Mainstream Ammonium Recovery to Advance Sustainable Urban Wastewater Management

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ABSTRACT: Throughout the 20th century, the prevailing approach toward nitrogen management in municipal wastewater treatment was to remove ammonium by transforming it into dinitrogen (N_2) using biological processes such as conventional activated sludge. While this has been a very successful strategy for safeguarding human health and protecting aquatic ecosystems, the conversion of ammonium into its elemental form is incompatible with the developing circular economy of the 21st century. Equally important, the activated sludge process and other emerging ammonium removal pathways have several environmental and technological limitations. Here, we assess that the theoretical energy embedded in ammonium in domestic wastewater represents roughly 38−48% of the embedded chemical energy available in the whole of the discharged bodily waste. The current routes for ammonium removal not only neglect the energy embedded in ammonium, but they can also produce N_2O, a very strong greenhouse gas, with such emissions comprising the equivalent of 14−26% of the overall carbon footprint of wastewater treatment plants. N_2O emissions often exceed the carbon emissions related to the electricity consumption for the process requirements of WWTPs. Considering these limitations, there is a need to develop alternative ammonium management approaches that center around recovery of ammonium from domestic wastewater rather than deal with its "destruction" into elemental dinitrogen. Current ammonium recovery techniques are applicable only at orders of magnitude above domestic wastewater strength, and so new techniques based on physicochemical adsorption are of particular interest. A new pathway is proposed that allows for mainstream ammonium recovery from wastewater based on physicochemical adsorption through development of polymer-based adsorbents. Provided adequate adsorbents corresponding to characteristics outlined in this paper are designed and brought to industrial production, this adsorption-based approach opens perspectives for mainstream continuous adsorption coupled with side-stream recovery of ammonium with minimal chemical requirements. This proposed pathway can bring forward an effective resource-oriented approach to upgrade the fate of ammonium in urban water management without generating hidden externalized environmental costs.
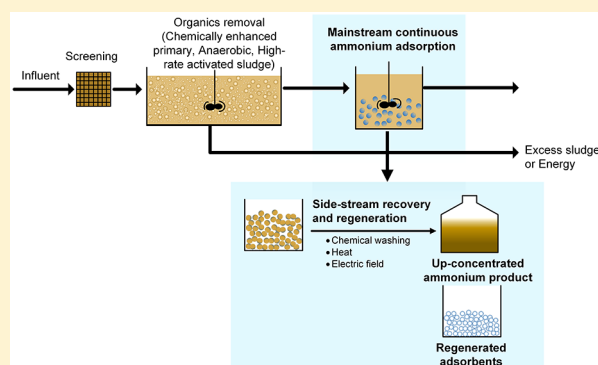
1. INTRODUCTION

Throughout history, the first and foremost role of urban water management has been to protect the environment and public health. To achieve this, management and engineering practice always had a strong focus on treating water by removing pollutants. Arguably the most well-known and widespread approach is the conventional activated sludge process. Since the introduction of the activated sludge process in 1914, it has had a major positive impact on our society and the environment in the 20th century.[1,2] One essential component and the process-limiting step of the activated sludge process in treating domestic wastewater is the conversion of reactive nitrogen (such as NH_4^+, NO_3^-, NO_2^-) into atmospheric nitrogen (N_2) through biological oxidation (i.e., nitrification) and reduction (i.e., denitrification) processes. Ammonium is an essential nutrient for agricultural production and for sustaining terrestrial and aquatic ecosystem functions, and most man-
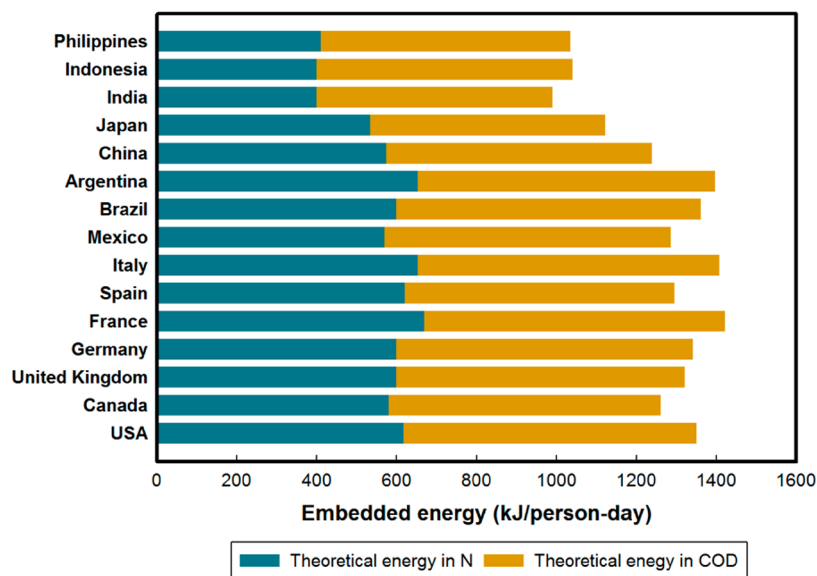
Figure 1. Theoretical energy embedded in one person's excreta as ammonium (blue bar) and organic carbon (yellow bar) for 15 representative countries per region. The total bar represents the maximum of energy that can be recovered. Data presented are 50th percentile values obtained from Trimmer et al.[37]

made reactive nitrogen entering our biosphere in the form of ammonium is produced by means of the Haber-Bosch process.[3−5] The Haber-Bosch production process, while highly optimized in terms of cost-effectiveness and maximum achievable energy efficiency with power consumptions approaching thermodynamic limits, is still energy intensive, with a typical energy usage of 12.1 kWh per kg NH_3-N.[3,6,7]

Ultimately, a substantial fraction of ammonium entering our biosphere ends up in domestic wastewater.[8] At present, domestic wastewater annually comprises some 20 million tons of ammonium, which is equivalent to ~19% of the annual ammonium production from the Haber-Bosch process.[8] Importantly, it is projected that the amount of ammonium that ends up in domestic wastewater will further increase to 35 million tons annually by 2050.[8]

While the introduction of the activated sludge process[9] is often regarded as one of the greatest engineering achievements of the 20th century, the underlying ammonium removal pathway will most likely not be considered sufficiently sustainable in the 21st century. A circular economy is developing where resources are recovered, not removed, as a means to create a more sustainable society.[10,11] Many water utilities and governments have set forward goals, with ambitions toward the circular use of resources being firmly anchored into national and international policies. Resource recovery from used water has gained significant interest not only in the academic world but also the water industry more generally and policy makers globally. A key challenge in the coming decades is how to re-envision the role of urban water management within the circular economy to become a more proactive economic force through the recovery of resources embedded in urban water. Due to the typically low ammonium concentrations in sewage and thus the inherent challenge of retrieving ammonium economically, current research efforts are still predominantly focused on more efficient ammonium removal, with, to the authors' best knowledge, only limited research efforts focusing on mainstream recovery of ammonium from domestic wastewater.

In this paper, the environmental and technological implications of ammonium removal approaches in our urban water infrastructure are assessed, followed by a critical review of the existing ammonium recovery methods and their limitations, and last an overview of the drivers behind the need to re-engineer the fate of ammonium in our urban water infrastructure. We will discuss how mainstream ammonium recovery from domestic wastewater can be achieved via adsorption oriented approaches. The technological and economic opportunities and challenges as well as the urgency to invest in novel approaches based around the development of next generation adsorbents are indicated.

2. THE LIMITATIONS OF AMMONIUM REMOVAL IN URBAN WATER MANAGEMENT

2.1. The Technological Limitations of Ammonium Removal. Recent alternative technologies to the conventional activated sludge process mainly aim to decrease energy demand by short-circuiting of the nitrification-denitrification pathway[12−17] through removal of organic carbon, followed by mainstream partial nitritation, and anaerobic ammonium oxidation (anammox).[15−17] The autotrophic nature of partial nitritation-anammox[18,19] requires that organic carbon and other reducing agents be removed prior to the process, generally through low-rate anaerobic treatment, A-stage biological treatment, or chemically enhanced primary treatment.[20−22] The process also requires less than half as much oxygen in comparison with the conventional nitrification−denitrification process[23,24] and produces less excess sludge, potentially lowering operational costs of ammonium removal by up to 90%.[17,25] Considering the above, the mainstream anammox approach is regarded as an important step forward for wastewater utilities, heading toward more sustainable urban water management.[16,26−28] However, the underlying principle (i.e., conversion of ammonium to nitrogen gas) remains unchanged. In addition, maintaining high and stable ammonium removal efficiencies is a challenge. Selective biomass retention is required to sustain sufficiently high anammox activity, especially at low temperatures.[24,29] This is

especially of concern for moderate climates such as parts of Europe and the United States, where it is not uncommon for sewage temperature to drop as low as 8 °C during the colder months of the year. In addition, partial nitritation−anammox systems are operationally difficult given that nitrite oxidizing bacteria (NOB) have to be eliminated without compromising the activity of aerobic ammonia oxidizers (AOB) and anammox bacteria. Selectively inhibiting NOB is complex given that a combination of selection pressure is likely required (e.g., solid retention time (SRT), dissolved oxygen set points and/or the use of free nitrous acid or free ammonia)[30−32] and is moreover system specific.[33] Therefore, despite significant research efforts, full-scale implementation of anammox has so far been mainly restricted to side-stream treatment of digestate and industrial wastewater streams with high ammonium concentrations and mesophilic temperatures.[23,28,34] Moreover, the nitritation−anammox system can give rise to considerable emission of N_2O.[35]

2.2. The Dissipation of the Energy Embedded in Reactive Nitrogen in the Form of Ammonium.

The energy requirements of the Haber-Bosch currently ranges between ~9.1 kWh (32.8 MJ) (best available technology) to 14.2 kWh (51.3 MJ) (current practice in China) per kg NH_3–N,[6] with a global average energy usage for the Haber-Bosch process of 12.1 kWh (43.7 MJ) per kg NH_3–N.[6] Adults are generally at steady-state in terms of total mass of nitrogen, with essentially all ingested nitrogen being excreted in urine and feces as ammonium.[36] Thus, ammonium excretion rates depend on diet.[37] Using the median ammonium content in one person's excreta of 8.2–13.8 g per person-day of 15 representative countries[37] (countries listed in Figure 1) along with the global average energy usage of nitrogen fixation via Haber-Bosch process (12.1 kWh per kg NH_3–N), the theoretical energy embedded in ammonium equals 0.11–0.19 kWh (399−670 kJ) per person-day (see Figure 1).

By comparison, the human body is quite effective in metabolizing organic carbon (only 2−10% of calories entering the body leave in excreta).[22,37,38] Based on caloric intake and utilization, the median energetic content in one person's excreted carbon is 0.16−0.21 kWh (588−761 kJ; across the same 15 countries) per person-day.[37] Ultimately, this means that ammonium represents roughly 38−48% of the embedded chemical energy available in discharged bodily waste (ammonium plus organic carbon). When considering what resource recovery processes would be implemented, this percentage may increase if the majority of ammonium can be recovered (e.g., a realistic energy recovery from organic carbon of 59% can be reached in the form of biomethane.[37]) The energetic content in ammonium is not just embedded energy, but also recoverable energy. If the ammonium were recovered in gaseous form as ammonia (NH_3), and subsequently burnt on-site in a CHP or fuel cell system, this energy 22 MJ/kg NH_3[39] is fully realizable.

In addition to the embedded energy lost by not recovering ammonium, the conventional nitrification−denitrification process is energy intensive, typically requiring about ~2.6−6.2 kWh/kg N.[40] Equally important, denitrification requires additional organic carbon. Considering the theoretical stoichiometric chemical oxygen demand of 2.86 kg COD per kg NO_3–N removed and assuming an energy content in the COD itself of 13.9 MJ/kg COD,[41,42] ~39.75 MJ/kg N is lost during denitrification which is equivalent to 91% of the energy to produce ammonium using the Haber-Bosch process (43.7

MJ/kg NH_3–N).[6] The supposed energy losses from denitrification can be avoided when mainstream anammox is implemented due to its autotrophic nature; however, it would still require electricity to match the oxygen requirements of the process. Considering the (i) energy requirements of the Haber-Bosch process to produce ammonium from elemental nitrogen (N_2), (ii) the electricity needed for the oxygen requirements for biological ammonium removal, and (iii) the energy embedded in COD consumed during denitrification, it is evident that a key feature for water utilities in realizing an overall lower energy footprint of their WWTPs would be to achieve energy-efficient recovery of ammonium from the mainstream.

2.3. The Environmental Limitations of Ammonium Removal.

In addition to the substantial amount of energy embedded in ammonium that is lost when it is biologically converted to N_2, there is another major disadvantage, namely the generation of nitrous oxide (N_2O). N_2O is a potent greenhouse gas (GHG) with a 300-fold stronger greenhouse effect than CO_2 (for a 100 year time horizon), and is also one of the most dominant ozone depleting substances.[43] Sewage treatment was estimated to emit 0.22 Tg N_2O–N year^{-1} in 1990, accounting for approximately 3.2% of the global anthropogenic N_2O emissions.[44] N_2O is a byproduct formed during nitrification produced by ammonium oxidizing bacteria (AOB) through incomplete oxidation of hydroxylamine (NH_2OH) or through nitrification−denitrification and it is a necessary intermediate during denitrification.[45−48] Intermediates such as NH_2OH and nitric oxide (NO) produced by AOB can also lead to abiotic N_2O production especially under low pH conditions.[49] Given the complexity of N_2O production mechanisms, N_2O emissions can vary significantly between biological nutrient removal (BNR) systems of different configuration and operating parameters.[50]

As seen in Figure 2, N_2O emissions from full-scale activated sludge treatment installations were found to vary between 0.01% up to 6.6% of the total ammonium removed (see
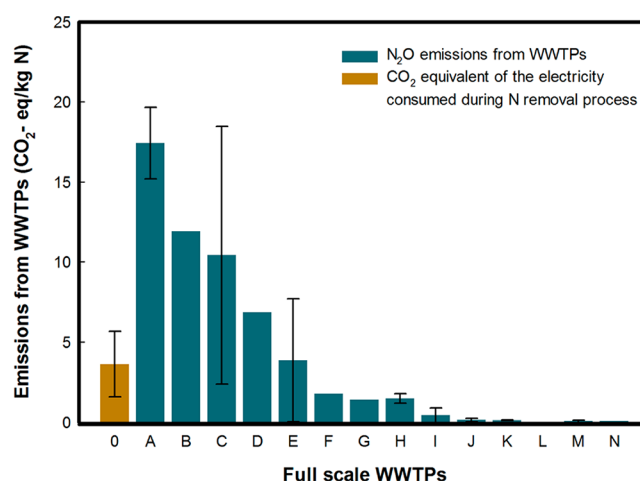
Figure 2. Comparison of carbon emissions (expressed as kg CO_2-equivalents per kg ammonium removed) as a result of electricity consumption for the process requirements in nitrification−denitrification (e.g., aeration, pumping, mixing) and nitrous oxide emissions from several full scale wastewater treatment plants. WWTPs are described in SI Table S1. Electricity consumption and N_2O emissions are expressed as kg CO_2-equivalents per kg N. All error bars represent minimum and maximum values.

Supporting Information (SI) Table S1). While these values seem less significant, N_2O emissions from domestic wastewater treatment is estimated to contribute about 14−26% of the total GHG emissions of the overall urban water infrastructure,[45,51] and up to 83% of the operational CO_2 footprint of BNR plants.[52,53] Intensive and tailored onsite measurement protocols are generally required to obtain accurate quantification.[50] Using a tracer gas dispersion method to measure whole-plant N_2O emissions, a recent study revealed that the contribution of wastewater treatment to global N_2O emissions has been underestimated.[54] GHG emissions were estimated to contribute from 44% to 71% of the carbon footprint of Scandinavian wastewater treatment plants, compared to 2−28% for electricity consumption.[55] Therefore, significant decrease in N_2O emissions will be required to achieve carbon-neutral wastewater treatment.

If nitrogen can be directly recovered in its reactive form (i.e., as ammonium), N_2O emissions can be prevented entirely, thereby substantially lowering the global warming potential (GWP) of WWTP operation. In a recent life cycle assessment, Lin et al.[56] found that recovering ammonium from domestic wastewater from the mainstream would result in the lowest environmental impact among different treatment schemes assessed including mainstream partial nitritation−anammox and the activated sludge process. Finally, in recent years, the scale of the externalities of N_2O emissions have become apparent with costs as high as 0.26−18 € per kg N_2O−N emitted (see SI Table S2). These externalities are burdens associated with the consequences of N_2O emissions for society which are not reflected in the price of fossil fuels such as health concerns, increased food security, and ecosystem destruction.[57,58] Although these studies clearly show that the environmental externalities of N_2O are significant, these externalities are not yet formally taken into account in decision-making processes and regulatory guidelines. Figure 2.

3. CURRENT TECHNOLOGIES FOR AMMONIUM RECOVERY FROM WASTEWATER

So far, we have highlighted the environmental and technological limitations of ammonium removal in our urban water infrastructure and the need to recover it. In general, the recovery of ammonium from wastewater streams is not new. In the past decades, several approaches to recover ammonium from wastewater have been proposed, as summarized in Table 1. We would like to refer to some excellent reviews in which the various established and emerging methods are discussed in detail.[59−62]

The only technique that is commonly implemented by the wastewater industry is volatilization (air or inert gas stripping) followed, normally, by recovery as ammonium sulfate. This is only really practically feasible at high concentrations above 2−3 g/L NH_4−N, and is generally not economically viable except where energy for temperature elevation is free (often with the digester being at 55 °C). Ammonia can be effectively precipitated as struvite (other ammonium precipitates have very high solubilities), but struvite is only 6% ammonium, and is practically used to recover phosphates instead. Reverse osmosis, electrodialysis, and other electrochemical processes rely on ammonium being the dominant cation, and will generally concentrate other cations also (particularly monovalents).[63] All of these methods have been demonstrated on streams with high ammonium concentrations (>2 g/L NH_4−N) such as digestate, source separated urine, and a limited range of industrial wastewater streams as shown in Table 1.[64] The only ammonium recovery techniques (apart from adsorption) that have shown feasibility at low concentrations of 40−60 mg/L NH_4−N are assimilative uptake in microbial cells, which recovers biomass, not ammonium, and reverse osmosis, which is nonselective toward ammonium, and requires substantial pretreatment.

Furthermore, as shown in SI Table S3, ammonium removal and recovery approaches from various wastewater streams have a substantial cost. Note that the cost estimates of these methods should be regarded as indicative only and should not be compared since they comprise different wastewater streams with highly fluctuating flows and ammonium concentration, both of which affect the practical feasibility and treatment costs. Considering that in practice it has been found that the user is willing to pay for recovered NH_4−N with only a value of some 20% of Haber-Bosch nitrogen, the latter having a market price of some 0.4−0.7 € per kg NH_4−N, it is evident that the economic potential of ammonium recovery approaches are not determined by the profit of the recovered ammonium, but by the treatment costs and performance (i.e., the costs to recover the ammonium cannot exceed that of the costs for ammonium removal). From SI Table S3, it is evident that in most cases the route of ammonium recovery is generally not economically attractive. To be cost-effective, existing recovery methods typically require concentrations above >2−3 g/L NH_4−N,[65−67] which is well above the dilute concentration of ammonium in domestic wastewater (40−60 mg/L NH_4−N).[68] Hence, we argue that the key technological challenge for ammonium recovery from domestic wastewater is mainly related to the up-concentration of ammonium to more than 2−3 g/L NH_4−N,[69] at which point the aforementioned technologies for ammonium recovery become cost-effective.[61]

3.1. Conventional Adsorptive Approaches. Among physicochemical techniques, adsorption-based processes have the potential to address the limitations of existing ammonium recovery methods. A key advantage lays in the fact that the process is suitable for and effective in removing ammonium at low initial concentrations.[77−82] In fact, since the 1970s, the feasibility of ammonium adsorption from domestic wastewater using zeolites has already been demonstrated in both lab- and pilot-scale studies, achieving excellent results in terms of ammonium removal (>98%) with effluent ammonium concentrations below 1 mg/L NH_4−N.[69,83,84] Other advantages of adsorption include, (i) it is a relatively simple and fast process that does not require any start up time (i.e., plug and play), (ii) it does not generate sludge,[85] (iii) some adsorbents are known to have high affinity and selectivity for ammonium,[77] (iv) high up-concentration factors can be achieved, thereby harvesting the ammonium from the mainstream into a (very) small side-stream suitable for subsequent recovery of ammonium using state-of-the art methods, and (v) fast adsorption kinetics that are independent of the wastewater temperature (within the typically observed range for domestic wastewater, 8−35 °C).[82] The latter makes adsorption especially attractive for colder climates.

In the past, significant research efforts have focused on the use of low cost adsorbents, with natural zeolites being arguably the most commonly explored material as reviewed elsewhere.[77,78,81,86] Natural zeolites are aluminum silicate materials that have high ion exchange properties for various wastewater ions.[78,79] The primary building block of zeolite is the aluminosilicate framework where the exchangeable cations

Table 1. Summary of Established and Emerging Approaches for Ammonium Recovery from Wastewater

technology	description	challenges	outlet concentration (mg/L NH_4-N)	ref
air stripping	caustic and heat is added to the wastewater to keep the pH within 10.8–11.5 in order to convert ammonium ions to free ammonia (NH_3); wastewater is pumped from the top of the column as the ammonia is stripped from the falling water by a counter current air-stream	• fouling of stripping towers • high chemical demands for raising the pH of the wastewater during stripping and for pH reduction after stripping • stripping at high pH is achievable but economically prohibitive due to the low NH_4^+ concentrations in sewage	500–1000	65
liquid–liquid membrane	reverse osmosis (RO) technology recovers all salts including ammonium	• RO is more selective for other salts than ammonium (pH dependent) • produces dilute concentrate stream, only concentrating max 1 order of magnitude • membrane fouling and chemical stability still remain unaddressed • high energy consumption	1	70
liquid–gas membrane	pervaporation membranes can recover ammonia gas to either an inert sweep gas or vacuum	• ammonia gas is excessively soluble meaning that pH or temperature elevation is still required • high energy consumption, particularly where vacuum is used	1000	71,72
electrochemical	ammonium is migrated to a central compartment or the cathode compartment in an electrochemical cell (via cation exchange membrane); rare earth electrodes are typically used to drive electrolysis in terminal reactions. Can be combined with pervaporation	• high power consumption • only viable where electrolytic byproducts have value • high capital costs due to ion selective membranes and electrodes	1000	71
bioelectro-chemical systems (BES)	similar to electrochemical, except that organic matter is biologically oxidized at the anode, while ammonium ions are transported over a cation exchange membrane to the cathode chamber, allowing for ammonium recovery	• there has been an enormous focus on BES in the past decade, but with limited success in development of BES approaches suitable for practical implementation for diluted and larger flows	1000	73,74
electrodialysis	ammonium (and other ions) are migrated to concentrate via a series of cathode and anode selective membranes with many cell pairs between electrodes; electrolytic terminal reactions. Can potentially achieve economical ammonium recovery at power consumptions of around 5 kWh/kg NH_4-N	• high selectivity toward monovalent ions which produces salty concentrate (Na^+, K^+, Cl^-) • phosphorus must be removed (as struvite) for scaling control • only relatively dilute streams (~1% NH_4-N) can be recovered	100	63
struvite precipitation	formation of ammonium containing precipitate struvite ($MgNH_4PO_4 \cdot 6H_2O$) through addition of magnesium and hydroxides	• very low ammonium concentration in product (max 6% dry weight) • needs phosphate to proceed • many competitors for phosphate (calcium, magnesium phosphates) • not a practical option for ammonium recovery	100	75
biological assimilation	growth of heterotrophic or photosynthetic (or phototrophic) algae or bacteria	• heterotrophic requires energy and high COD:N ratios	Het ~1–5	76

Table 1. continued

technology	description	challenges	outlet concentration (mg/L NH$_4$–N)	ref
		• phototrophic requires large land area and expensive process • produces biomass, not ammonium, not readily usable • only operates at low input/output concentrations	Photo <0.1	
ion exchange and adsorption	adsorption and ion exchange are often grouped together as a "sorption" process; adsorption involves the accumulation of target molecules from a gas or liquid to a surface while ion exchange, true to its name, involves a reversible replacement of ions of the same charge that is initially in the solid; one of the most promising physicochemical methods for removal and recovery for diluted streams	• commonly used adsorbents for wastewater applications such as activated carbon are not suited for ammonium recovery due to their nonselectivity and energy-intensive regeneration (500–900 °C) • zeolites for ammonium recovery has been extensively studied for several decades but have not found widespread implementation, which are discussed in detail in the next section	1	77–82

are attached and are readily available for ion exchange with an external medium.[78] Owing to their ion exchange properties, zeolites have been widely used for environmental cleanup processes such as removal of ammonium, heavy metals, and other contaminants (e.g., dyes and inorganic anions) from wastewater.[77−79,81,86] Zeolites have a high affinity for ammonium ions with typical ion exchange capacities of 2.7−53.9 mg/g,[78,87] depending on the initial ammonium concentrations and presence of competing cations.

Despite its low cost, widespread availability on the market, and effectiveness in terms of removing ammonium to very low levels, the use of (natural) zeolite for treatment of domestic wastewater came with some serious drawbacks that hindered the adoption of zeolite (and zeolite-like materials) as a full-scale technology. First, in terms of operation, the characteristic granular, sand-like structure of zeolites requires operation of adsorption in conventional packed-bed columns, thereby normally needing periodic backwashing to remove accumulated solids.[83] Packed-bed columns are, therefore, not suitable for continuous operation and difficult to retro-fit within existing WWTPs. It should, however, be emphasized that operating in a plug-flow configuration has an important advantage in terms of the retention of a large concentration gradient, thereby increasing the ammonium adsorption efficiency. Second, the mode of operation of packed-bed columns implies that the zeolite is almost continuously exposed to the sewage, despite the fact that the ammonium adsorption process only requires a very short contact time (i.e., 5−30 min). Consequently, the zeolite is more susceptible to biofouling resulting in a strong drop in adsorption capacity over time.[88,89] This can potentially be mitigated by increasing the frequency of regeneration or by applying chemical washing strategies similar to membrane fouling, but this further lowers the practical and economic feasibility and comes with chemical usage costs. Third, the high chemical requirements for regeneration was also considered a major drawback. Typically, salt is used for regeneration. Since ion exchange is the predominant adsorption mechanism for zeolites, this implies that equimolar amounts of Na$^+$ are required to displace the NH$_4^+$ attached to the zeolites.[78,90] Thus, the theoretical salt demand (as NaCl) for every ton of ammonium removed equals to 4.17 tons NaCl per ton of NH$_4$–N. In practice, considering a WWTP with a capacity of 250 000 persons equivalent (PE) and average NH$_4$–N loads of 8.8−13.8 g per person-day,[37] and assuming 80% adsorption of the incoming NH$_4$–N, it would require 7.33−11.5 tons per day of NaCl to displace the adsorbed NH$_4$–N (assuming an efficiency of 100%). While, in theory, seawater can be used as a cheap alternative to purchased salt, this would only be cost-effective at a proximate distance from the seawater source. Furthermore, scaling and fouling are serious concerns due to the universal presence of divalent cations like calcium and magnesium in seawater, besides particles and organics.

Technically, to potentially address some of these issues, zeolites can be modified through a number of ways such as (a) preconditioning with NaCl to improve the ion exchange capacity and efficiency,[91] (b) incorporation of magnetic particles for added adsorption sites and magnetic properties,[92] (c) surfactant coating for surface modifications,[93] and (d) synthesis of zeolites with controlled pore and particle size distribution.[94] To decrease the salt requirements, new strategies have been developed to recover and reuse the spent regenerant from ion exchange processes.[95−97]

Table 2. Overview of Ammonium Adsorption Performance of Zeolites and Polymer-Based Adsorbents[a]

adsorbent	influent	concentration range (mg/L NH$_4$−N)	contact time	adsorption capacity (mg/g NH$_4$−N)	ref
Gordes clinoptilolite	landfill leachate	100−1000	3 h	16.32	117
Natural Western Azerbaijan zeolite	synthetic NH$_4$Cl solution	10−200	45 min	43.47	118
Chinese zeolite	rainfall runoff	20−49	5−600 min	12.60	119
NaCl modified clinoptilolite	municipal secondary effluent	50		11.44	120
NaOH modified mordenite	fish pond water	10	24 h	53.91	87
microwave-treated zeolite	synthetic NH$_4$Cl solution	0−200	4 h	23.83	121
poly(acrylic acid)/ biotite	synthetic NH$_4$Cl solution	100	15 min	32.87	122
chitosan-g-poly(acrylic acid)/rectorite	lake water	100	30 min	34.26	123
poly(vinyl acohol)/poly(acrylic acid)/tourmaline	synthetic NH$_4$Cl solution	13−130	30 min	42.74	124
chitosan-g-poly(acrylic acid)/unexpanded vermiculite	synthetic NH$_4$Cl solution	100	30 min	21.7	125
poly(dimethyl diallyl ammonium chloride)/poly(arylic acid)/starch	synthetic NH$_4$Cl solution	50	10 min	33.98	126
carboxymethyl chitosan-g-poly(acrylic acid)/ palygorskite	synthetic NH$_4$Cl solution	100	12 min	237.6	127
amphoteric straw cellulose derived from wheat straw	synthetic NH$_4$Cl solution	50−200	30 min	68.4	128
commercial poly(acrylic acid)	raw sewage	50−180	10−30 min	8.8−32.2	129

[a]Please refer to Huang et al.,[116] and Wang et al.[78] for a comprehensive summary of zeolite adsorption studies.

Despite their disadvantages, the fact that ammonium can be removed from dilute streams with low initial ammonium concentration in a very rapid and temperature-independent manner means that zeolite-based processes form an excellent basis for the development of novel adsorbents that can be modified to suit mainstream ammonium recovery from domestic wastewater.

4. TOWARD MAINSTREAM AMMONIUM RECOVERY FROM DOMESTIC WASTEWATER THROUGH THE DEVELOPMENT OF TAILORED ADSORBENTS

To suit implementation for domestic wastewater applications, adsorbents need not only high selectivity and excellent ammonium adsorption properties, but also need to be (i) suitable for operation in continuous mode in CSTR type reactors (e.g., carousel type reactors, activated sludge tanks, and sequence batch reactors (SBRs) rather than column type reactors) in order to be retro-fitted in existing WWTP infrastructure, (ii) easy to separate from the wastewater, (iii) resistant against biofouling, (iv) amenable to modification for varying surface chemistry, and (v) efficient and cost-effective with respect to release of the ammonium and regeneration of the adsorbent, without the need for large amounts of chemicals. Considering the above-described required characteristics, polymer-based materials are of special interest. Polymer science and engineering is a field that holds significant potential and has undergone enormous progress in recent years.[98−104] Advancements in polymer science and engineering have greatly increased the sophistication and complex functions of new generation materials, including polymer membranes, biopolymers, composites, conducting materials for energy storage, smart sensors, electronics, and controlled drug delivery systems, as reviewed elsewhere.[105−112]

The use of polymers in wastewater applications is not new. Polymer adsorbents with high surface area and readily exchangeable charged ions, having the same working and operational mechanism as zeolites, are popularly known in the wastewater field as ion exchange resins.[82] In ion exchange, the polymer has a fixed total capacity and merely exchanges ions while conserving charge. On the other hand, adsorbents have an open pore network allowing free diffusion of liquids into the matrix. Hence, the target ions can freely access the functional groups within the interior of the polymer and can bind onto the surface as long as the target ions have an affinity for the functional groups, and the mesh size of the polymer allows the ions inside.[82]

Polymer-based adsorbents can exhibit different behaviors and adsorption mechanisms depending on the chemical nature of the monomer units, method of synthesis, and subsequent modifications. It can consist either of one, two, or more monomer species having different molecular architectures, final form, and functionalities.[113] Depending on the functional groups, polymer adsorbents can also be classified as nonionic, cationic or anionic, which can therefore impart an affinity for target species.[114] Nonionic cross-linked polymers such as poly(ethylene oxide) can serve as size-exclusion media.[115] On the other hand, ionic cross-linked polymers can be used for selective binding of oppositely charged molecules (i.e., cations binding onto anionic polymers) without the need for ion displacement (such as is needed for zeolites and ion exchange resins) to facilitate the binding of target ions.[114]

4.1. Toward High Ammonium Selectivity and Adsorption Capacity.
The potential for polymer-based adsorbents for ammonium recovery is driven by their versatile and tunable molecular properties that can impart a range of adsorbent properties such as physical rigidity and/or flexibility, stimulus response (e.g., to pH, temperature, electric field), and affinity to or rejection of specific molecules depending on the selected monomer and synthesis modifications.[110,111,130−136] For ammonium recovery applications, ionic polymers—those

containing acidic pendant groups (e.g., carboxylic acids and sulfonic acids)—can be useful due to their high affinity for oppositely charged molecules such as NH$_4^+$ and amenability for mild acid/base regeneration.

Recent studies with new polymer-based ammonium adsorbents suggest more efficient alternatives to zeolite adsorption as shown in Table 2. For example, initial laboratory studies using polymer-based adsorbents in synthetic wastewater reported rapid ammonium adsorption operating in a wide pH range of 4.0−9.0 with adsorption capacities of 22−86.4 mg/g NH$_4$−N achieved within 30 min.[122−124,126−129,137] In addition, a very recent proof-of-concept using commercial polymer hydrogels, which are polymer materials designed to absorb water, demonstrated rapid ammonium removal from real domestic wastewater coupled with effective regeneration using mild acid washing.[129] The study reported adsorption capacities of 8.8−32.2 mg/g NH$_4$−N depending on the initial ammonium concentration (50−180 mg/L NH$_4$N), bringing down the effluent concentrations from 50 to 16 mg/L NH$_4$−N in under 30 min, with minimal loss of performance after multiple adsorption/desorption cycles. The adsorption performance of these ionic adsorbents were attributed to the attraction of NH$_4^+$ in the charged adsorption sites within the negatively charged −COOH groups in the polymer backbones.[125,127,129] While the findings in Table 2 showed satisfactory performance in terms of ammonium adsorption capacity, a conclusion cannot be drawn by directly comparing the adsorption capacity values from studies that used different hydrogel loading and type of influents. Furthermore, the experiments conducted in these studies are preliminary in nature, only testing the performance of the adsorbents in ammonium chloride and/or synthetic solutions in short-term batch experiments.

In addition, the studies in Table 2 reported a decrease in ammonium adsorption capacity in proportion to the increasing presence of competing ions, especially divalent cations, following an order of preference of Ca^{2+} > Mg^{2+} > K$^+$ > Na$^+$.[125,127,128] The latter is important as these cations are almost universally present in domestic wastewater, and their concentration can differ depending on the source water used for drinking water production, discharge of industrial wastewater into the sewer network and infiltration of seawater in coastal regions.[138] While polymer adsorbents are still effective in adsorbing NH$_4^+$ even at higher counterion concentrations,[127] high selectivity toward NH$_4^+$ is a very important feature in the implementation of adsorption-based ammonium recovery, and one that will require significant research effort. Interestingly, monovalent selectivity has already been widely reported in membrane applications using various methodologies such as (i) sieving of monovalent and divalent ions on the basis of their hydrated size[139,140] and hydration energy;[141] and (ii) introducing a polymer membrane layer containing charged functional groups.[142−144] The latter achieved monovalent selectivity due to the higher electrostatic repulsion between divalent ions and the charged membrane layer, hence achieving a higher rejection of divalent ions than of monovalent ions.[142−144] Such promising approaches, in theory, could also be used to increase the selectivity of polymer adsorbents for ammonium, and as such warrant further exploration.

4.2. Antifouling Capability. Real domestic wastewater contains a wide array of constituents other than NH$_4^+$ and ions that affect adsorption capacity and cause biofouling. This is a widely known issue not only in ion exchange and adsorption processes but also in operations employing membranes. A polymer with low propensity for fouling ideally has the following characteristics: (i) hydrophilicity, thus a resistance to hydrophobic organic foulants; (ii) smooth topography to avoid the clogging of foulants; and (iii) amenability to surface modifications to increase selectivity.[145] Adjustments to the cross-linking density of polymers can also create size-exclusion at a molecular level which increases resistance to fouling by larger molecules and naturally occurring organic constituents.[146−149]

Recent studies have made considerable efforts to develop antifouling membranes for forward osmosis (FO) using polymers with low propensity for organic foulants. The use of hydrophilic cross-linked polymers for surface coatings has been extensively studied as a means to minimize natural organic matter induced fouling during membrane filtration[150,151] as well marine biofouling applications.[152−154] In a recent study, an antifouling hydrogel membrane designed for treating high-strength organic wastewaters exhibited superior antifouling capability against typical organic antifoulants (such as protein, alginate, humic acid, and oil) and could be regenerated by simply flushing the surface with deionized water. The study further highlighted that excellent antifouling capability and maximal separation efficiency can both be achieved by controlling the cross-linking degree of the hydrogel membrane.[151] Taken this into account, the rapid adsorption performance of polymer adsorbents that was demonstrated in preliminary studies (at under 30 min) and the frequency of subsequent adsorbent regeneration can also potentially reduce the degree of biofouling, as discussed in detail in the next section.

4.3. Ease of Fabrication for Continuous Mainstream Operation. Polymer-based adsorbents can be formulated in nearly any form such as granules, powder, films, and beads.[155−157] This is an important feature that will allow for the development of adsorbents that can be used in CSTR type reactors, thereby opening up opportunities to be retro-fitted into existing activated sludge tanks, SBRs, and carousel type wastewater treatment.

Recently, innovative polymer-based adsorbents have seen important applications in water and wastewater treatment. In 2016, a new class of cyclodextrin-based polymers, marketed as "Dexsorb", was reported to selectively and instantaneously adsorb micropollutants in trace concentrations of as low as one part per billion or less, followed by simple methanol washing for regeneration.[158] Moreover, MIEX resins, a new generation of cross-linked acrylic-based magnetic resins designed for the removal of dissolved organic carbon (DOC) in municipal water treatment, have been successfully commercialized and implemented at full-scale.[159,160] This new class of adsorbents offers a unique and innovative approach to treating DOC and other anionic pollutants due to their micro size, macro porous, and magnetic properties which circumvent the need for packed columns, thereby allowing a continuous process in mixed tanks operated at very short HRTs (i.e., 5−30 min).[159,161,162] Alternatively one could also consider packed columns operated in plug-flow similar to that of traditional zeolite columns.[83] However, their associated operational issues such as periodic backwashing and susceptibility to biofouling cannot be ignored. An interesting approach that potentially can overcome some of these issues that warrants further exploration is the use of packed columns that can be operated in continuous mode
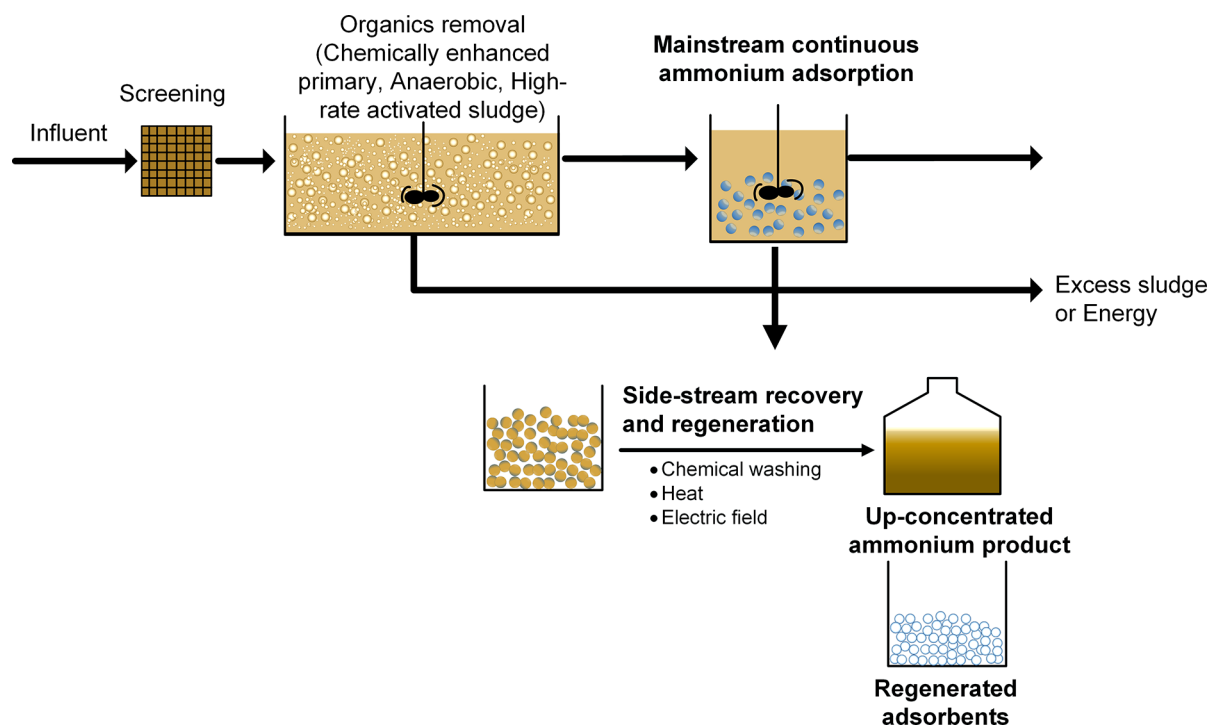
Figure 3. Schematic diagram for mainstream continuous ammonium adsorption followed by side-stream regeneration using polymer adsorbents.

without the need for periodic back-washing, similar to that of continuous sand filtration.[163]

Important challenges in using adsorption-based ammonium recovery strategies are nontarget adsorption and biofouling. This means that adsorption can be preferentially placed after the carbon removal step. As shown in this paper, adsorptive-based ammonium removal processes can effectively treat 40−60 mg/L NH_4−N solutions (relevant to anaerobically treated domestic wastewater),[22] readily achieving discharge limits of 1 mg/L NH_4−N and thus be a drop-in and more effective replacement than mainline anammox, which has typically a limit of approximately 10 mg/L NH_4−N. Final biological polishing can be done if necessary through trickling filters or moving bed bioreactors (MBBR). This results in a schematic as shown in Figure 3.

4.4. Regeneration Ability without Large Chemical Requirements. The next generation ammonium adsorbents need to not only have excellent adsorption properties, but also good regeneration ability for reuse. To ensure their cost-effectiveness, the key is to develop adsorbents that are viable for regeneration that would yield a concentrated ammonium stream and completely desorb the ammonium without affecting the material's structural integrity and adsorption performance over a guaranteed service life.[164]

Available regeneration methods such as mild chemical washing, heat, and electric field are well-demonstrated options for polymer-based materials.[158,165−168] Chemical washing involves displacement of the target ions into the acid/caustic/salt solution and has been the most commonly used method for regenerating adsorbents.[165] This method, however, requires recoverability of the regenerant chemicals to be cost-effective. Regeneration of polymer adsorbents using methanol was recently demonstrated by washing the adsorbents using methanol.[158] The adsorbed products can be separated from the methanol solution by heating at 65 °C (boiling point of methanol), followed by distillation to recover the methanol.

Thermal regeneration of polymer-based materials is also an interesting option. Depending on the binding strength of NH_4^+ ions onto the functional groups in the polymer, the removal of NH_4^+ ions can be initiated by heat through the thermal decomposition of NH_4^+ into NH_3.[169] In particular, the fact that heat can be used for regeneration purposes offers opportunities to beneficially reuse low value heat released during electricity generation using combined heat power (CHP) systems at WWTPs that implement anaerobic digestion. Given careful research, cost-effective regeneration methods that do not rely heavily on chemical dosing could likely be developed for ammonium adsorbents for WWTP applications, provided that the structural integrity of the polymer remains intact after multiple regeneration cycles. This is a major concern that needs to be taken into consideration during material development. Lastly, electrochemical regeneration involves desorption of spent adsorbents using an electrolytic cell. Various studies have demonstrated that this technique using carbon-based adsorbents,[168,170,171] can achieve up to near complete regeneration efficiencies with minimal loss in adsorbent capacity after multiple regeneration cycles.[168] A similar approach was conducted with polymer hydrogels, materials that absorb water, wherein 80% of the absorbed water was released by applying 5 V electric field.[167]

5. CONCLUDING REMARKS

In order to find a long-term sustainable solution for the anthropogenic nitrogen cycle, it is evident that we need to reduce our dependence on the energy-intensive Haber-Bosch process for the production of ammonium using natural gas. In the coming years, population growth and urbanization are driving the realization of thousands of new WWTP's in emerging economies. In accordance to UN Sustainable Development Goals (SDG) Target 6.2 that endeavors to achieve "adequate and equitable sanitation and hygiene for all and end open defecation" by 2030,[172] an estimated 1000−

15 000 new WWTP's are going to be constructed in the coming years.

In addition, many wastewater utilities in more developed countries are nearing their end-of-life in the next 10−15 years, which will require very large capital investments.[173] For example, many WWTPs in Europe were built in the 1970−1990 era, implying that their technical and economic lifetime will end from 2020 onward. Moreover, in Europe, many wastewater facilities[174] still need to comply with the EU treatment directives and are required to be upgraded to achieve sufficient nutrient removal. This offers opportunities for transitioning to more sustainable technologies for newly built WWTPs as well as for retro-fitting of existing WWTPs that require upgrading into resource recovery facilities. While the above highlights the opportunities for uptake of ammonium recovery approaches, more importantly, it highlights the importance and urgency to start investing in research that will deliver efficient and cost-effective recovery of ammonium from domestic wastewater. In this paper, we have highlighted physicochemical adsorption techniques, through development of next generation adsorbents, which warrant further exploration as effective alternatives to emerging biological ammonium removal methods such as mainstream anammox. In order for these approaches to become attractive and viable alternatives, a crucial factor will be the development of processes that, from a technological point of view, are more robust and reliable than current practice or other emerging ammonium dissipative technologies. Furthermore, from an economic point of view, due to the widespread availability and low cost of Haber-Bosch nitrogen and the perceived low market value of recovered ammonium, the processes need to be competitive with current and emerging treatment methods without relying on the potential market value of the recovered ammonium.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b00603.

> Nitrous oxide emissions reported for several full-scale wastewater treatment plants (Table S1); Environmental externalities of reactive nitrogen (Table S2); and Typical costs for nitrogen production, dissipation, and recovery processes that have been implemented at full-scale (Table S3) (PDF)

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Notes

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