam supply cost (Moore and Auty, 2013). The low G/L ratio will boost the gas-phase ammonia concentration (~1–3 %wt) in the stripped vapour and can simplify product capture and purification (Fig. 5). In industrial applications, the output from steam stripping is often condensed to form an aqueous concentrate and can facilitate the extraction and recycling of organic solvents from process wastewater (Leonhard et al., 1994). Zeng et al. (2006) investigated ammonia recovery from digested dairy manure by steam stripping and condensation and recovered an aqueous ammonia product which was 10 times greater than the feed. Through steam stripping, rectification and condensation, the recovery of aqueous ammonia at 12–20 %wt could be achieved from digested sludge liquors (100–150 times greater than the feed concentration) (Teichgraber and Stein, 1994). Upgrading the concentrated aqueous stream into anhydrous ammonia (<0.5 %wt H_2O) requires a further fractionation stage. Compared to thermal and ambient air stripping, the higher gas-phase ammonia concentration exiting the steam stripper will require less energy to dehydrate the ammonia, requiring a smaller separator with fewer stages (Hassan and Timberlake, 1992; Kohl and Nielsen, 1997).

Unlike air or steam stripping, vacuum stripping does not require a sweep gas (G/L = 0) and so the production of a highly concentrated ammonia gas-phase is possible. Previous researchers have paired vacuum thermal stripping with an acid scrubber for ammonium sulphate production (Han et al., 2022; Tian et al., 2019; Ukwuani and Tao, 2016), or directly condensed the vapours to form concentrated aqueous ammonia (Davey et al., 2022; Guida et al., 2022). For example, a 9 %wt aqueous ammonia condensate was produced during vacuum thermal stripping of synthetic wastewater at 0.42 bar (Bavarella et al., 2020). The condensate concentration coincided with the solubility limit at the operating temperature of 80 °C. This limited ammonia collection in the aqueous product and therefore around 40 % of the gas-phase ammonia 'slipped' through the condenser (Bavarella et al., 2020). By considering both aqueous and gaseous ammonia in a total mass balance, it can be inferred that a 17 %wt gas-phase ammonia was produced at the stripper outlet which represented a 20-factor increase in concentration from the treated wastewater. Through the use of vacuum as the driving force, a higher gas-phase ammonia concentration can be achieved using only a single stage of stripping, creating a simpler design than is required for air or steam stripping. If the intent is to produce an anhydrous ammonia product, this further decreases the energy demand and size of the fractionation separator required downstream (Kohl and Nielsen, 1997). Alternatively, an option is to dehumidify the non-condensable gas-phase stream recovered using a desiccant coated heat exchanger (Sieres et al., 2008; Venegas et al., 2021). Davey et al. (2022) estimated that ammonia recovery from digested sludge liquors at 65ºC and 0.25 bar would require 44 kWh kg_N^{-1}, which accounted for sensible heat recovery between the incoming and outgoing wastewater feed. Over 95 % of the total energy demand for vacuum thermal stripping was attributed to the latent heat of water vaporisation in the stripper (Davey et al., 2022). Reducing water vaporisation (i.e., increasing ammonia selectivity) in the stripper could reduce the energy demand whilst simultaneously increasing the ammonia concentration, energy density and value of the recovered vapour. By increasing ammonia selectivity with refined vacuum control, Luqmani et al. (2024) was able to demonstrate an increase in gas-phase ammonia concentration from 1–5wt % to >43wt % whilst

Table 6
Alternative ammonia stripping processes.

Process / feed	Reactor /configuration	Feed NH_3 kg m^{-3}	NH_3 removal %	pH	T °C	G/L ratio m^3 m^{-3}	HRT h	kLa h^{-1}	Refs.
Vacuum thermal stripping[a]/ synthetic wastewater	Membrane/batch (continuous fed)	10	14 %	10	35[b]	N/A	0.3	0.5[c]	(van Linden et al., 2022)
Air stripping/ synthetic wastewater	Jet loop reactor/ batch	0.5	61 %	11	20	2250	7.5	0.2	(Değermenci and Yildiz, 2021)
Thermal air stripping/ synthetic wastewater	Jet loop reactor/ batch	0.5	88 %	11	50	2250	7.5	1.0	(Değermenci and Yildiz, 2021)
Air stripping/ UASB effluent	Jet loop reactor/ batch	0.05	99 %	7.0	23	-	5.0	0.8	(Tai et al., 2006)
Air stripping/ synthetic wastewater	WSA/ batch	1.2–5.5	> 99 %	> 11	15	2850[d]	4.2	1.2	(Quan et al., 2009)
Air stripping/ digested swine liquor	WSA/ batch	0.1	96 %	> 11	~30	855[d]	1.5	2.1	(Quan et al., 2009)
Air stripping/ synthetic wastewater	HRC/ Batch	2.5	97 %	11	20	1200	20	0.2	(Taşdemir et al., 2020)
Thermal air stripping/ digested swine slurry	Thin film column/ batch	3.7	> 99 %	9.5	80	1.2[d]	4.0	0.9[c]	(Bonmatı and Flotats, 2003)
Thermal air stripping/ synthetic wastewater	Rotating bed/ continuous	1.0	81 %	11	40	1600	0.004	18	(Yuan et al., 2016)
Thermal air stripping/ synthetic wastewater	Rotating bed/ six passes	13	> 99 %	11	90	1600	< 0.001	22	(Yin et al., 2018)

TAN – Total ammoniacal nitrogen; G/L – Gas/liquid ratio; HRT – hydraulic residence time; UASB – upflow anaerobic sludge blanket bioreactor; WSA – water-sparged aerocyclone; HDR – hydraulic cavitation reactor.
[a] Calculations based on reported NH_3 and H_2O flux data over a 15 min sampling interval
[b] Permeate-side pressure = 0.02 bar
[c] k_La estimated from experimental data
[d] Calculated value

reducing thermal demand from 91 kWh_{th} kg_N^{-1} down to 1 kWh_{th} kg_N^{-1} (Table 6). Since vacuum suppresses the boiling temperature, the feed temperature can be reduced to facilitate better heat integration with low-grade waste sources thereby supplementing thermal demand (Anwar and Tao, 2016). For example, a heat audit for a centralised wastewater treatment works indicated that 40–50 kWh of low-grade heat (85 °C) could be recovered per m^3 digested sludge liquor from biogas turbines, which can contribute significantly to the thermal demand for all thermal stripping systems (Davey et al., 2022; Moore and Auty, 2013; Ndam, 2017).

2.3. Process resilience and reactor configuration

Packed columns are widely utilised and provide high interfacial areas (200–600 m^2 m^{-3}) to encourage greater gas-liquid contact which enhances the rate of ammonia mass transfer from the liquid to gas phase

Table 7
Ammonia product removal/recovery technology.

	Thermal oxidation	Acid scrubbing	Water scrubbing	Distillation	Condensation
Process description	Oxidation of ammonia in off-gas occurs at ~300°C using a catalyst before flaring. Ammonia is converted primarily to dinitrogen (N_2) gas and vented.	Dilute ammonia in sweep-gas from stripper is contacted with a concentrated acid solution (i.e. sulphuric acid) in absorption column to produce ammonium sulphate.	Ammonia in off-gas is absorbed when passed through water in absorption column to produce dilute aqueous ammonia solution.	Ammonia in off-gas is separated from components such as water by relative volatility to produce a concentrated ammonia product.	Off-gas is cooled to temperatures that condense water which then solubilise ammonia. An aqueous ammonia solution is produced with remaining ammonia in the vapour.
Advantages	• Oxidation is exothermic and generates heat that can be used to reduce energy heating off-gas	• Ammonium sulphate product can generate additional income as fertiliser • Heat of absorption can be used to elevate co-located stripping column temperature	• Relative low cost of scrubbing solvent • Cooling water increases absorption capacity without requiring chemical • Provides some concentration of ammonia when placed downstream of air strippers	• Capable of producing anhydrous ammonia (<1.5wt % H_2O, <1500ppm H_2S) and thereby improve recovered product value	• Significant condensation of water using ambient/sub ambient temperatures for low energy ancillary cooling • When complemented with vacuum upstream, rich ammonia gas can be produced with low energy requirement (low latency)
Disadvantages	• >2 % of ammonia nitrogen entering catalyst converts to nitrogen oxides; as a greenhouse gas, it must be removed by additional selective catalytic reduction equipment	• Chemical cost of scrubbing acid is significant • Selling ammonium sulphate as fertiliser is challenging due to 'end of waste' and receptivity • Produces dissolved ammonium sulphate in an acid solution, which is more challenging to use as a final product (vs. crystalline) and increases cost of shipment	• Dilute product recovered of little value without further concentration • Biological fouling in absorption column • Relative larger absorption column due to lower ammonia solubility in scrubbing solvent • Cooling can be energetically costly	• Significant energy demanded by low temperature ancillary cooling and/or by operating at raised pressures • Overcome high latent heat to vaporise water in column reboiler • May require multiple distillation columns depending on the composition of ammonia fed	• Depending on ammonia-water composition and condensation temperature, ammonia solubility in water is limited. Therefore ammonia vapour can slip through and is lost without additional capture stage

during stripping (Eq. (1)) (Boardman and McVeigh, 1998; Organics Group, 2020; Zeng et al., 2006). These facilitate high liquid loading rates (2.5–6.0 m^3 m^{-2} h^{-1}) which enable reduction in process size, associated infrastucture and capital cost compared to slower biological nitrogen removal processes which have hydraulic residence times of several hours (Table 4) (Boardman and McVeigh, 1998; Teichgraber and Stein, 1994; Ramalingam et al., 2017; Metcalf and Eddy, 2014). Sidestream biological reactors such as deammonification continuous stirred tank or nitrification/denitrification sequencing batch reactors achieve around 1 kg_N m^{-3} d^{-1} whereas thermally-driven ammonia stripping can reach up to 35 kg_N m^{-3} d^{-1} (Ochs, et al., 2023). However, they are vulnerable to fouling and scaling when treating wastewater (Table 7). Multi-stage clarification of the feed has been proposed, since suspended solids will cause clogging and provide a nutrient source which stimulates the growth of biofilms on the packing (Huang and Shang, 2006). In a pilot study, Gopalakrishnan et al. (2000) employed a settlement stage (0.75 h) followed by coarse (4.8 mm) and fine (1.2 mm) filtration to clarify sludge liquors prior to steam stripping. Hourly intervention was required to clean the filters and keep the system operational (Gopalakrishnan et al., 2000). In low temperature strippers, the compensatory rise in pH and G/L ratio can cause inorganic fouling. A higher pH encourages carbonate salts to precipitate out of solution whilst in the presence of air, sulphides (i.e. hydrogen sulphide) may oxidise into elemental sulphur (Huang and Shang, 2006). During ammonia stripping from leachate (pH 11, 2400 m^3 m^{-3}), an 18 % reduction in ammonia removal efficiency was observed over a 6-month period due to scaling which increased the packing weight up to 7-times and restricted surface area for mass transfer. The formation of calcium carbonate scale on packing is caused by the absorption of carbon dioxide from the air stream used for stripping (Viotti and Gavasci, 2015). Regular acid washing cycles were necessary to maintain performance, mandating two or more stripping columns in a duty/standby configuration to provide a continuous service (Viotti and Gavasci, 2015). During steam stripping of sludge liquor, severe process blockages occurred within the media and pipework due to the precipitation of ammonium bicarbonate (Teichgraber and Stein, 1994). Steam and air stripping both use sweep gas to continually renew partial pressure of ammonia which also facilitates scaling in the presence of stripped chemical species whereas vacuum stripping instead reduces total pressure to drive ammonia transfer. Due to the difference in driving force, vacuum stripping may mitigate scaling while the amelioration of organic fouling may benefit from rethinking conventional packed column geometric design.

Table 8
Ammonia-water stripping technology product and energy.

Stripping technology	Feed concentration $kgNH_3$ m^{-3}	Recovered ammonia product quality wt %	Removal energy demand kWh kg_N^{-1}	Refs.
Ambient air stripping[a]	0.1–3	0.01–0.16 (g)	<3	Jiang et al. (2010), Quan et al. (2014), Değermenci et al. (2012), Boardman and McVeigh (1998), Grasham et al. (2019)
Hot air stripping	0.427–2.2	0.01–1.25 (g)	5–20	Jiang et al. (2010), Guštin and Marinšek-Logar (2011), Bonmatı and Flotats (2003)
Steam stripping	0.8–5	0.41–1.79 (g)	35–160	Gopalakrisnan et al. (2000), EPA (1992), Teichgraber and Stein (1994)
Vacuum thermal stripping	0.6–8.5	0.4–10 (aq) 1–64 (g)	1–91	Guida et al. (2022), Davey et al. (2022), Bavarella et al. (2020), Luqmani et al. (2024)

[a] ≤25 °C operation

Emerging reactor technologies could offer greater resilience to fouling and scaling during air or steam stripping and/or achieve competitive rates of mass transfer to conventional packed columns (Table 8). For example, high turbulence systems have been developed which create greater interfacial areas without packing and reduce the thickness of the gas-film to intensify ammonia mass transfer (Eq. (1)) (Değermenci and Yildiz, 2021). These include jet-loop reactors, hydrodynamic cavitation reactors and water-sparged aerocyclones, each following similar principles of operation where a pressurised feed is sprayed through venturi nozzles into a gas-liquid contacting chamber (Değermenci and Yildiz, 2021; Quan et al., 2009; Taşdemir et al., 2020). Jet-loop reactors and hydrodynamic cavitation reactors have demonstrated liquid-phase volumetric mass transfer coefficients of 0.2–0.8 h^{-1} at ambient temperatures and up to 1.0 h^{-1} at 50 °C (Değermenci and Yildiz, 2021; Tai et al., 2006). Up to 2.1 h^{-1} has been reported for a water-sparged aerocyclone at 15 °C which exceeds conventional air stripping transfer when operated at similar ambient temperatures (Table 4) (Quan et al., 2009). Turbulent reactors are actively 'self-cleaning' which can prevent fouling and scaling over time. This has been evidenced by the continuous operation of a jet-loop reactor fed with unfiltered effluent (100 mg L^{-1} TSS) over almost 200 days (Tai et al., 2006), and the treatment of digested swine manure in a water-sparged aerocyclone (Quan et al., 2011). Thin-film columns can provide moderate interfacial area for stripping high solids feeds, such as digested swine slurry (32000 mg L^{-1} total solids), which would be impractical to treat in packed columns due to media clogging (Bonmatı and Flotats, 2003). Rotating packed bed reactors utilise centrifugal force to reduce thickness of the gas-film and enhance interfacial area to intensify ammonia mass transfer (Eq. (1)) (Yuan et al., 2016). Liquid-phase volumetric mass transfer coefficients of up to 22 h^{-1} were reported when thermal stripping in lab-scale rotating packed bed reactors at 1200–1600 rpm, indicating that mass transfer rates could greatly exceed conventional packed column strippers (Table 4) (Yin et al., 2018; Yuan et al., 2016). Higher rotation rates also mitigate fouling of packing material where above 900 rpm significantly more solid mass is discharged during ammonia stripping from landfill leachate (Trinh, et al., 2023). Hot microbubble stripping is another intensified processes which utilises a sparger to pass high interfacial area air bubbles up through a liquid and recover ammonia. Very large overall volumetric mass transfer coefficients approaching 79.2 h^{-1} are reported for a synthetic ammonia-water feed albeit demanding hot air at 140 °C (Desai, et al., 2022).

Evidence for vacuum thermal stripping used to recover ammonia is currently limited to boiling vessels operated in batch-mode (Table 4). When running batch processes, the presence of down-time can facilitate regular cleaning thereby providing resilience to fouling which has enabled the direct treatment of unfiltered concentrated wastewaters and digestate slurries (Han et al., 2022; Tao et al., 2018). However, the low interfacial areas (<40 m^2 m^{-3}) produce inferior liquid-phase volumetric mass transfer coefficients (0.4–1.5 h^{-1}) relative to packed column strippers at equivalent temperatures (Davey et al., 2022; Guida et al., 2022; Han et al., 2022). To intensify mass transfer and achieve hydraulic loading rates which are competitive with established processes, vacuum thermal stripping requires translation to gas-liquid contacting reactors. Industrially established processes for the removal of aromatics and dissolved gases from wastewater and slurry feeds could be adapted for ammonia recovery by vacuum thermal stripping. For example,

ELO-VAC® is a continuous batch system for dissolved methane recovery from digested sludge, which enhances the interfacial area for mass transfer by spraying sludge into a vacuum vessel and can treat up to 50 m^3 h^{-1} (Eq. (1)) (ELIQUO Water Group, 2023). Continuous vacuum stripping systems (~0.05 bar) have also been incorporated at the outlet of biological nitrification processes at full-scale to mitigate 'bulking' during the secondary settlement of activated sludge (Gnida and Student, 2021). Vacuum distillation within thin film columns is employed for the removal of volatile compounds and the partial evaporation of industrial wastewaters. These systems can internally recycle heat by mechanical recompression of flash vapours to lower the thermal demand for distillation (McCabe and Vivona, 1999). Spinning cone columns (SCC) are established in the food and beverage industry for removing volatile compounds such as aromatics and ethanol by steam distillation under vacuum conditions (Huerta-Pérez and Pérez-Correa, 2018; Riley and Sykes, 2002). The feed, which can contain up to 20 % suspended solids, cascades down a stack of rotating cones (~200 m^2 m^{-3}) in counter-current to the steam flow (Makarytchev et al., 2004). Vacuum membrane stripping (VMS), which employs a gas-permeable membrane to separate liquid and vapour phases, has been explored directly for the recovery of ammonia from synthetic wastewater (van Linden et al., 2022; 2022). Ammonia vapours up to 11 %wt have been generated during VMS using a 35 ºC feed and 0.02 bar permeate pressure (van Linden et al., 2022). The future development of dense polymers with greater ammonia-water selectivity could promote a higher permeate concentration and limit the thermal energy demanded by water vaporisation (van Linden et al., 2022). Regarding VMS application in real wastewaters, the removal and recovery of ammonia from digested sludge has been demonstrated at pilot scale. Further work into the impact of membrane fouling during prolonged operation has been acknowledged despite no significant defects reported after several days of operation (Dow et al., 2022).

2.4. Feed pH amendment

For stripping processes which require a high pH feed (i.e., air and vacuum), substantial alkali dosage is needed to overcome buffering capacities for concentrated wastewater. In dilute wastewater, pH amendment can be achieved by the addition of lime ($CaOH_2$) which yields 2 moles of hydroxide per mole of calcium (Huang and Shang, 2006). However, calcium addition to wastewater produces a fouling sludge and so the application of sodium hydroxide is often recommended. Due to the 1:1 hydroxide to sodium ratio, the operating cost increases (Limoli et al., 2016). For example, 8 kg_{NaOH} m^{-3} (3.9 EUR m^{-3}) was required to raise swine wastewater to pH 11 (ChemAnalyst, 2022; Zhang et al., 2012). Introducing a decarbonisation pre-treatment could reduce or eliminate the alkali demand associated with ammonia stripping. Dissolved CO_2 contributes to wastewater acidity and is much less soluble than ammonia, and can therefore be efficiently stripped from solution at a low G/L ratio (<10 m^3_{gas} m^{-3}_{liquid}) (Heile et al., 2017; Kang et al., 2017). Decarbonisation has been demonstrated to increase wastewater and digestate slurries from 7.8 to pH 8.5 using air (containing 0.03 %vol CO_2) and up to pH 10 with nitrogen (Cohen and Kirchmann, 2004; Kang et al., 2017). Hence, this could facilitate chemical-free stripping for thermal air or vacuum thermal stripping. Using a batch thermal stripper, Luqmani et al. (2024) investigated vacuum degassing CO_2 whilst stripping ammonia from wastewater and observed a rapid rise in pH during the first 10 min of operation stabilising at pH ~9.3. This demonstrates both CO_2 degassing and ammonia stripping can take place in one system. Degassing of CO_2 is already established at full-scale in the aquaculture sector where cascade stripping columns can process 80 m^3 m^{-2} h^{-1} which exceed hydraulic loading rates for many stripping configurations (Table 4) (Summerfelt et al., 2003).

2.5. Extractive technologies for ammonia recovery from dilute wastewater sources

Extractive technologies make use of affinity, chemical or electrical gradients to partition the ammonia onto a solid or into a segregated liquid phase. Unlike stripping, these technologies often exploit the cationic charge in the ammonium (or protonated) form to separate ammonium, which reduces the reliance on pH amendment to facilitate separation. Therefore, ammonia recovery can be applied to a wider range of wastewaters, particularly those of lower ammonia concentration (e.g. secondary effluent) where pH amendment is not economically achievable due to the size of the flow, and due to the regulated pH range for discharge.

Ion-exchange can offer targeted, high efficiency ammonium (>98 %) removal from wastewaters. Natural zeolites (e.g. Clinoptilolite) and synthetic zeolites (e.g. Mesolite) have been widely explored for ammonium removal, due to their high exchange capacities of up to 21.5 g kg^{-1} and 55 g kg^{-1} respectively (Mackinnon et al., 2003; Sprynskyy et al., 2005; Ashrafizadeh et al., 2008). Surface area and pore diameter of exchange media also controls the kinetics for ammonium adsorption and the media capacity (Deus, et al., 2021). Once saturated, the ion-exchange resin is regenerated using sodium or calcium hydroxide and their salts to subsequently produce a brine rich in ammonium (Cooney et al., 1999; Zhou et al., 2021). These bases are used to amend the regenerant up to pH 11 which enables the transformation of ammonium to ammonia to prevent re-adsorption on the resin (Bobleter and Bonn, 2011; Canellas-Garriga, 2018). High volumes of regenerant are required to desorb ammonium and regenerate the media, with regeneration ratios exceeding 300 eq_{Na2+} eq^{-1}_{NH4+} (Canellas-Garriga, 2018). The purchase of regenerant chemicals and the subsequent disposal of brine generated can account for 60–80 % of total operating costs for IEX which can threaten the economic viability of the process and has stimulated interest in the extraction of ammonia to enable brine reuse (Green et al., 1996; Milán et al., 2011). Brine can accumulate 10-times the influent ammonia concentration after a single regeneration cycle (Cooney et al., 1999; Deng et al., 2014) and up to 30-times after 5 cycles (Canellas-Garriga, 2018). For instance, up to 1.2 gN L^{-1} brine could be achieved from a 40 mgN L^{-1} feed equivalent to crude wastewater (Pinelli et al., 2022) and modified natural zeolites equipped with magnesium can additionally recover phosphate which facilitates precipitation of struvite in brine (You et al., 2017). The high pH and raised ammonia concentration of brine resemble side-stream wastewater chemistry (i.e. centrate) which suggests stripping technologies could be used to separate and concentrate the ammonia while also restoring the brine for use in further IEX regeneration cycles. An integrated IEX-air stripping process to treat sludge liquor was investigated for ammonia recovery from brine during media regeneration (Ellersdorfer, 2018). The continuous extraction of ammonia increased the efficiency and rate of regeneration whilst producing gas-phase ammonia in the stripping exhaust (Ellersdorfer, 2018). IEX-air stripping was also effective at extracting ammonia from dilute wastewaters (0.05 kg m^{-3}) yet utilisation of air strip gas limits recovery as a fertiliser via acid scrubbing (Maghfiroh et al., 2023; Deng et al., 2016) and could encourage scaling of carbonate species (Viotti and Gavasci, 2015) when carbon dioxide passes through the concentrated cationic brine. A similar product is obtained using hollow fibre membrane contactors that selectively extract ammonia from brine yet without energy demanded for strip gas (Sheikh et al., 2023). Guida et al. (2022) extracted ammonia from wastewater (<0.05 kg m^{-3}) to produce a pH 10 brine containing 0.7 kg m^{-3} aqueous ammonia which was subsequently recovered using vacuum thermal stripping and the vapour product condensed to produce 5 kg m^{-3} aqueous ammonia. Therefore, strong synergies have been demonstrated by integrating IEX and vacuum thermal stripping for simultaneous brine recovery and ammonia extraction from dilute wastewater to recover higher quality products (Fig. 8).

Separation via electrical gradient has also been proposed primarily

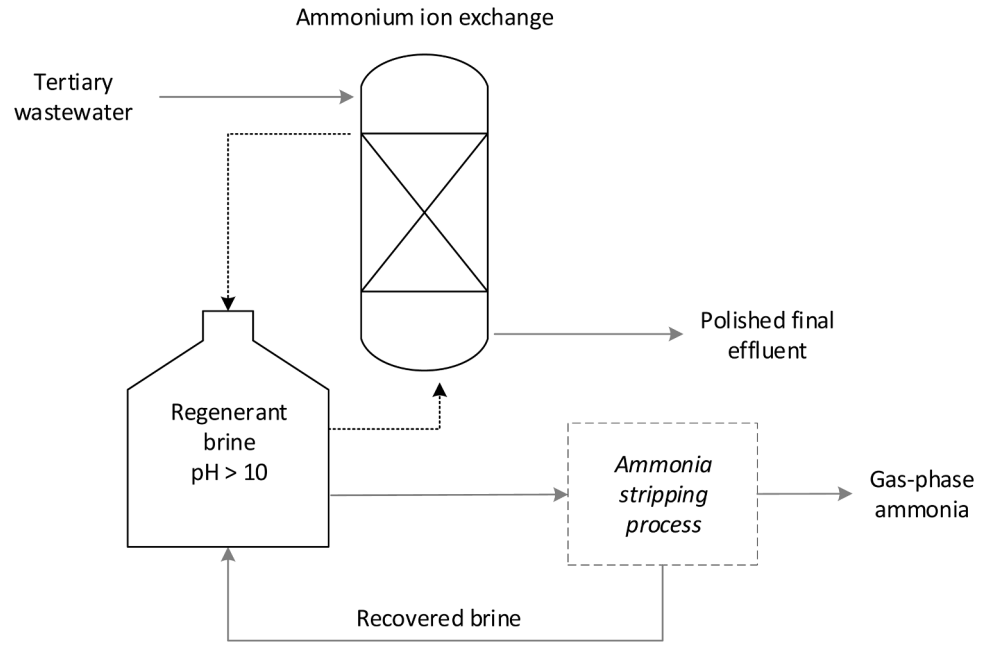


Fig. 8. Integrated ion-exhange-stripping process for ammonia recovery and wastewater polishing.

for industrial desalination, making use of the valency of ammonium and other molecules for extraction from water and wastewaters with an electrical current (Chen et al., 2021). In electrodialysis (ED), anions and cations migrate towards their respective electrodes and pass through charged ion exchange membranes designed to trap and channel the respective ions into concentrated reject streams (Ward et al., 2018). Zheng et al. (2017) treated dilute wastewater (0.02 kg m^{-3}) in an ED cell, which concentrated 90 % of the initial ammonium within a 0.2 kg m^{-3} aqueous ammonia reject stream. The high separation energy for stripping (52 kWh kg_N^{-1}) indicated the reject stream was too dilute for economic stripping (Zheng et al., 2017). However, multi-stage approaches could be explored for further concentration and gas-phase recovery. To increase energy efficiency and viability, ED is often applied to higher concentration wastewaters which have a greater electrical conductivity. Since ED cells are vulnerable to fouling, concentrated wastewaters will require a high degree of clarification, and struvite precipitation has been proposed to reduce the scaling potential (Brewster, 2017). Ward et al. (2018) treated digested sludge liquor (0.8 kg m^{-3}) in a single-pass ED cell at pilot scale. An 8.6 kg m^{-3} aqueous ammonia reject stream could be produced at an energy consumption competitive with biological processes (4.9 kWh kg_N^{-1}) (Ward et al., 2018). Bioelectroconcentration cells (BEC) operate on a similar principle to ED, but manipulate electrochemically active bacteria within wastewater to generate electricity and reduce external energy demand (Koskue et al., 2021). Koskue et al. (2021) treated digested sludge liquor (0.7 kg m^{-3}) in a BEC and produced a 6.5 kg m^{-3} aqueous ammonia reject stream at an energy consumption of 6.1 kWh kg_N^{-1}. Bipolar membranes can be incorporated within electrodialysis cells (BMED), which simultaneously separate water into OH^- and H^+ to produce alkaline cationic and acidic anion concentrates (van Linden et al., 2020; Zhang et al., 2020a). This has been applied to synthetic wastewater (1.5 kg m^{-3}) to generate an aqueous ammonia concentrate (7.3 kg m^{-3}) at pH 9.8 suitable for stripping, for a competitive energy consumption of 5.3 kWh kg_N^{-1} (van Linden et al., 2020). In membrane capacitive deionisation (MCDI), migrating anions and cations pass through selective ion exchange membranes and are absorbed at the surface of porous carbon electrodes (Chen et al., 2021). The electrodes are periodically discharged which releases the ionic species to produce concentrated solutions. A novel MCDI cell incorporated a gas permeable membrane and acid chamber at the cathode to harvest ammonium ions by liquid-liquid absorption (Z. Wang et al., 2017). This enabled 80 % recovery of ammonia from AnMBR wastewater into an acid solution which was at 3–4 times the influent concentration (Wang et al., 2017). Similar to other electrically driven processes, operating MCDI with higher-strength synthetic urine (3.8 kg m^{-3}) lowered the energy demand for ammonia recovery from 20.4 to 7.8 kWh kg_N^{-1} (Wang et al., 2017). Compared to steam stripping (35–160 kWh_{th} kg_N^{-1}), which can achieve a similar %wt ammonia product, the fall in MCDI power demand facilitates an energetically cheaper recovery technology despite the cost of power typically 3–4 times more expensive than heat. Interestingly, ammonia was harnessed from urine (4.6 kg m^{-3}) using electrochemical recovery integrated with stripping (Christiaens, et al., 2019). Electrochemical (and bio-electrochemical) recovery utilises a cation exchange membrane to facilitate the transfer of ammonium into an alkaline solution. The high pH of solution is maintained by hydroxyl ions generated from the reduction of water at the cathode to produce concentrated gas-phase ammonia that can be more efficiently stripped (Yang and Qin, 2021). Electrokinetic systems are developing rapidly, and the ongoing innovation in materials and cell configurations could eventually lower the energy consumption associated with dilute wastewater feeds to enable viable integration with stripping for gas-phase recovery. In its current state, the technology is best positioned as a pre-treatment for concentrated wastewater stripping, which could reduce the energy demand, alkali demand and increase the gas-phase ammonia concentration generated.

Liquid-liquid hollow fibre membrane contactors (HFMC) have been investigated as a polishing step for the removal of ammonia from dilute secondary or tertiary wastewater (Licon Bernal et al., 2016; Licon et al., 2015). HFMC comprise a semi-permeable hydrophobic microporous polymeric membrane which permits the transport of gas across from the liquid feed side. Similar to stripping, which utilises the relative high volatility of ammonia, wastewater pH is raised (>9) by alkali addition or decarbonisation to increase the free ammonia fraction. Ammonia gas then diffuses across the membrane which offers favourable characteristics for mass transfer (Darestani et al., 2017; Hasanoğlu et al., 2010). The ammonia gas is captured within a liquid absorbent. Sulphuric acid is commonly used due to its affinity for ammonia (Darestani et al., 2017). Within the conditions studied, mass transfer has been shown to be less dependent on the feed-side concentration, due to the slow diffusion of ammonia in liquid, which results in a mass transfer coefficient in liquid-liquid extraction around two orders of magnitude lower than in

gas phase mass transfer within the same technology (Davey et al., 2020).. However, the HFMC offers high interfacial areas (1000–2000 m^2 m^{-3}) thereby compensating for the decline in mass transfer (Belaissaoui et al., 2016). The use of a reactant to encourage ammonia separation in liquid-liquid membrane contactors, enables efficient treatment from dilute sources and the attainment of excellent effluent quality which could meet stringent nitrogen discharge limits (<0.001 kg m^{-3}) (Licon Bernal et al., 2016). When operated in a closed loop, the final absorbent can contain more than 35 times the treated wastewater ammonia concentration (Licon Bernal et al., 2016; Lin et al., 2018). However, at an industrial scale, the vapour pressure gradient that may arise from a difference in temperatures between phases, could induce significant water transport across the membrane and dilute the acid product (Davey et al., 2022). Chilled water (10ºC) has been investigated as an ammonia absorbent within HFMC, which could provide a suitable medium for downstream stripping (Lin et al., 2018; Christiaens et al., 2019).

3. Pathways for ammonia to energy

A range of technological routes exist for energy or hydrogen generation from ammonia and these have different requirements for the state and quality of the ammonia fuel. These include the combustion in engines alongside biogas, high and low temperature fuel cells that can exceed the Carnot limit, and conversion to hydrogen fuel which facilitates access to an even wider range of technologically mature and novel routes (Table 9). Low temperature alkaline fuel cells (AFC) could generate power from the oxidation of ammonia in aqueous solutions (Guo et al., 2020). This technology has been applied for energy generation from unrefined leachate and synthetic wastewater as dilute as 0.3 kg m^{-3} aqueous ammonia (Zhang et al., 2020b). Hence, AFC could be fuelled by unrefined condensate from steam or vacuum stripping or by dilute ammonia captured during water scrubbing of thermal stripping off-gases. Higher efficiency solid oxide fuel cells (SOFC) operate at high temperatures to generate power from gas-phase ammonia by firstly cracking it into hydrogen fuel (Lan and Tao, 2014). Efficient power generation in SOFC has been demonstrated using ammonia-water vapour (5–25 %wt) of comparable concentration to that produced directly from vacuum stripping (van Linden et al., 2022). Direct utilisation of vapour-phase ammonia from these processes at the treatment works would eliminate any condensation stage and liquid handling which is required when deploying it instead as an energy vector to decarbonise a wider range of sectors (Grasham et al., 2019). This means that associated energy demand and ammonia losses of direct utilisation are lower overall compared to the case where this ammonia is

Table 9
Ammonia to energy technology overview.

Technology	Fuel state	Fuel quality %wt NH_3	Scale tested	Temperature ºC	Electrical efficiency %LHV	Energy consumption kWh kg_{H2}^{-2}	Emissions ppmv[a]
Ammonia to energy							
Pure NH_3 gas turbine	Gaseous/ Anhydrous Liquid[b,c]	100 %[b,c]	0.2 MW[c]	COT 650–800[b,e]	30–40 %[f]	-	$NO_X < 10$[b]; $NH_3 < 5$[g]
Co-fired NH_3-CH_4 gas turbine	Gaseous/ Anhydrous Liquid[b,c]	32–100 %[b,c,h]	2.0 MW[i]	COT 650–800[b,e]	30–40 %[f,h]	-	$NO_X < 10$[d]; $NH_3 < 5$[e]
SOFC	Gaseous[j]	5–100 %[j,k]	1–14 kW m^{-2} [j,l]	600–850[l,m]	50–70 %[f,n]	-	$NO_X < 4$[k]; $NH_3 < 2$[k]
AFC	Gaseous/ aqueous[o,p]	0.01 - 100 %[o,p]	1×10^{-5}-4 kW m^{-2} [q,r]	20–100[q,r]	50–60 %[f,o]	-	-
Ammonia to hydrogen							
Catalytic cracking	Gaseous[s,t]	5–100 %[j,s,t]	-	450–700[s,t]	-	4.3[s], 33–42[u,v]	-
Alkaline electro-oxidation	Aqueous	0.01 – 35 %[w,o]	0.12 kW m^{-2} [x]	20–55[s,y]	-	10–17[z,aa]	- $NO_X < 0.2$[ab]; $NH_3 < 4.5$[ab]

SOFC – solid oxide fuel cell; AFC – alkaline fuel cell; COT – combustor outlet temperature

[a] At 16 % O_2
[b] Kurata et al. (2017)
[c] Okafor et al. (2021)
[d] Uchida et al. (2019)
[e] Okafor et al. (2020)
[f] The Royal, 2020
[g] Okafor et al. (2019)
[h] Hewlett et al. (2019)
[i] Uchida et al. (2019)
[j] van Linden et al. (2022)
[k] Dekker and Rietveld (2006)
[l] Shy et al. (2018)
[m] Guo et al. (2020)
[n] Saadabadi et al. (2020)
[o] Siddiqui and Dincer (2019)
[p] Zhang et al., 2020a
[q] Davey et al. (2022)
[r] Gottesfeld (2018)
[s] Membrane reactor for H_2 generation and purification (Jackson et al., 2015)
[t] Li et al. (2017)
[u] H_2 generation, NH_3 removal and cryogenic separation (Nasharuddin et al., 2019)
[v] H_2 generation and cryogenic separation (Makhloufi and Kezibri, 2021)
[w] Diaz and Botte (2015)
[x] Latvyte et al. (2024)
[y] Modisha and Bessarabov (2016)
[z] Vitse et al. (2005)
[aa] Cooper and Botte (2006)
[ab] Huang et al. (2019)

Table 10
Characterisation of methane, CO_2, H_2S and siloxanes in stripped off-gas and conventional biofuels.

Gas product	CH_4 %vol	CO_2 %vol	H_2S mg m^{-3}	Siloxanes mg m^{-3}	Halogens mg m^{-3}
Wastewater stripping off-gas[a]	<1 %[b]	-	140–1000[b,c]	0.5–0.6[d]	-
Biogas (municipal sludge)	58–67 %[e,f,g]	33–40 %[e,f,g]	1–90[e,h,i]	4–400[d,j,k,l]	<0.1–7[h,g]
Landfill gas	37–68 %[e,g]	24–43 %[e,g]	40–1000[e,h]	1–18[e,j,m]	0.3–1.3[g]
Biomethane	95–98 %[n,o]	1–5 %[n,o]	<5[p]	0.23[q]	<1.5[p]

[a] Data available for air stripping UASB and AnMBR effluents
[b] Glória et al. (2016)
[c] Centeno Mora et al. (2023)
[d] Galdi et al. (2022)
[e] Rasi et al. (2010)
[f] Oshita et al. (2014)
[g] Rasi et al. (2007)
[h] Arnold and Kajolinna (2010)
[i] Spiegel and Preston (2003)
[j] McBean (2008)
[k] Dewil et al. (2006)
[l] Hepburn et al. (2015a)
[m] Tansel and Surita (2019)
[n] Angelidaki et al. (2018)
[o] Bauer et al. (2013)
[p] Environment, 2013
[q] Energy Networks Association, 2021

condensed, transported and fed to the same fuel technology. The combustion of anhydrous ammonia has been demonstrated in gas turbines for combined heat and power generation (Okafor et al., 2019; 2021). Pertinently for wastewater applications, the co-combustion with ammonia and hydrocarbon fuels (i.e. biogas or biomethane) will enhance the stability of combustion and this could support the utilisation of ammonia vapours (30–40 %wt) in gas turbines (Hewlett et al., 2019; 2020; Uchida et al., 2019). This could facilitate the use of existing combined heat and power assets for ammonia to energy. Finally, ammonia recovered in an aqueous or gas-phase could be transformed into hydrogen by electrolysis or catalytic cracking respectively (Grasham et al., 2020; Jackson et al., 2015; Vitse et al., 2005). There are several review papers in the literature on ammonia to power and hydrogen generation (Elbaz et al., 2022; Asif et al., 2023; Jeerh et al., 2021) but most of the work focused on pure ammonia or ammonia blending with other fuels (e.g. hydrogen and natural gas) in the context of the hydrogen economy and renewable energy storage (Tawalbeh et al., 2022). This section is aimed to discuss potential application of wastewater-derived ammonia for power generation. The robustness and tolerance of each power generation technology to contaminants which may be present in wastewater-derived ammonia fuels will be the focus and compared against conventional biofuels in wastewater treatment (Table 10).

3.1. Combustion in gas-turbines

In recent years, there has been rapid progress in the development of ammonia fuelled gas-turbines for heat and power generation (Eq. (3)). The key challenges for ammonia combustion have been its low flame velocity which leads to flame instability and poor combustion efficiency (Kobayashi et al., 2019; Okafor et al., 2019), and high NO_x potential due to competing side reactions during ammonia oxidation (Hayakawa et al., 2015; Zamfirescu and Dincer, 2008). In the past few years, there have been significant research progress to address these issues such as using staged combustion (Okafor et al., 2019; 2020), partially cracked ammonia combustion (Shi, et al., 2024), ammonia blending up to 40 % vol with hydrogen and natural gas (Uchida et al., 2019; Montgomery et al., 2021), development of swirl burner to enhance stability (Kurata et al., 2017), plasma assisted combustion (Taneja et al., 2022), and moderate and intense low oxygen dilution (MILD) combustion (Liu et al., 2022; Rocha et al., 2021; Ariemma et al., 2021). NO_x could be reduced below 10 ppmv by selective catalytic reduction (SCR) exhaust treatment which consumes a fraction of the ammonia fuel (Uchida et al., 2019).

Limited experimental data is available for the combustion of lower quality ammonia vapour which could be generated from wastewater stripping with partial or no purification. Ammonia fed for co-combustion is typically pure (Montgomery et al., 2021) yet a 25 %wt ammonia aqueous solution resembling the product quality of stripped wastewater has been fed to an engine alongside commercial diesel fuel despite giving rise to CO_2 and CO alongside NO_x (Pyrc, et al., 2020). Instead, the co-combustion with humidified ammonia originating from wastewater stripping mitigates these emissions, since the addition of water to the ammonia-air mixture can lower flame temperature and scavenge oxygen radicals which limits the reaction rate of N_2O and NO generation (Law, 2006). However, the water content should not exceed 3 %vol for combustion efficiency unless MILD combustion is used, which is not significantly affected by water vapour content (Pugh et al., 2021; Maab et al., 2023; Ariemma et al., 2021). Ariemma et al. (2021) observed a 36 % decrease in NO_X after adding water from a 25 %wt ammonia feed composition, which is of comparable quality to ammonia vapour (43–64 %wt) recovered from wastewater stripping (Luqmani et al., 2024). Recent research has seen possibility of burning liquified ammonia directly in gas turbines which may open a new route for the use of wastewater-derived ammonia. The liquid ammonia spray combustion demonstrated experimentally so far could reduce cost and energy associated with the vaporisation of liquid fuel and subsequent compression required to be compatible with ammonia gas combustion systems discussed thus far (Somarathne et al., 2023).

In addition to water in the wastewater-derived ammonia fuel there are also contaminants present which are carried over from liquid wastewater to the gas phase during stripping. The contaminants influence gas turbine performance, lifespan and emissions. Stripping of ammonia from the relatively concentrated advanced anaerobic digestion centrate (digested sludge liquor in Fig. 1) is proposed. The characterisation of trace contaminants in the stripped gas are therefore potentially similar to that from anaerobic digester effluent, due to their shared origin, where high concentrations of hydrogen sulphide (up to 1000 mg m^{-3}) exist alongside other trace gases including siloxanes (Table 10). While the implications of these contaminants has not been directly investigated either during combustion or co-combustion, they can be inferred from the combustion of established biofuels such as

biogas and landfill gas which contain sulphur, silicon and volatile organic compounds (including those halogenated) (McBean, 2008; Rasi et al., 2007; 2010). Corrosive acids (e.g. HCl, HF) formed during the combustion of halogenated volatile organic compounds in the stripping off gas can inflict damage to the engine itself. Damage is worsened in the presence of water which may be added as steam to suppress NO_x by transforming post-combustion sulphur dioxide into sulphuric acid (Schweigkofler and Niessner, 2001). Moreover, siloxanes that are oxidised in the combustion chamber form silicates and quartz which are deposited on the engine surface and severely decrease operational lifetime (McBean, 2008). Many of the remaining trace contaminants identified in the vapour exhaust of vacuum stripping digested sludge liquor (e.g. phenolic compounds) are not reported to be of concern (Ukwuani and Tao, 2016; Tao et al., 2024). If not managed upstream, post-combustion products may also be yielded. The combustion of trace hydrogen sulphide produces sulphur dioxide which is then converted to corrosive sulphuric acid when exposed to moisture in the atmosphere whilst NO_x emissions negatively contribute to air quality and global warming (Deed et al., 2004).

The probability for partitioning of these trace compounds into the strip gas is determined by the concentration and chemistry of the trace compounds present but may also be determined by conditions specific to the stripping technology selected. For example, the increase in pH imposed during stripping, transforms hydrogen sulphide into more water soluble and less volatile species thereby limiting transfer to the vapour phase (Tao et al., 2024). The concentration and composition of trace contaminants will also depends on where it is integrated into the treatment works. In the case of siloxanes, the more volatile cyclic siloxanes will partition into the biogas (e.g. D4, D5), while the cyclic and linear compounds partition into the sludge due to their hydrophobicity (Hepburn et al., 2015a; 2015b; Tansel and Surita, 2014). Since stripping will be based downstream of an AD, the concentration of these trace compounds within the stripped gas phase is likely to be less than experienced with biogas. Importantly, numerous technologies have been developed to selectively separate these compounds from biogas at treatment works (Bauer, et al., 2013), whether to pretreat biogas before combustion in a CHP engine (Hepburn et al., 2015a), to comply with engine manufacturer warranty specifications, or to ensure compliance with regulatory standards during the upgrading of biogas to biomethane before injection into the national gas grid or for use as vehicle fuel (Table 11) (Legislation, 1996; Legislation, 2023). Technological approaches have also been introduced for post-combustion gases (Deed, et al., 2004) to meet emissions regulations (European Parliament. Council of the European Union (2015)). However, in the case of ammonia to energy, best engineering practice should be implemented to limit partitioning and to adopt effective pretreatment where warranted to mitigate the demand for post-combustion abatement or to derisk the exploitation of ammonia fuel for other applications that may possess greater sensitivity to the presence of trace compounds (Shareefdeen and Mishu, 2023).

3.2. Solid oxide fuel cells

Solid oxide fuel cells (SOFC) have higher power conversion efficiencies than gas turbines because they can exceed the Carnot limit (The Royal Society, 2020). Peak power densities in the range 1–14 kW m^{-2} are typical for hydrogen SOFC (Saadabadi et al., 2020; Shy et al., 2018; Stoeckl et al., 2020). Broadly, there are two types of SOFC, SOFC(O) and SOFC (H). In SOFC-O, oxygen anions are produced at the cathode and are transported to the anode to oxidise hydrogen and generate water vapour (Eqs. (5) and (6)) (Afif et al., 2016). In SOFC-H, hydrogen is oxidised at the anode and protons are transported to the cathode to react with oxygen and form water vapour (Eqs. (7) and (8)) (Afif et al., 2016). Ammonia can be directly used as a fuel for both SOFC. Mechanistic studies have shown that direct ammonia SOFC undergoes ammonia *in-situ* cracking to produce hydrogen followed by hydrogen SOFC process (Eq. (4)) (Cinti et al., 2016; Kishimoto, et al., 2017; Meng, et al., 2007).

$$2NH_3 \rightarrow 3H_2 + N_2 \ \Delta H = 92.4\ kJ \quad (4)$$

$$SOFC(O)\ Cathode:\ O_2 + 4e^- \rightarrow 2O^{2-} \quad (5)$$

$$SOFC(O)\ Anode:\ H_2 + O^{2-} \rightarrow H_2O + 2e^- \quad (6)$$

$$SOFC\ (H)\ Cathode:\ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (7)$$

$$SOFC\ (H)\ Anode:\ 3H_2 \rightarrow 6H^+ + 6e^- \quad (8)$$

An SOFC fed with pure ammonia gas could achieve an electrical efficiency of 67 % at temperature of ca. 750ºC, based upon 80 % fuel utilisation and accounting for the parasitic energy demand of cooling air blowers (Cinti et al., 2016). When the same system was fed with ammonia-water vapour (27 %wt), an electrical efficiency of up to 58 % was demonstrated (Cinti et al., 2016). This indicates overall performance was not substantially decreased despite the presence of water vapour which reduces potential by diluting hydrogen at the anode (Rainwater et al., 2012). van Linden (2022) investigated power generation in an SOFC(O) using ammonia-water vapour compositions characteristic of those recovered when vacuum stripping wastewater. Increasing the ammonia fraction from 5 to 25 %wt enhanced the peak power density from 1 to 3 kW m^{-2} (van Linden et al., 2022). Notably, an unstable open circuit voltage was observed for 5 %wt vapour which indicated that excess water vapour disrupted the *in-situ* cracking of ammonia and can denote the minimum concentration for efficient SOFC use (van Linden et al., 2022). Since the anode exhaust represents a source of high-grade heat (>600ºC), it has been proposed that SOFC could replace the functionality of existing gas turbines for combined heat and power generation in wastewater treatment (Trendewicz and Braun, 2013). High-grade waste heat from SOFC could supplement the energy required for thermal stripping of ammonia fuel from wastewater in an integrated vision for nitrogen removal. Un-utilised fuel and the hot exhaust exiting the SOFC have been combined in a combustion chamber (Patel et al., 2012). These hybrid SOFC-gas turbine systems fuelled with

Table 11
Overview of acceptable contaminant concentrations in fuel for energy applications.

Fuel source (energy application)	Minimum fuel content	H_2S mg m^{-3}	Siloxanes mg m^{-3}	Halogens mg m^{-3}	Refs.
Municipal sludge and landfill biogases (commercial gas turbine)	14.4–23.6 MJ m^{-3}	1150–2140[a]	5–50[a]	100–700[a]	(Deed et al., 2004; Wheless and Pierce, 2004)
Biomethane (UK gas grid)	35–44 MJ m^{-3}	≤5	-	<1.5	(Environment Agency, 2013; Legislation, 1996)
Gaseous ammonia (Solid Oxide Fuel Cell)	-	1–3	2–30	-	(Papadias and Ahmed, 2012; Sasaki et al., 2011)
Gaseous hydrogen (Transport fuel)	99.97 mol %	0.006[b]	-	0.07[b]	(European Standards, 2018)

[a] Value quoted mg per m^3 CH_4
[b] Original value in μmol/mol for both gaseous and liquid application

ammonia gas have been thermodynamically projected to achieve high electrical (55 %–66 %) and overall energy efficiencies (70 %) (Duong et al., 2022; Patel et al., 2012).

The long-term resilience of ammonia SOFC presents the primary developmental challenge. High activity nickel-based anodes have been applied widely during the development of SOFC due to their availability and low cost (Ganley et al., 2004; Guo et al., 2020). However, nickel-based anodes can suffer poisoning during ammonia oxidation and this can lead to degradation in performance over time where for example, a 4 % decline in cell voltage was observed over 100 h (Zhang et al., 2007). In the lower operating temperature range (<700 °C), voltage degradation was observed because of the formation of Ni-nitrides on the anode surface during incomplete ammonia decomposition (Stoeckl et al., 2019). Although higher temperatures avoids Ni-nitride formation, thermal stresses can cause sintering and agglomeration of nickel particles on the anode surface which will reduce catalytic activity (Stoeckl et al., 2019; Yang et al., 2015a). Pathways to improve SOFC stability include the decomposition of ammonia using the heat from high temperature anode gas prior to entering the cell, and the development of bi-metallic catalysts which could enhance resilience (Guo et al., 2020). Despite numerous proposed schemes, there is limited data for SOFC operation using real wastewater-derived ammonia. Recently, Xu et al. (2022) reported that power density for an SOFC(O) fed with ammonia-hydrogen gas mixtures generated from digested pickling wastewater were 3-times lower than for synthetic gas mixtures. This was attributed to the presence of water and hydrogen sulphide (Xu et al., 2022). Solid oxide cells are highly vulnerable to degradation by both hydrogen sulphide and siloxanes that may be present in wastewater-derived ammonia (Table 10). Trace amounts of hydrogen sulphide (7 mg m^{-3}) react with conventional nickel anodes to form dense Ni-sulphides on their surface which reduce electrochemical activity (Sasaki et al., 2006). Siloxanes in the feed will be oxidised in the SOFC at high temperatures to form silicates on the surface of the anode and result in fatal degradation of cell performance (Sasaki et al., 2011). Consequently, thresholds of 1–3 mg m^{-3} hydrogen sulphide and 2–30 mg m^{-3} siloxanes are recommended for the feed gas which will necessitate high efficiency removal of contaminants during pre-treatment (Table 11) (Papadias and Ahmed, 2012; Sasaki et al., 2011). Although water is responsible for a reduction in overall SOFC performance, similar to combustion, it is reported to suppress generation of NO_x which is of particular concern when ammonia is present with the oxygen anion electrolyte (Eq. (6)) (Yang et al., 2015b).

3.3. Low temperature alkaline fuel cells

In contrast to SOFC, low temperature AFC can generate power directly from the electrochemical oxidation of ammonia and so cracking is not required. Consequently, they can operate at lower temperatures (25–100 °C) and can accept a wide range of feeds from dilute aqueous to pure gas-phase ammonia (Gottesfeld, 2018; Siddiqui and Dincer, 2019; Zhang et al., 2020b). In a typical AFC, oxygen and water vapour react together at the cathode to form hydroxide ions, which are transported through an anion exchange membrane to oxidise ammonia at the anode and produce electrons (Guo et al., 2020) (Eqs. (9) and (10)):

$$Cathode: \ 1.5O_2 + 3H_2O + 6e^- \rightarrow 6OH^- \quad (9)$$

$$Anode: \ 2NH_3 + 6OH^- \rightarrow N_2 + 6H_2O + 6e^- \quad (10)$$

Power densities in AFC tend to be 2–3 orders of magnitude lower than SOFC (Siddiqui and Dincer, 2018; 2019; Suzuki et al., 2012), indicating that much higher installed capacities would be required to process the same quantity of fuel (Table 9). In a notable exception, Gottesfeld (2018) reported a power density of 4 kW m^{-2} when operating with a pure ammonia gas feed at 100°C. This has been attributed to the high ammonia concentration which will lower the onset potential for ammonia oxidation, coupled with the high operating temperature which increases catalytic activity and the kinetics of ammonia oxidation (Guo et al., 2020). However, in a wastewater context, the major advantage of AFC is their potential for power generation from dilute aqueous solutions and the avoidance of energy intensive ammonia purification. For example, Zhang et al. (2020b) used an AFC to oxidise 97 % ammonia from landfill leachate (3 kg m^{-3}) whilst generating 8 × 10^{-4} kW m^{-2}. Increasing the feed ammonia concentration to 51 kg m^{-3} more than quadrupled power density, highlighting why the recovery and concentration of ammonia could be advantageous to lowering the capital cost for an AFC system (Zhang et al., 2020b).

Platinum-based catalysts are widely employed due to their high activity for ammonia oxidation however, platinum is expensive and vulnerable to poisoning by intermediate species formed during oxidation (N_{ads}) which adsorb to its surface and reduce activity (De Vooys et al., 2001). Nickel, copper and iron-based catalysts could be resilient to N_{ads} poisoning and achieve high activities for ammonia oxidation in the low operating temperature range. Investigating these alternative catalysts is crucial for reducing the cost and enhancing the long term stability of AFC (Jeerh et al., 2021). Siddiqui and Dincer (2018) reported an electrical efficiency of just 12 % for an AFC fuelled with 17 kg m^{-3} aqueous ammonia at ambient temperature (0.07 kW m^{-2} power density), which is similar in concentration to an aqueous ammonia product formed through steam or vacuum stripping. Low electrical efficiencies can arise from the relatively poor conductivity of hydroxide ions in solution and so highly conductive exchange membranes (AEM) must be applied to counter this (Marino et al., 2014). Reducing the AEM thickness can also limit ohmic losses and increase overall efficiency (Jeerh et al., 2021), but this could facilitate ammonia crossover and the consequent poisoning of the cathode and a reduction in open current voltage (Siddiqui and Dincer, 2018). Therefore, the manufacture of very thin AEM which maintain mechanical robustness is the subject of continual development.

The presence of contaminants in wastewater-derived ammonia could indirectly lower cell performance. Davey et al. (2022) explored power generation in AFC using a 17 kg m^{-3} aqueous ammonia solution recovered from digested sludge liquor by vacuum thermal stripping. A lower power density was achieved for the recovered ammonia (5 × 10^{-5} kW m^{-2}) than for a synthetic feed at the same concentration (1 × 10^{-4} kW m^{-2}) (Davey et al., 2022). This was attributed to the carryover of volatile compounds from wastewater which lowered the pH for the recovered solution, and thus limited the concentration of free ammonia (Fig. 3) and OH^- necessary for ammonia oxidation at the anode (Eq. (10)) (Davey et al., 2022). A commonly reported performance inhibiting volatile compound is CO_2 which reacts with OH^- electrolytes to produce the carbonate anion that then forms carbonic acid in water (Jeerh et al., 2021). Rather than utilising CO_2 sequestration technology upstream, anodic carbonate decomposition could be induced by operating nearer the upper range of 100 °C to facilitate the removal of dissolved CO_2 (Gottesfeld, 2018). Other contaminants including siloxanes are less likely to be converted to and deposited as silicates on the AFC anode surface compared to SOFCs which adopt significantly higher operating temperatures (>600 °C) (Lan and Tao, 2014). Likewise, NO_x formation is mitigated at temperatures well below those utilised in gas turbines and therefore the cost of post-combustion technologies at treatment works is lowered by adopting an AFC (Law, 2006; Shareefdeen and Mishu, 2023).

3.4. Carbon-free hydrogen generation

Hydrogen generation by catalytic cracking of gas-phase ammonia (Eq. (4)) is an alternative route to steam methane reforming (SMR). Ruthenium-based catalysts, commonly applied for ammonia catalytic cracking, exhibit higher activity than those used in SOFC and therefore enable efficient ammonia decomposition (>99.9 %) at 450–700 °C (Jackson et al., 2015; Li et al., 2017; Wang et al., 2004). Due to the rarity and cost of ruthenium, there is a focus on the development of catalysts based on cheaper materials such as nickel which are active at higher

temperatures and metal amides which offer high activities below 500 °C but may be limited by poor thermal stability (Makepeace et al., 2015; Mukherjee et al., 2018). Catalytic cracking can be conducted using feeds with low gas-phase ammonia concentrations (5–10 %wt) (Chellappa et al., 2002; van Linden et al., 2022). However, reducing the concentration will slow the decomposition kinetics and is counteracted by increasing the reactor temperature and residence time using a larger reactor (Chellappa et al., 2002; Hossein Ali and Shin, 2022). Catalytic cracking, commonly conducted within fixed bed reactors, will produce a gas blend containing trace contaminants depending on the feed gas quality (Hossein Ali and Shin, 2022). For example, an SMR reactor charged with synthetic biogas revealed that trace levels (~0.5 ppm) of hydrogen sulphide and siloxane D5 were capable of poisoning the catalyst and reducing activity (Chiodo, et al., 2017). These contaminants may exist in ammonia products recovered from wastewater by stripping, and could thus pose a risk for ammonia catalytic cracking which, similar to SMR reactor, employs a commercial nickel catalyst and alumina support at >800 °C (Lee et al., 2021; Ashcroft and Goddin, 2022). On the other hand, ruthenium exhibits lower hydrogen sulphide adsorption (Oliphant et al., 1978). Transport-grade hydrogen fuel, suitable for sensitive polymer electrolyte membrane (PEM) fuel cells, must meet stringent international quality standards which include <0.1 ppm of unreacted ammonia and <4 ppb hydrogen sulphide (EN 17124:2018) (European Standards, 2018). In a conventional flowsheet, ammonia is removed by water scrubbing and then hydrogen is purified in a pressurised cryogenic cycle (240 bar, <-210 °C) to liquefy the nitrogen component or by pressure-swing adsorption to produce a high purity final product (>99.97 %vol H_2) (Makhloufi and Kezibri, 2021; Nasharuddin et al., 2019). These are analogous to technologies that have been employed in the wastewater sector for the treatment of biogas (Bauer, et al., 2013).

The total energy demand for hydrogen production by catalytic cracking is estimated to be 33–42 kWh kg_{H2}^{-1}, where 30–40 % is associated with the energy-intensive purification (Makhloufi and Kezibri, 2021; Nasharuddin et al., 2019; Naquash et al., 2024). This can exceed the intrinsic energy of the purified hydrogen product (33.3 kWh kg_{H2}^{-1}), highlighting that net energy losses can occur during the conversion. Catalytic membrane reactors in development could facilitate ammonia decomposition and hydrogen purification in a single unit to lower the overall energy requirement further below that of SMR (>44.5 kWh kg_{H2}^{-1}) (Cechetto et al., 2021; Jackson et al., 2015; International Energy Association, 2023). Energy demand can decrease to 8 kWh kg_{H2}^{-1} whilst high purity hydrogen (>99.99 %) is produced (Giddey et al., 2017; Jackson et al., 2015). Catalytic cracking is the most developed technology for hydrogen production from ammonia, and demonstration projects for the generation of 200–400 kg_{H2} d^{-1} transport-grade hydrogen are underway to evaluate commercial viability at scale (Siemens, 2022; The Royal Society, 2020; Tyseley Energy Park, 2022; AFC Energy, 2024). For a 1.2 million P.E. treatment works (Fig. 1), the potentially recoverable 210 kg_{H2} d^{-1} within demonstration scale capacity may produce up to 7 MWh d^{-1} and offset 1/3rd of power demanded by aeration for ammonia.

Alternatively, hydrogen could be produced from the electro-oxidation of ammonia (Modisha and Bessarabov, 2016; Vitse et al., 2005). Similar to AFC, this can utilise aqueous ammonia feeds at low temperatures (typically ambient) (Cooper and Botte, 2006; Palaniappan, 2013). Since hydrogen and nitrogen generation occurs at the anode and cathode respectively, the gases can be segregated within the cell and energy intensive downstream hydrogen purification is avoided (Eqs. (11) and (12)) (Modisha and Bessarabov, 2016).

$$Cathode: \ 6H_2O + 6e^- \rightarrow 3H_{2(g)} + 6OH^- \quad (11)$$

$$Anode: \ 2NH_3 + 6OH^- \rightarrow N_{2(g)} + 6H_2O + 6e^- \quad (12)$$

This process has garnered particular interest since, thermodynamically, it requires 95 % lower energy consumption for hydrogen production than the conventional electrolysis of water (1.6 kWh kg_{H2}^{-1} and 33 kWh kg_{H2}^{-1} respectively) (Vitse et al., 2005). In practice, the energy efficiency is limited by poisoning of platinum-based catalysts at the anode by N_{ads} and therefore the development of cheap, resilient catalysts like nickel-copper that has been demonstrated on synthetic wastewater is necessary for commercialisation (Adli et al., 2018; Latvyte, et al., 2024). An identical anodic reaction to AFC under similar conditions and catalyst denote that with the exception of carbon dioxide, which reacts with OH^- electrolytes to limit oxidation, other contaminants transferred across from stripping real wastewater are unlikely to significantly impact performance or emissions (Jeerh et al., 2021). Limited experimental data is available on any direct impact. Conversely, the ammonia catalytic crackers are likely more susceptible at much higher temperatures (Chiodo, et al., 2017; Shareefdeen and Mishu, 2023). Promisingly, the production of high purity hydrogen (<1 ppm NH_3) has been demonstrated by the electro-oxidation of 17 kg m^{-3} aqueous ammonia over platinum-based catalysts at 25°C and associated with 10–17 kWh kg_{H2}^{-1} (Cooper and Botte, 2006; Vitse et al., 2005). Increasing the feed concentrations for hydrogen production will substantially enhance current density within the cell (16-fold increase from 0.02 to 34 kg m^{-3}) whilst a high pH maximises free ammonia available at the anode (Fig. 3) (Li et al., 2017; Adli et al., 2018). Therefore, technologies capable of recovering a high-quality ammonia product from wastewater like low energy vacuum thermal stripping (Luqmani et al., 2024) could therefore promote more efficient, lower capital cost electrolytic cells for onsite hydrogen generation.

4. Future outlook

Decarbonisation is an emerging contemporary challenge for the water sector that places emphasis on: (i) the reduction in electrical energy derived from fossil sources; (ii) the mitigation of fugitive carbon emissions, and (iii) investment in renewable energy. To meet stricter regulations on ammonia (Urban Wastewater Treatment Directive; 91/271/EEC), water utilities are upgrading carbonaceous activated sludge wastewater treatment works, or underperforming nitrifying wastewater treatment works with biological sidestream processes for return liquor treatment that offer lower capital investment versus an upgrade to the mainstream treatment process. However, this increases power requirements and nitrous oxide emissions therefore making the transition to net zero a greater challenge. By implementing thermal ammonia stripping into the sidestream for return liquor treatment, up to 50 % of net CO_2 emissions associated with mainstream wastewater treatment could be reduced by avoiding nitrous oxide formation (Davey et al., 2022). This review evidences that ammonia recovery technologies for return liquors are technically mature, but to produce an ammonia product that can be exploited for energy applications, innovation is warranted to reduce the separation energy and chemical demand. Grasham et al. (2019) modelled a scheme to recover ammonia from digested sludge liquor by thermal stripping and distillation, and subsequently combined the ammonia with biomethane produced on-site (4.8 MW) to co-fuel an SOFC and furnace (Table 12). The electrical energy balance demonstrated a net gain of approximately 1–1.5 kWh kg_N (Grasham et al., 2019), indicating the potential to achieve energy neutral ammonia recovery. However, this did not consider the thermal energy demand which was assumed to be offset from recycling heat from the furnace exhaust.

Full-scale site audit of biogas combustion in a combined heat and power (CHP) system at a conventional AD installation, has been shown to produce a total thermal output of 3.0 MW in waste heat, including 1.5 MW high-grade heat (Moore and Auty, 2013), which illustrates the opportunity to integrate thermal stripping with existing on-site waste heat. However, for thermal stripping systems that require a higher heat quality (i.e. raising steam for distillation or steam stripping stages), natural gas or liquified fuels may be required to supplement. Vacuum stripping has been shown to mitigate the thermal demand for ammonia stripping, where operation at the bubble point of the mixture incurs a

Table 12
Overview of schemes proposed for waste ammonia to energy or hydrogen.

Waste source (ammonia concentration)	Ammonia removal, capture and/or concentration	Utilisation	Performance	Refs.
Ammonia vapour from steel manufacture [a] (32–38 % wt)	Optional: blend with green ammonia gas source to increase up to 70 %wt $NH_{3(v)}$	Co-fuel gas turbine with methane or coke oven gas	36–39 % electrical efficiency	(Hewlett et al., 2019, 2020)
Synthetic wastewater (1–10 kg m^{-3})	Vacuum membrane stripping (25–55°C, 0.02 bar), generation of 1–11 % wt $NH_{3(v)}$	SOFC	1–2 kW m^{-2}[b] 30–43 % electrical efficiency[b]	(van Linden et al., 2022)
Primary sludge liqour[a,c]	Struvite precipitation and thermal degradation, distillation of vapours up to 30–90 %wt $NH_{3(v)}$	SOFC	1 kW m^{-2} up to 53 % electrical efficiency	(Saadabadi et al., 2020)
Wastewater[a,c]	Vacuum membrane stripping[d], generation of 3–100 % $NH3_{(v)}$	SOFC	2–3 kW m^{-2}	(Stoeckl et al., 2020)
Digested sludge liquor [a] (1.8 kg m^{-3})	Thermal air stripping (7 5°C), water scrubbing for ammonia capture, flash distillation to form 3.9 %wt $NH_{3(v)}$	Co-fuel SOFC with biomethane	1 kW m^{-2} 48 % electrical efficiency	(Grasham et al., 2019)
Landfill leachate (3 kg m^{-3})	Electrodeionisation, capture of NH_3-H_2 gas formed at cathode	Co-fuel SOFC with biogas	10–12 kW m^{-2} 50 % electrical efficiency	(Xu et al., 2017)
Pickling wastewater (0.5 kg m^{-3})	Bipolar membrane electrodialysis, capture of NH_3-H_2 gas formed at cathode	Co-fuel SOFC with biogas	5 kW m^{-2e} 60 % electrical efficiency	(Xu et al., 2022)
Leachate (3 kg m^{-3})	N/A	Low-temperature AFC	8×10^{-4} kW m^{-2}	(Zhang et al., 2020b)
Digested sludge liquor (2 kg m^{-3})	Vacuum thermal stripping (65 °C, 0.25 bar), condensation to form 17 kg m^{-3} $NH_{3(aq)}$	Low-temperature AFC	5×10^{-5} kW m^{-2}	(Davey et al., 2022)
Digested sludge liquor[a] (1.5 kg m^{-3})	Thermal air stripping (64 °C), water scrubbing for ammonia capture, distillation to produce $NH_{3(v)}$[c], combine with biogas in steam reformer and water-gas shift reactor to produce hydrogen	PSA to purify hydrogen for export	-	(Grasham et al., 2020)

[a] Modelled results.
[b] Based on outcomes for 5–10 %wt $NH_{3(v)}$.
[c] Concentration not specified.
[d] Operating conditions not specified [e] Based on real gas mixtures.

latent heat penalty as low as 1 kWh_{th} kgN^{-1} (Luqmani et al., 2024). This is comparable to the energy demand of 3–5 kWh_e kgN^{-1} for mainstream biological nitrogen removal (Garrido et al., 2013; Wett, 2006). Heat is typically three to four times cheaper than electrical power, and as such vacuum thermal stripping may be more economically competitive, while producing an rich ammonia product that can be directly exploited as a fuel (Bavarella et al., 2020; Davey et al., 2022; van Linden et al., 2022). With such low total thermal and heat quality requirements, the use of biogas, renewable power or waste heat represent low carbon and economically viable primary fuel sources. Recent evidence also proposes that the co-stripping of CO_2, complemented with the addition of sensible heat, is sufficient to raise pH for effective ammonia stripping without the demand for chemicals (Luqmani et al., 2024), which offers further transformation of the economics beyond the current state-of-the-art, in mitigating chemical costs and facilitating all separations needed to recover and transform ammonia as a fuel into a single stage.

Extractive technologies have been demonstrated to separate ammonia at low concentrations in mainstream wastewater. These technologies are presently less mature but can work synergistically with thermal stripping to access the full ammonia quotient of wastewater, which is sufficient in energy to offset 40 % of sector wide energy consumption (Davey et al., 2022), and when complemented with the energy saved from avoiding aeration for nitrification, represents a major decarbonisation opportunity for the water sector. Three critical criteria must be achieved in any single technology: (i) a high rate of mass transfer to limit process footprint; (ii) robustness to water quality; and (iii) the production of an ammonia stream that can used for energy generation. Robustness can be garnered through pretreatment technologies (McAdam et al., 2011), whereas the production of an immediately applicable ammonia product is more challenging. Thermal stripping of the ammonia liquid stream arising from extractive technologies has been shown to produce an ammonia concentrate that is amenable for use in energy generation (Guida et al., 2022). This highlights complementarity between the two technologies in enabling an alternate low carbon strategy to the attainment of strict nitrogen discharge standards in the final effluent. Further to stricter wastewater regulations, clean air quality standards introduced to mitigate the causal link between ammonia air emissions and the formation of harmful $PM_{2.5}$, will indirectly drive further uptake of stripping solutions into the municipal and industrial wastewater sectors to abate fugitive ammonia air emissions from the storage of ammonia rich slurries which has been identified as a critical sink (Cheng et al., 2021; Department for Environment Food and Rural Affairs, 2019; European Commission, 2013; Vrontisi et al., 2016).

Purified ammonia could be exported and sold to provide a revenue. Ammonia is regarded as a critical zero-carbon energy vector within the hydrogen economy due its favourable liquefaction properties and high hydrogen density (Table 2) (Valera-Medina et al., 2018). This has led to an expansion in the production of 'green' ammonia to create a 100 % renewable and zero carbon product for use in fuel technologies of contrasting maturity and efficiency (Table 13). The levelised cost of 'green' ammonia production from wastewater could compete with standard approaches, and align with Europe's target for low-carbon and renewable hydrogen production, which is expected to deliver 24 % of total energy demand (2250 TWh y^{-1}) by 2050 (Department for Business Energy and Industrial Strategy, 2021; Fuel Cells and Hydrogen Joint Undertaking, 2019; Nayak-Luke et al., 2018). While ammonia as an energy commodity will be subject to waste classification under European law (Directive 2008/98/EC, 2008) which introduces a market barrier, entry into the supply chain is likely to be easier than for other ammonia based products derived from wastewater that are proposed for use as fertilisers in agriculture, or the wider food chain (Sfetsas et al., 2022). Financial incentives have also been levied in Europe for the production of zero carbon fuels for the decarbonisation of transportation and heating that can further motivate investments into ammonia recovery for energy (Jacobs, 2022), similar to those which have stimulated the transition away from the use of biogas for combined heat and power (CHP) generation toward biomethane production (Angelidaki et al., 2018). In analogy to biogas, ammonia could be exploited as an energy vector internally by water utilities, which could aid decarbonisation and reduce the risk on investment through decreasing dependence on an external market to drive demand. This is particularly timely, due to the net-zero ambitions for the water sector (Water UK, 2020), but also due to the contemporary challenges emerging for renewable energy generation. The incentives originally in place to support CHP engines such as the UK's Renewable Obligation Certificates (ROCs) are reaching end of life

Table 13
Ammonia fuel technology comparison.

	Combustion in gas turbine/ furnaces/internal combustion engines	Solid oxide fuel cells (SOFC)	Low temperature alkaline fuel cells (AFC)	Carbon-free hydrogen generation – catalytic cracking
Process description	During combustion ammonia is oxidised in the presence of oxygen to form nitrogen, water and NO_x. Other fuels such as methane and hydrogen can be blended with ammonia.	Ammonia fed to an SOFC is cracked *in-situ* between 600 and 850 °C to produce H_2 as fuel. The anode oxidises the fuel to generate electrons for power before they are transferred to an oxidising agent at the cathode. Electrolytes used to maintain these reactions depend on the type of SOFC.	AFC can generate power directly from the electrochemical oxidation of ammonia at the anode and operate between 25 and 100 °C. Electrons at the anode are transferred to the cathode where water vapour and oxygen react together. Hydroxyl ions are used as electrolytes to maintain these reactions.	Hydrogen alongside nitrogen is generated from the catalytic cracking of gas-phase ammonia between 450 and 700 °C. Hydrogen must then be purified from the nitrogen and unreacted ammonia for the use in fuel cell.
Advantages	• Oxidation is exothermic and can generate significant quantity of useful heat alongside the power from • Existing combustors at wastewater treatment works for combined heat and power from biogas are of similar scale that can be retrofitted to support ammonia combustion • Small quantity of water (<3 %vol) present in ammonia fuel may reduce NO_x emissions	• Fuel cells have higher power conversion efficiencies than traditional gas turbines/engines because they can exceed the Carnot limit (i.e. 50–70 %LHV) • Can accept humidified vapour fuel down to 5 %wt ammonia before *in-situ* cracking is disrupted thereby reducing pre-treatment ammonia purification. Water vapour also reduces NO_x emissions • Useful high-grade heat (>600 °C) from anode exhaust	• Fuel cells have higher power conversion efficiencies than traditional gas turbines/engines because they can exceed the Carnot limit (i.e. 50–60 %LHV) • Can accept humidified fuel down to very low ammonia concentrations thereby reducing pre-treatment ammonia purification • Low operating temperatures reduce likelihood of contaminants impacting cell performance (e.g. siloxanes). NOx emissions are decreased and exhaust treatment technology is mitigated	• Nickel/Ruthenium catalysts enable highly efficient ammonia decomposition (>99.9 %) • Can accept humidified vapour fuel down to 5 %wt ammonia before cracking is disrupted thereby reducing pre-treatment ammonia purification. Water vapour also reduces NO_x emissions • Green hydrogen in high demand by UK government and mature hydrogen fuel technology exists
Disadvantages	• Contaminants carried over with ammonia in wastewater can influence engine performance (e.g. siloxanes into silicates) and emissions (e.g. hydrogen sulphide into sulphur dioxide) under the high temperatures used • NO_x emissions must be reduced before exhaust to atmosphere. For example, selective catalytic reduction treatment yet it also consumes ammonia fuel • To ensure flame stability and sufficient efficiency either co-combustion alongside methane or utilisation of novel combustion technologies (e.g. MILD) is required	• Contaminants carried over with ammonia in wastewater can influence cell performance (e.g. siloxanes into silicates) and emissions (e.g. hydrogen sulphide into sulphur dioxide) under the high temperatures used • Long-term resilience of ammonia SOFC nickel catalyst is challenging and leads to degradation in performance • NO_x can be formed during oxidation of un-cracked ammonia at anode. Emissions must be reduced before exhaust to atmosphere. For example, selective catalytic reduction treatment yet it also consumes ammonia fuel • Additional energy consumed to maintain endothermic cracking with cooling air blowers	• Contaminants carried over with ammonia in wastewater can influence cell performance. For example, carbon dioxide decreases pH of fuel solution which reduced both the free ammonia fraction and hydroxyl ions available as fuel and electrolytes, respectively • Comparatively low ammonia fuel concentration and operating temperature decrease power density and therefore demand greater installed capacities • Platinum-based catalysts typically employed are expensive and vulnerable to poisoning. Minimal investigation into cheaper catalysts	• Ruthenium catalysts commonly used are expensive • Contaminants carried over with ammonia in wastewater can influence catalyst performance (e.g. siloxanes into silicates) and emissions (e.g. hydrogen sulphide into sulphur dioxide) under the high temperatures used • Energy-intensive purification demands up to 40 % of total energy which can exceed intrinsic energy of purified hydrogen fuel • Hydrogen must be stored at very high pressures (>350 bar) or low temperatures (-253 °C) before transport

(Houlker, 2019), while many existing CHP engines will require future investment in order to meet stricter NO_x emission standards (EU Directive 2015/2193) (Anglian Water, 2018; European Parliament. Council of the European Union (2015)). Ageing CHP engines could be replaced with higher efficiency SOFC or SOFC-gas turbine combined heat and power assets run exclusively on recovered ammonia, which would reduce the cost and complexity of conventional CHP engine operation, while offering opportunity for a wider range of financial benefits (Stoeckl et al., 2019; van Linden et al., 2022). Through the use of ammonia rather than biogas for the generation of heat (mainly used for heating AD), the export of biomethane could also increase, which is a major driver for decarbonisation set out within the EU's Renewable Energy Directive. Ammonia can therefore be regarded as a highly flexible product, whose value can be exploited for both existing and emerging energy opportunities that can help transition the water sector toward net-zero.

5. Conclusion

Ammonia is a zero-carbon energy vector with an emerging role in decarbonising heat, power and transport applications. The recovery of ammonia from wastewater can serve to sustainably meet the growing demand for ammonia as a fuel, reducing the need to expand production from the energy-intensive Haber-Bosch process. This approach also facilitates a triple carbon benefit for the water sector by avoiding the energy required for conventional biological ammonia oxidation, mitigating the nitrous oxide emissions attributed to biological oxidation, and producing a zero-carbon energy source that can decarbonise energy use. This review has presented established and novel technologies for the recovery and concentration of wastewater, and related the quality of these ammonia products to methods for zero-carbon energy generation by the water sector who urgently seek to migrate to net-zero. Sidestream ammonia recovery represents the most technically mature pathway for ammonia to energy, where the aspiration to be energetically competitive with the Haber-Bosch process could be met with vacuum thermal stripping and without requiring chemical use. The rationalised design for vacuum thermal stripping is impingent on using the ammonia-water vapour-liquid equilibrium for process design to improve the selectivity for separation, and reducing the energy requirements for separation. This should be complemented with innovation around its application to continuous processing in reactor geometries that would enable scale-up. For the separation of ammonia from dilute sources (i.e. raw wastewater), extractive technologies must produce an ammonia solution suitable for concentration via stripping to achieve a fuel quality that is economically and thermodynamically favourable for use. The synergistic relationship between extractive and stripping technologies has

been demonstrated, where the maturation of extractive technologies could substantially broaden the triple carbon benefit ammonia as an energy vector could have for the water sector. While some fuel pre-conditioning may be required for ammonia produce from wastewater to protect downstream energy production assets, this is equivalent to the technology demands for biomethane production which has become a standard approach for the European water sector.

CRediT authorship contribution statement

M.T. Powders: Writing – review & editing, Writing – original draft, Visualization, Investigation, Data curation, Conceptualization. **B.A. Luqmani:** Writing – original draft, Visualization, Investigation, Data curation, Conceptualization. **M. Pidou:** Writing – review & editing, Supervision, Conceptualization. **M. Zhu:** Writing – review & editing, Supervision, Conceptualization. **E.J. McAdam:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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The use of ammonia recovered from wastewater as a zero-carbon energy vector to decarbonise heat, power and transport – a review

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