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Membrane-based Processes for Wastewater Nutrient Recovery: Technology, Challenges, and Future Direction

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ABSTRACT

Wastewater nutrient recovery holds promise for more sustainable water and agricultural industries. We critically review three emerging membrane processes – forward osmosis (FO), membrane distillation (MD) and electrodialysis (ED) – that can advance wastewater nutrient recovery. Challenges associated with wastewater nutrient recovery were identified. The advantages and challenges of applying FO, MD, and ED technologies to wastewater nutrient recovery are discussed, and directions for future research and development are identified. Emphasis is given to exploration of the unique mass transfer properties of these membrane processes in the context of wastewater nutrient recovery. We highlight that hybridising these membrane processes with existing nutrient precipitation process will lead to better management of and more diverse pathways for near complete nutrient recovery in wastewater treatment facilities.

1. Introduction

We face a major grand challenge in the twenty-first century: sustainably meeting food demands while simultaneously reducing agriculture's environmental harm (Foley et al. 2011, West et al. 2014). This challenge is being exemplified as an annual increase of 4% in fertiliser demand to feed additional 2.3 billion people by 2050, thereby requiring a sustained supply of fertilisers (Elser and Bennett 2011).

Current fertiliser production heavily relies on the consumption of non-renewable energy and finite mineral resources. For example, the generation of ammonia from air in the Haber-Bosch process requires 35-50 MJ per kg nitrogen in the form of fossil fuel for energy supply (Desloover et al. 2012), which accounts for 2% of the world energy use. Phosphorus mining leads to a huge amount of gypsum by-products that are contaminated with heavy metals and radioactive elements (Ashley et al. 2011). More alarming, the forecasted phosphorus production peak is approaching in 2030, with an accelerated depletion of minable phosphorus rock (Elser and Bennett 2011).

The use of fertiliser to meet food demand also carries a heavy burden for wastewater treatment processes. Once through production and application of fertilisers results in major nutrients (nitrogen and phosphorus) being primarily found in wastewater. It is estimated that 30% of nitrogen and 16% of phosphorus in fertilisers ends up in wastewater (Rahman et al. 2014, Verstraete et al. 2009). Consequently, wastewater treatment facilities consume up to 4% electrical energy in the United States (Energy 2006, EPA and Water 2006), more than 77% of which is used for activated sludge aeration for nitrification (McCarty et al. 2011, Svardal and Kroiss 2011). The removal of nitrogen from wastewater requires substantial energy, 45 MJ per kg nitrogen, only to release it back as gaseous nitrogen into the atmosphere. This energy-intense nutrient removal also contributes to greenhouse gas emission of 0.9 kg CO_2 per cubic litre of treated wastewater (Hall et al. 2011, Rothausen and Conway 2011). The large energy and environmental footprint of nutrient removal from wastewater, in turn, aggravates the sustainability of fertiliser production for food security. As a result, wastewater nutrient recovery is anticipated to become a promising strategy to sustain fertiliser and food production, and at the same time, potentially bring benefits to wastewater treatment facilities (Grant et al. 2012, Guest et al. 2009, Verstraete et al. 2009).

High-rejection membrane processes, such as nanofiltration (NF) and reverse osmosis (RO), have demonstrated huge potential in wastewater nutrient recovery. For example, RO was applied for urine concentration in a source-separation toilet system, achieving a concentration factor of five and high rejection of ammonium, phosphate and potassium (Maurer et al. 2006). NF separation also exhibited medium to high rejection of a range of nutrients, such as urea (Pronk et al. 2006b), ammonium, phosphate and potassium (Blöcher et al. 2012, Niewersch et al. 2014). Despite the potential of NF and RO processes in wastewater nutrient recovery, current pressure-driven membrane processes are not without limitations. NF and RO processes are prone to membrane fouling in wastewater nutrient recovery where the feed streams are challenging and difficult to treat, such as urine and digested sludge. Fouling of NF and RO membranes impairs membrane performance and shortens membrane lifetime, thereby restraining productivity in nutrient recovery. Hence, there is a critical need for robust separation processes for nutrient recovery from challenging wastewater streams.

We critically review membrane processes that enable the reclamation of nutrients from wastewater and illustrate the challenges for membrane processes in wastewater nutrient recovery. Emerging membrane processes — forward osmosis (FO), membrane distillation (MD), and electrodialysis (ED) — are discussed and evaluated based on their applications, nutrient recovery potential, and process limitations. Unique challenges associated with the agricultural application of recovered nutrients are also elucidated.

2. Existing technology illustrates challenges for wastewater nutrient recovery

Struvite ($MgNH_4PO_4{\cdot}6H_2O$) precipitation is widely accepted as the most promising technology in wastewater nutrient recovery (de-Bashan and Bashan 2004). Struvite is a slow-release fertiliser, applicable to crops in soils with relatively low pH value. In the process of nutrient recovery via struvite precipitation, an alkaline solution is obtained either by addition of basic solution or aeration stripping of CO_2, and followed by the introduction of magnesium salts for struvite precipitation. Previous studies have demonstrated nutrient recovery via struvite precipitation from various nutrient-rich streams, such as wastewater (Gerardo et al. 2013, Ichihashi and Hirooka 2012), anaerobically digested sludge (Battistoni et al. 2005, Lahav et al. 2013, Marti et al. 2008, Pastor et al. 2010, Quintana et al. 2003), and urine (Ronteltap et al. 2010, Triger et al. 2012). Despite the struvite precipitation reaching commercial implementation for nutrient recovery, there remains two critical challenges in wastewater nutrient recovery via struvite precipitation.

The efficiency of nutrient recovery via struvite precipitation is limited by the phosphorus concentration in wastewater. The driving force and kinetics for struvite precipitation are significantly influenced by the phosphorus concentration. Extensive experimental results showed that effective struvite precipitation could only be achieved when the phosphorus concentration was above 100 mg/L (Figure 1A) (Çelen et al. 2007, Guadie et al. 2014, Jaffer et al. 2002, Liu et al. 2011, Münch and Barr 2001, Pastor et al. 2008, Pastor et al. 2010, Ronteltap et al. 2010, Song et al. 2011). Low phosphorus concentration resulted in either low (<40%) struvite recovery or a longer precipitation reaction time, which substantially impaired the economic feasibility of nutrient recovery via struvite precipitation. The demand for high phosphorus concentration is challenging for wastewater where typical phosphorus concentrations for wastewater influent and digested sludge supernatant were 6 and 56 mg/L, respectively (Jaffer et al. 2002, Münch and Barr 2001). As a result, it is desirable to enrich nutrients in the waste stream prior to struvite precipitation, thereby significantly enhancing the struvite precipitation potential and efficiency.

Struvite precipitation for nutrient recovery is also challenged by the presence of toxic heavy metal ions and emerging organic contaminants in wastewater (Pronk et al. 2006b), which substantially compromises struvite purity and safe agricultural application. For example, a close examination of recovered struvite crystals revealed the presence of toxic heavy metals in struvite, with arsenic concentration up to 570 mg/kg (Figure 1B) (Lin et al. 2013, Ma and Rouff 2012, Pizzol et al. 2014, Rouff 2012, Rouff and Juarez 2014). The presence of such contaminants in struvite fertiliser is strictly regulated and excessive amounts can result in the fertiliser being banned from agricultural application.

Alternative nutrient recovery approaches with better selectivity should be considered to improve the nutrient product quality. For example, instead of struvite precipitation, ammonium can be recovered under alkaline condition by membrane distillation as 10% ammonia solution (Bonmatí and Flotats 2003, Jorgensen and Weatherley 2003); and phosphorus can be fractionated as phosphoric acid by electrodialysis (Wang et al. 2013, Zhang et al. 2013a). These nutrient recovery technologies targeting specific nutrient ions demonstrated better selectivity and resulted in nutrient products with higher quality.

[Figure 1]

3. Emerging membrane processes advance wastewater nutrient recovery

The challenges of higher nutrient enrichment and membrane selectivity discussed above (Section 2) open opportunities for emerging membrane processes to advance wastewater nutrient recovery. Forward osmosis (FO), membrane distillation (MD) and electrodialysis (ED) are three membrane-based processes that are best suited to overcome the challenges in wastewater nutrient recovery, and could potentially represent a paradigm shift in wastewater nutrient management (Table 1). As described herein, these technologies can achieve high concentration factor for struvite precipitation, their selectivity is conducive to the fraction of valuable nutrient substances in various formats, and their energy requirements and associated costs are competitive with more conventional, pressure-driven membrane processes. A process overview of the three technologies is presented below and the advantages and disadvantages of each for wastewater nutrient recovery are discussed.

[Table 1]

3.1. Forward osmosis

Forward osmosis (FO) could substantially enhance wastewater nutrient recovery via struvite precipitation by its unique mass transfer properties: lack of hydraulic pressure and the occurrence of reverse draw solute flux. In FO, a semipermeable membrane is placed between two solutions of different concentrations: a concentrated draw solution and a more dilute feed solution. Instead of hydraulic pressure, FO employs an osmotic pressure difference to drive the permeation of water across the membrane. As a result, FO has demonstrated a lower fouling propensity and higher fouling reversibility in comparison with pressure-driven RO membrane filtration (Lee et al. 2010, Mi and Elimelech 2010). Consequently, FO enables concentration of a range of challenging, nutrient-rich streams, achieving high enrichment factors for streams (Table 1), such as anaerobically digested sludge (Holloway et al. 2007), activated sludge (Achilli et al. 2009, Cornelissen et al. 2008) and raw sewage (Cath et al. 2005, Xie et al. 2013, 2014a, Xue et al. 2015).

Reverse draw solute diffusion, an inherent phenomenon commonly considered detrimental to FO (Boo et al. 2012, Xie et al. 2014b), can be beneficial by elevating struvite precipitation potential via supplementing magnesium cation into the feed when magnesium-based draw solution is used (Figure 2). Recent studies demonstrated this proof-of-concept of FO in nutrient recovery (Xie et al. 2013, 2014a). Feed sludge centrate was concentrated by FO driven by $MgCl_2$ draw solution and achieved a concentration factor of five, resulting in a high strength stream comprising ammonium (1210 mg/L), phosphate (615 mg/L), and magnesium from reverse magnesium flux. As a result, the $MgCl_2$ draw solution not only provides the driving force for nutrient enrichment, but also can be incorporated into the nutrient precipitate, which makes beneficial use of lost draw solution. These unique mass transfer properties of FO motivate nutrient recovery from various waste streams such as urine (Gormly and Flynn 2007, Michael et al. 2012, Zhang et al. 2014a), sewage (Ge et al. 2012, Hancock et al. 2013, Phuntsho et al. 2012, Wang et al. 2011a, Xie et al. 2013, Zhang et al. 2014b, Zhang et al. 2013b), and sludge (Hau et al. 2014, Holloway et al. 2007, Nguyen et al. 2013).

[Figure 2]

Experimental results from the aforementioned literature were corroborated by mathematical modelling, illustrating promising potential and capacity of the FO process in wastewater nutrient recovery. For instance, Xue et al. (2015) calculated theoretical water recovery of 93% in an FO process using seawater draw solution, thereby achieving ten-fold concentration of ammonium and phosphate in the secondary treated municipal wastewater. This high nutrient enrichment factor also agreed with the solution-diffusion model for FO filtration (Zhang et al. 2014a), yielding 50−80% rejection of ammonium and above 90% rejection of phosphate and potassium.

Despite the feasibility of nutrient recovery by FO, membrane performance is constrained by the water permeability – solute selectivity tradeoff (Yip and Elimelech 2011), an intrinsic property of water and solute transport through polymeric membranes. This tradeoff restricts attainment of high water permeability for FO membrane materials without decreasing solute selectivity (Freeman 1999, Geise et al. 2011), which limits the achievement of high nutrient concentration factor. For nutrient recovery, a membrane with high solute selectivity effectively enriches ammonium and phosphate, and hence, yields a high strength nutrient-rich stream. However, lack of sufficient cations, particularly magnesium supplemented into this stream via reverse salt flux, reduces struvite precipitation potential. By contrast, a membrane with high water permeability produces a higher water flux, and the concomitant decline in membrane selectivity simultaneously provides more draw solution cations to the feed due to higher reverse salt flux, while also causing significant loss of nutrient solutes into the draw. Such detrimental effects work against the benefit of a more permeable but less selective membrane to enhance struvite product yield. Therefore, further understanding membrane permeability – selectivity tradeoff is crucial to nutrient recovery by FO process.

3.2. Membrane distillation

Membrane distillation (MD) is a thermally-driven membrane process that can utilise low-grade heat to drive separation (Alkhudhiri et al. 2012, Alklaibi and Lior 2005). In MD, the aqueous feed stream is separated from the distillate by a hydrophobic, microporous membrane. Liquid is unable to penetrate the membrane pores due to the hydrophobic nature of the membrane, and a difference in the partial vapour pressure drives the transport of water vapour across the membrane pores. Because water is transported through the membrane only in a vapour phase, MD can offer complete rejection of all non-volatile constituents in the feed solution. More importantly, MD could achieve high water recovery because water vapour transport through MD membrane is not significantly influenced by the feed osmotic pressure.

Due to this unique transport mechanism, MD processes have been explored for the recovery of valuable components. Based on the volatility and vapour pressure, these components can be concentrated either in the feed stream or permeate streams. For example, non-volatile inorganic nutrient ions, such as potassium and phosphate, can be concentrated in the feed stream to facilitate subsequent nutrient precipitation. Indeed, the MD process achieved a high concentration factor of three for seawater RO brine volume reduction (Martinetti et al. 2009). Similar high enrichment performance could also be observed for mineral acids (Elkina et al. 2013, Tomaszewska et al. 1995, Tomaszewska 2000) and fruit juices (Mohammadi and Bakhteyari 2006). Concentration of sulphuric acid by MD from 16% until 40% was reported with a separation coefficient of above 98% (Tomaszewska and Mientka 2009).

Ammonia recovery can be one important application of MD process in wastewater nutrient recovery where ammonia is more volatile than water and can be enriched in the permeate stream of MD processes (du Preez et al. 2005, Zarebska et al. 2014, Zhao et al. 2013). Ammonia recovery exemplifies the selectivity of MD membrane process, an approach that is different from aiming for high nutrient concentration factor. MD processes were configured as vacuum MD, gas sweeping MD and direct contact MD for ammonia recovery from varying waste streams, such as urine (Zhao et al. 2013), wastewater (Ahn et al. 2011, Ding et al. 2006, El-Bourawi et al. 2007, Qu et al. 2013, Xie et al. 2009), and swine manure (Thygesen et al. 2014, Zarebska et al. 2014). These MD processes achieved more than 96% ammonia recovery in the form of aqueous solution, which can be conveniently processed as commercial fertiliser. More importantly, in direct contact MD, low concentration of sulphuric acid was used as stripping solution on the permeate side to further enhance the capture of ammonia vapour. The application of acidic stripping solution in the MD permeate stream substantially improves ammonia recovery to 99%, with ammonium sulphate being produced as fertiliser.

Varying composition of nutrient-rich waste stream can pose distinctive challenges to MD in nutrient recovery (Meng et al. 2014, Tijing et al. 2015, Van der Bruggen 2013). The volatile organic compounds, such as volatile fatty acids that exert partial vapour pressures comparable to or higher than water are transported across the MD membrane with the water vapour, causing contamination of the permeate stream and jeopardising the quality of recovered ammonia fertiliser. Certain components in wastewater, such as surfactants, can lower the liquid surface tension of the feed solution and cause wetting of the membrane pores. Membrane pore wetting will result in a direct liquid flow from feed through the wetted pores, substantially deteriorating distillate quality. To restore the vapour-liquid interface at the pores, the wetted membrane must be taken out of operation and dried completely, resulting in process downtime and potential membrane degradation. Dissolved organic matters and colloids present in the nutrient-rich waste streams can lead to MD membrane fouling. Fouling clogs membrane pores, which leads to flux decline and pore wetting and imposes additional hindrance to heat and mass transfer, thereby diminishing the MD process productivity in nutrient recovery. Indeed, in ammonia recovery from wastewater by MD process, MD membrane fouling was initiated by adsorption of peptides and proteins on MD membrane surface, and thus reduced Gibbs free energy and hydrophilised the membrane surface, thereby hindering ammonia vapour permeation (Thygesen et al. 2014, Zarebska et al. 2014).

[Figure 3]

Fabrication of MD membranes with special wettability, such as superhydrophobic or omniphobic property, imparts membrane anti-fouling property and mitigates deleterious membrane fouling and wetting, thereby improving the nutrient recovery efficiency of MD in processing challenging waste streams (Liao et al. 2013, 2014, Lin et al. 2014). Increasing the hydrophobicity of an MD membrane leads to higher liquid entry pressure and consequently more resistance to pore wetting. For example, Razmjou et al. (2012) fabricated a superhydrophobic polyvinylidene fluoride (PVDF) MD membrane with TiO_2 nanoparticles providing hierarchical structures with multilevel roughness on the membrane surface. The resultant MD membrane, possessing high liquid entry pressure of 195 kPa, demonstrated a much higher water flux recovery after humic acid fouling in comparison to the pristine PVDF membrane. Another strategy for preventing membrane fouling and wetting is fabrication of MD membrane with omniphobic property that repels both water and low surface tension liquids such as surfactants. Indeed, Lin and coworkers (2014) fabricated an omniphobic MD membrane with silica nanoparticles via surface fluorination and polymer coating, and demonstrated anti-wetting MD membrane performance maintaining water flux and salt rejection, even with the presence of surfactant. The advancement of MD membrane fabrication with special wettability can open up vast opportunities for MD application for beneficial nutrient recovery, particularly ammonia, from challenging waste streams.

3.3. Electrodialysis

Electrodialysis (ED), which arranges ion-exchange membranes alternately in a direct current field (Xu and Huang 2008), could selectively fraction nutrients from wastewater streams into high quality nutrient products. The direct current field is the driving force in an ED process where cations and anions migrate towards the cathode and anodes, respectively. The ion separation in ED process is achieved by ion-exchange membranes that comprise cation-selective, anion-selective, and bipolar membranes. Cation- and anion-selective membranes are widely used in conventional ED to hinder the passage of co-ions (anions and cations, respectively) by virtue of Donnan repulsion. When bipolar membranes comprising a cation-selective layer and an anion-selective layer are used in an ED process, dissociation of solvent molecules, such as water, into H^+ and OH^- can be realised.

The unique ion separation mechanism of ED process provides a selective mechanism for wastewater nutrient recovery. ED process selectively partitioned phosphate from wastewater effluent containing various ions as a concentrated phosphate solution, achieving a concentration factor of up to 7 (Zhang et al. 2012, Zhang et al. 2013a). Similar selective phosphate enrichment by ED process was also observed in urine nutrient recovery, resulting in a purified phosphate concentrate (Escher et al. 2006, Pronk et al. 2006a). Phosphate selectivity in an ED process can be further enhanced by either adjusting the feed stream to the alkaline pH range or increasing current density (Tran et al. 2014, Tran et al. 2015). Better performance was expected based on the ED separation mechanisms where multivalent phosphate migrates more slowly than monovalent ions under the current field (Zhang et al. 2012).

Nutrient recovery efficiency and product purity could be significantly improved when bipolar membrane was employed in an ED process. The ED process with bipolar membrane integrates solvent (water) and salt dissociation (Bailly 2002); it provides H^+ and OH^- *in situ* without the introduction of salts (Huang and Xu 2006, Huang et al. 2006, Huang et al. 2007).

The combination of H^+ and anions in certain chambers leads to production of acid, while the combination of OH^- ions and cations in other chambers leads to production of the corresponding base. As a result, this ED process with bipolar membrane concept could diversify the final products and enhance purity for nutrient recovery. For example, Wang et al. (2013) employed the ED process with bipolar membrane to convert phosphate in sludge supernatant to purified phosphoric acid of 0.075 mol/L, which provided an approach for wastewater nutrient recovery.

Despite the high purity and diverse product extracted by ED process, it suffers from membrane fouling during wastewater nutrient recovery. The build-up of fouling layers in ED process increases the cell resistance (current drop), decreases migration yield and ion selectivity, and eventually alters membranes due to irreversible fouling (Mondor et al. 2009). Unlike fouling in RO and FO membranes, the fouling of ion-exchange membrane in ED process is significantly dependent on the charge of the membrane (Wang et al. 2011b). Specifically, more sever fouling was observed in anion-selective membrane when negatively charged humic substance, protein and surfactant were presented (James Watkins and Pfromm 1999, Lee et al. 2009, Lindstrand et al. 2000). By contrast, cation-selective membrane could be hampered by calcium-dominated scaling (Ayala-Bribiesca et al. 2006, Bazinet and Araya-Farias 2005). Abating ED membrane fouling could be achieved by periodically reversing the polarity of electrodes, decreasing current density, improving hydraulic conditions in stack compartment by increasing flowrate or gasket with flow pattern, and in-place cleaning with acidic or basic solutions (Lee et al. 2002, Mondor et al. 2009, Ruiz et al. 2007).

[Figure 4]

4. Path forward

4.1. 1+1>2

The emerging membrane processes discussed above have demonstrated their capacity to advance wastewater nutrient recovery by either maximising nutrient concentration factors, such as FO and MD, or enhancing nutrient selectivity, for instance MD and ED. Hybrid membrane processes complement each other, thereby maximising overall nutrient recovery efficiency.

For example, the requirement for concentrating the diluted draw solution in an FO process opens opportunity for coupling with other membrane processes (e.g., RO or MD) to simultaneously restore the FO driving force and to produce high quality freshwater (Hoover et al. 2011, Xie et al. 2013, 2014a). Integration of FO with other processes could not only re-concentrate diluted draw solution for sustainable process performance, but also complement wastewater nutrient recovery with freshwater production. This concept motivates coupling FO with different membrane processes, such as RO, MD, and ED (Figure 5). For example, an FO-RO hybrid system can achieve high rejections of phosphate and ammonium (99.9% and 92%, respectively) from wastewater effluent (Hancock et al. 2013, Holloway et al. 2007) or nutrient-rich sludge (Nguyen et al. 2013). More importantly, this hybrid system also simultaneously produces high quality permeate water. In an FO-MD hybrid system, FO concentrated orthophosphate and ammonium for subsequent phosphorus recovery in the form of struvite ($MgNH_4PO_4 \cdot 6H_2O$), while MD was used to recover the draw solution and extract clean water from the digested sludge centrate (Xie et al. 2013, 2014a). The MD unit in the hybrid system can also be powered by solar energy, thereby reducing the overall operating cost for wastewater nutrient recovery (Qtaishat and Banat 2013). Similarly, ED can also levy solar photovoltaic energy to re-concentrate draw solution in an FO-ED hybrid system (Zhang et al. 2013b), thereby simultaneously concentrating nutrient from the feed waste, and producing freshwater from the draw solution.

Coupling FO with a membrane bioreactor (MBR) is also becoming attractive for wastewater nutrient recovery (Holloway et al. 2014, Holloway et al. 2015). This osmotic MBR concept substantially benefits from the high nutrient rejection by the FO membrane in MBR, high concentration factor due to low FO fouling propensity, and supply of magnesium ions to facilitate nutrient precipitation via reverse draw solution diffusion (Figure 3). Recently, Qiu and Ting (2014) applied an osmotic MBR using $MgCl_2$ draw solution to directly extract phosphorus from wastewater, achieving 95% phosphorus recovery via calcium phosphate precipitation. Subsequently, Qiu and coworkers employed an OMBR with seawater brine draw to achieve 90% phosphorus recovery in the form of amorphous calcium phosphate (Qiu et al. 2015).

[Figure 5]

Despite the versatility and robustness of hybridized FO system for wastewater nutrient recovery, this technology is not without limitations. One significant hindrance is contaminant accumulation in the draw solution. In the closed-loop FO hybrid system, contaminants that permeate through the FO but not the downstream RO or MD process can accumulate in the draw solution, leading to a build-up of unfavourable contaminants in the draw solution (D'Haese et al. 2013, Shaffer et al. 2012). Significant accumulation of organic foulants in the draw solution was observed in an FO-RO hybrid system (Coday et al. 2015, Hancock et al. 2013). Similarly, this detrimental effect was also found in an FO-MD hybrid system where micropollutant concentrations increased in the draw solution as the cumulative permeate volume increased (Xie et al. 2013, 2014a). Therefore, it is of paramount importance to manage this detrimental contaminant accumulation to ensure system performance and reliability.

Struvite precipitation, a key step for phosphorus nutrient recovery, could also benefit from coupling with membrane processes to improve precipitation efficiency. For example, ED process was operated with struvite precipitation reactor in tandem, which enhanced the selective capture of phosphate from the effluent of the struvite reactor (Zhang et al. 2013a). As a result, the phosphate from struvite reactor effluent was further concentrated in ED stack and recirculated into the struvite reactor, thereby improving the overall phosphorus recovery to 97%.

Ammonia recovery, which could result in high quality liquid fertiliser, can be substantially advanced by hybrid membrane processes. In an ED-RO hybrid system, the ammonium was fractioned by cation-selective membrane in an ED unit where the ammonium-rich stream from concentrate compartments was further concentrated by RO membrane. This ED-RO hybrid process produced highly concentrated ammonium solution up to 13 g/L (Mondor et al. 2008), which is beneficial in agricultural application. On the other hand, the volatile ammonia could be captured in an ED-MD hybrid process (Ali et al. 2004, Graillon et al. 1996, Udert and Wächter 2012). For instance, ED process with bipolar membranes produced ammonia from ammonium nitrate waste stream via splitting water solvent. The produced ammonia was recovered by stripping under vacuum membrane distillation, achieving an ammonia concentration of 2 mol/L.

4.2. Decentralised or centralised?

Key nutrient concentrations – ammonium and phosphate – decrease along the sewer system from household to a centralised wastewater treatment facilities, with phosphate concentration being 100 times higher from single household in comparison to the concentration at the wastewater treatment plant (1991, Carroll et al. 2006, Chanan and Woods 2006, Maurer et al. 2003). This significant variation of nutrient concentration gradient unlocks opportunities for tailoring nutrient recovery approaches with varying membrane processes for both decentralised (e.g., single household) and centralised (e.g., wastewater treatment plant) applications.

On-site urine separation and recovery via struvite precipitation is one promising strategy for decentralised, small-scale wastewater nutrient recovery (Larsen et al. 2009). In particular, the urine stream contributes a large proportion of nutrients from household (81% nitrogen, 50% phosphorus, and 55% potassium), but less than 1% of the total volume of municipal wastewater (Karak and Bhattacharyya 2011). More importantly, via nutrient recovery, on-site urine separation can significantly reduce nutrient loadings to the wastewater treatment plants and downstream effluent-receiving water bodies (Ishii and Boyer 2013, Wilsenach and Loosdrecht 2003). As such, on-site nutrient recovery from urine can be more energetically efficient than nutrient removal and recovery in centralised wastewater treatment process, despite low economic efficacy of small-scale system. However, the deployment of urine source separation requires substantial change to existing infrastructure, such as varying flush water from urine diverting toilets (Wilsenach and Van Loosdrecht 2004), proper urine storage for urea hydrolysis (Ishii and Boyer 2015), and precipitation in urine-separating toilets (Udert et al. 2003). In addition, the deployment of on-site nutrient recovery from urine also encounters varying degree of acceptance. For example, fertiliser produced by urine was less accepted by farmers in comparison with the public, where more than 50% farmers have concerns in technical feasibility as well as nutrient product quality (Lienert and Larsen 2010).

Emerging membrane processes discussed above also exhibit satisfactory performance in urine separation. For instance, FO process mined macronutrients (nitrogen, phosphate and potassium) from urine after hydrolysis, achieving significant volume reduction, and high rejection of ammonium (50-80%), phosphate and potassium (>90%) (Zhang et al. 2014a). A higher ammonia separation factor from urine could be observed in a vacuum MD process where rejection of ammonia reached 99% (El-Bourawi et al. 2007, Zhao et al. 2013). ED process is also capable of recovering and concentrating nutrient ions from urine contaminated by micropollutants (Pronk et al. 2006a).

Wastewater nutrient recovery has been practised in centralised wastewater treatment facility (Cote et al. 2013, Kuzma et al. 2012). However, the benefit of upgrading conventional wastewater treatment process goes beyond economic gains (McConville et al. 2014), as re-engineering the existing nutrient recovery process by a suite of membrane processes offers more sustainable sewage management and nutrient cycling.

4.3. Energy consumption and bioavailability for recovered nutrients

The reviewed three emerging membrane processes for wastewater nutrient recovery could utilise a range of renewable energy to further enhance the process sustainability and substantially reduce the carbon footprint. For instance, via powering the ED process by solar energy, the operating cost for an FO-ED hybrid process was €3.32 to 4.92 per cubic meter treated water (considering the investment for membranes and solar panel) for a small size (Zhang et al. 2013b). In addition, levying waste heat generated by a power plant (Zhou et al. 2015) or introducing the biogas produced by the wastewater treatment plant (Qin and He 2014) can be an important alternative to drive the MD process with less cost in wastewater nutrient recovery. Furthermore, a life cycle assessment showed that more than 25% reduction of the environmental impact could be achieved when incorporating FO process into traditional seawater desalination or wastewater reclamation process (Hancock et al. 2012).

Producing agriculturally applicable fertiliser is the final goal for wastewater nutrient recovery. Apart from the technological aspect of wastewater nutrient recovery, more attention should be also paid to the agronomic efficacy and crop uptake of the fertiliser produced from recovered nutrients (Withers et al. 2014). Phosphorus plant availability of struvite precipitate recovered from waste stream was compared with a well-established, water-soluble fertiliser, triple superphosphate, using pot experiments with isotope ^{32}P-labelled soil, suggesting negligible difference in plant phosphorus nutrition and growth (Achat et al. 2014). However, despite the abundance of phosphorus availability for plant growth, the recovered nutrient fertiliser showed poor nitrogen uptake for plant growth (Ganrot et al. 2007, Matassa et al. 2015). In addition, phosphorus that was recovered in the form of amorphous calcium phosphate precipitate, exhibited less water solubility, thereby hindering the crop uptake (Plaza et al. 2007). As a result, wastewater nutrient recovery is a multi-dimensional challenge, with considerable requirements to find a suitable market to distribute recovered nutrient product with proven agronomic efficacy.

5. Conclusion

Three emerging membrane processes – FO, MD and ED – can advance wastewater nutrient recovery with their unique mass transfer properties. FO, demonstrating low fouling propensity and supplementing magnesium ion via reverse salt flux, is able to maximise nutrient enrichment prior to struvite precipitation. MD, driven by vapour pressure difference, is not only capable of achieving a high concentration factor, but also can recover volatile ammonia as a high quality fertiliser. ED can selectively partition phosphate with an anion-selective membrane, or produce phosphoric acid or ammonia with a bipolar membrane that splits water solvent into proton and hydroxide. In addition, integration of these membrane processes with existing nutrient precipitation processes could substantially improve nutrient recovery efficiency, and diversify the nutrient product that can be extracted, even achieving a near complete wastewater nutrient recovery. For the future, detailed techno-economic analysis of these hybridised membrane-based processes in wastewater nutrient recovery should be performed, such as process energy demand, CO_2 footprint, system robustness, operating costs, product quality and market demands.

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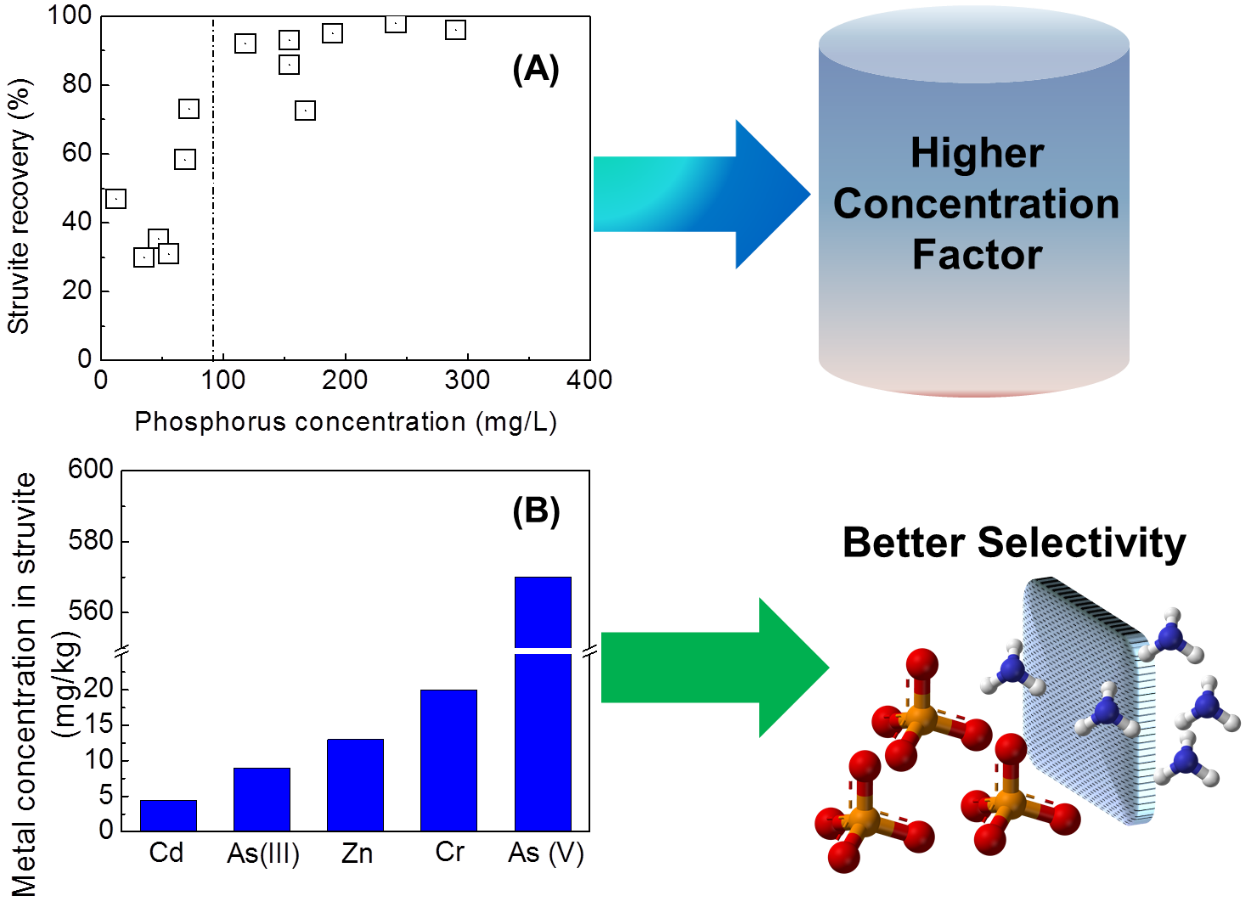

Figure 1: Illustrations of the critical challenges in wastewater nutrient recovery. (A) Struvite precipitation efficiency as a function of initial phosphate concentration; there is a critical need for membrane processes enabling higher concentration factor. Data points were summarised from literatures (Çelen et al. 2007, Guadie et al. 2014, Jaffer et al. 2002, Liu et al. 2011, Münch and Barr 2001, Pastor et al. 2008, Pastor et al. 2010, Ronteltap et al. 2010, Song et al. 2011) (B) Presence of toxic heavy metal ions in struvite precipitates from waste streams; there is a critical need for membrane processes with high selectivity. Data points were collected from literatures (Lin et al. 2013, Ma and Rouff 2012, Pizzol et al. 2014, Rouff 2012, Rouff and Juarez 2014).

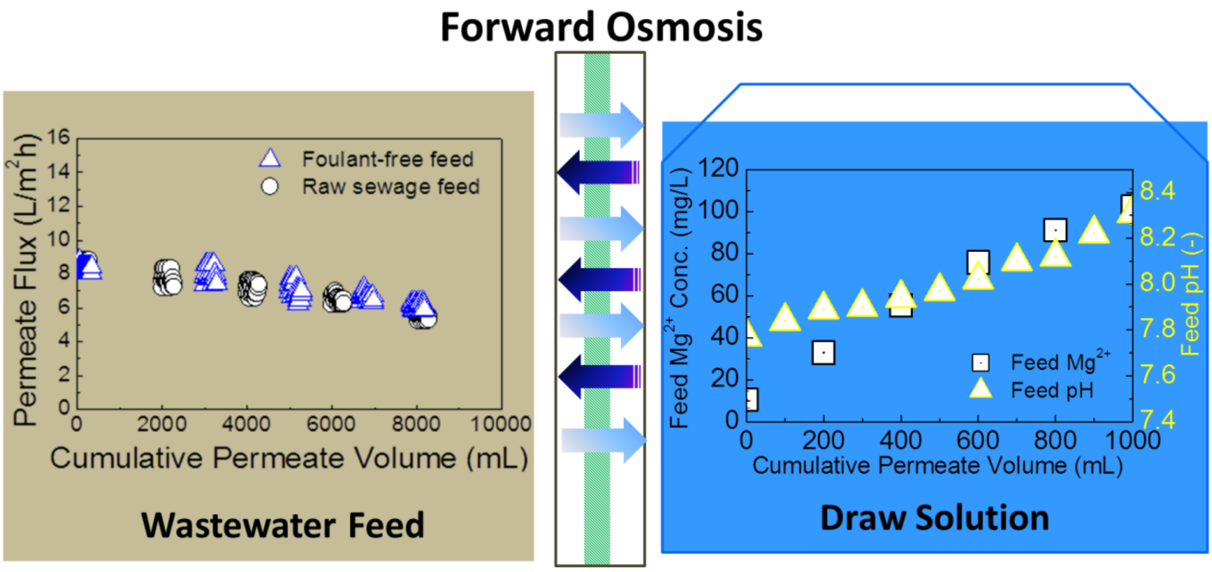

Figure 2: Unique mass transfer properties of forward osmosis (FO) enhance nutrient recovery efficiency from wastewater. Data reproduced from (Xie et al. 2014a, Xie et al. 2014b).

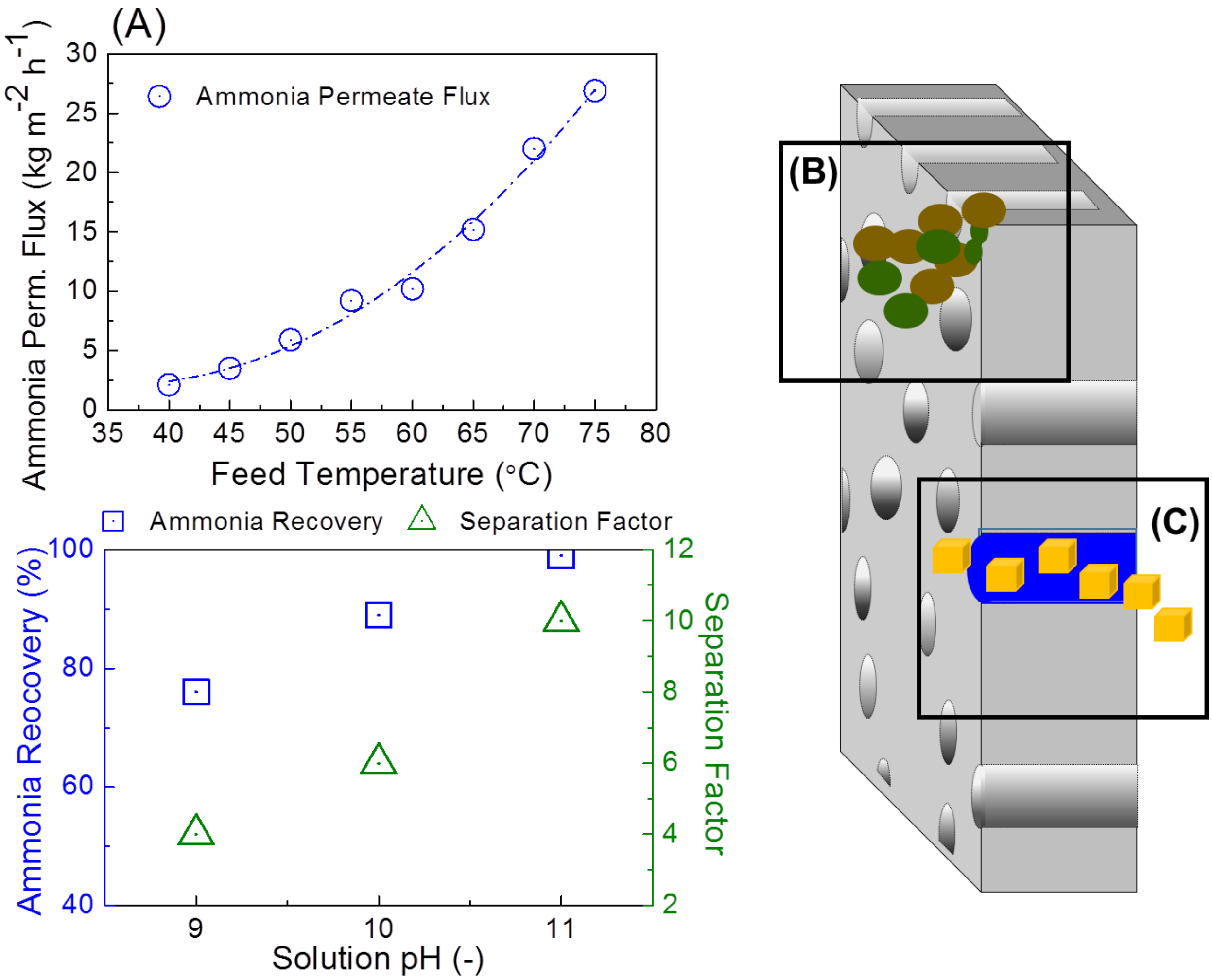

Figure 3: Conceptual illustration of membrane distillation (MD) for wastewater nutrient recovery. (A) Ammonia vapour selectively permeates through the membrane pores as a function of feed temperature (upper panel) and solution pH (lower panel where separation factor was calculated as the ratio of ammonia concentration in the feed and permeate); experimental data were reproduced from references (Ding et al. 2006, El-Bourawi et al. 2007, Qu et al. 2013, Xie et al. 2009). (B) Fouling of MD membrane leading to detrimental effect on process productivity (such as flux decline). (C) Wetting of MD membrane pores and permeate quality, such as feed solute (yellow cubes) flowing directly across membrane.

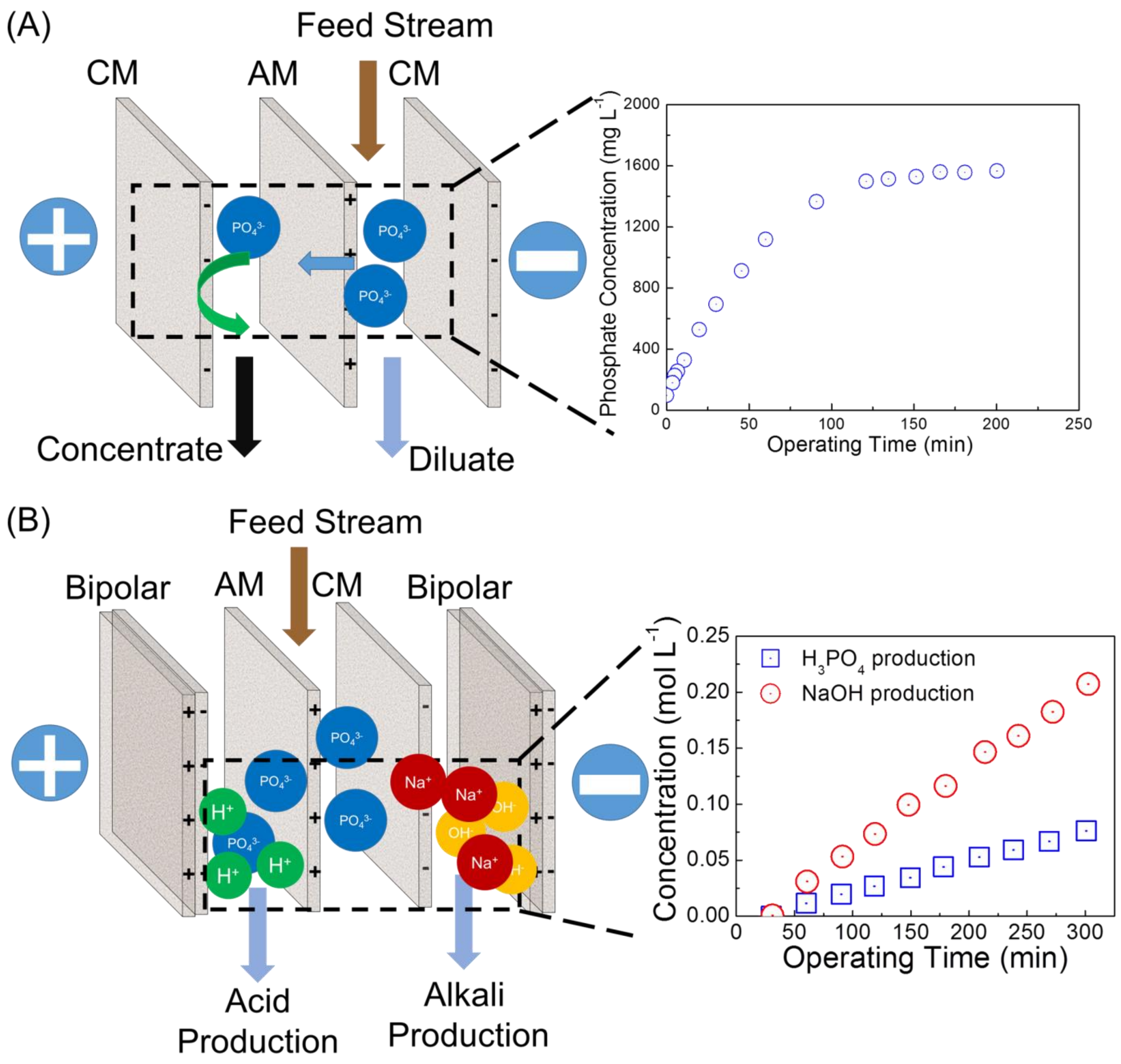

Figure 4: Conceptual illustration of electrodialysis (ED) for wastewater nutrient recovery. (A) Conventional ED process selectively concentrates phosphate in waste stream, where phosphate ion concentration in the concentrate stream increased as a function of time. (B) ED process with bipolar membrane selectively produces phosphoric acid from waste stream, where phosphoric acid concentration increases as a function of operating time. Data reproduced from Wang et al. 2013.

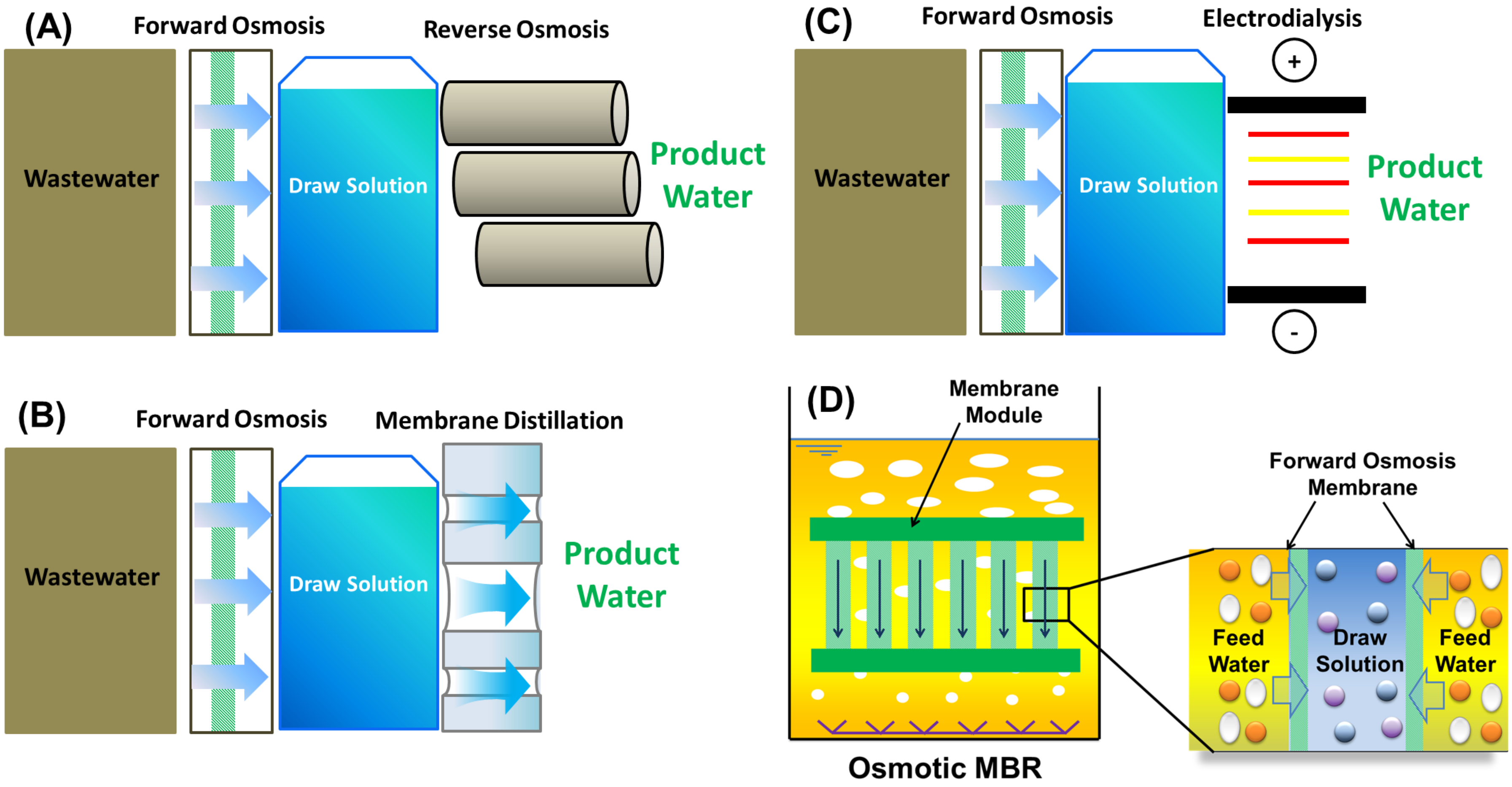

Figure 5: Conceptual illustrations of forward osmosis (FO)-based membrane processes for wastewater nutrient recovery: (A) FO-RO hybrid process; (B) FO-MD hybrid process; (C) FO-ED hybrid process; and (D) Osmotic MBR with FO membrane.

Table 1: Summary of nutrient and water recovery by pressure- (nanofiltration and reverse osmosis), osmotically- (forward osmosis), thermally- (membrane distillation) and electrically- (electrodialysis) driven membrane processes in terms of process performance, membrane fouling, and operating cost and energy consumption.

Driving force	Source water	Nutrient recovered	Key membrane process	Performance	Membrane fouling	Operating cost and energy consumption
Pressure-driven	Urine (Maurer et al. 2006)	Ammonium, phosphate, potassium	RO	Concentration factor up to 5. Ammonium: 70%; phosphate: 73%; potassium: 71%.	Membrane scaling	Operating pressure of 50 bar
	Synthetic urine (Pronk et al. 2006b)	Urea, ammonium, phosphate	NF	Urea: 10% ammonium: 55% phosphate: 94%	N.A.*	Operating pressure of 20 bar
	Synthetic wastewater (Niewersch et al. 2014)	Phosphate, potassium	NF	Phosphoric acid: 50% potassium: 30%	N.A.	Operating pressure of 12 bar
	Digested sludge (Blöcher et al. 2012)	Phosphate	NF	phosphate: 50%	N.A.	Operating pressure of 25 bar Operating cost can be covered by phosphate recovery revenue
Osmotically-driven	Urine (Zhang et al. 2014a)	Ammonium, phosphate, potassium	FO	Ammonium: 50-80% phosphate: >90% potassium: >90%	N.A.	N.A.
	Urine (Gormly and Flynn 2007, Michael et al. 2012)	Water	FO (X-Pack™, Water Well®)	Total nitrogen >95% urea > 93% total organic carbon > 95%	N.A.	N.A.
	Synthetic	Water	FO with	Diluted fertilizer for	N.A.	N.A.

	wastewater (Phuntsho et al. 2012)		fertilizer draw solution	agricultural irrigation		
	Secondary treated effluent (Hancock et al. 2013)	Water	FO-RO	Nitrate >72% phosphate >99% dissolved organic carbon > 98%	Cake layer formation	N.A.
	Raw sewage (Xie et al. 2013)	Water	FO-MD	Total organic carbon > 99% total nitrogen >99%	Cake layer formation	Draw solution temperature 40 °C
	Secondary treated effluent (Zhang et al. 2013b)	Water	FO-ED	Total organic carbon >90% Near 100% rejection of heavy metal ions (Cd, As, Pb)	N.A.	€3.32-4.92 per m^3 product water
	Activated sludge (Nguyen et al. 2013)	Water, ammonium, phosphate	FO	Ammonium >96%, phosphate >98% dissolved organic carbon > 99%	Cake formation	N.A.
	Activated sludge (Hau et al. 2014)	Water, ammonium, phosphate	FO-NF	Ammonium >97% phosphate >99%	Cake formation	NF operating pressure: 80 psi
	Activated sludge (Holloway et al. 2007)	Water, ammonium, phosphate	FO-RO	Ammonium >92.1% phosphate >99.8%	Pore blocking and surface fouling	4 kWh/m^3 at 75% water recovery
	Anaerobic sludge (Xie et al. 2014a)	Water, phosphate	FO-MD	Ammonium >90% phosphate >97% struvite product	Cake formation	Draw solution temperature 40 °C
Thermally-driven	Urine(Zhao et al. 2013)	Water, ammonia, organic matters	Vacuum MD	Organic matter: >99% Ammonia: 41-75% Water: 32-49%	Organic fouling with salt crystallization	Feed temperature: 50-70 °C Vacuum pressure: 9.5kPa.

	Synthetic wastewater (Xie et al. 2009)	Ammonia	Sweep gas MD	Ammonia: >96%	N.A.	Feed temperature: 65°C sweep gas flowrate: 3 L/min
	Synthetic wastewater (El-Bourawi et al. 2007)	Ammonia	Vacuum MD	Ammonia: >90%	N.A.	Feed temperature: 50 °C Vacuum pressure: 6.3kPa.
	Synthetic wastewater (Ahn et al. 2011)	Ammonia	Direct contact MD	Ammonia: >92%	N.A.	Feed temperature: 35°C Ammonia stripping solution: 1 M H_2SO_4
	Synthetic wastewater (Qu et al. 2013)	Ammonia	Direct contact MD	Ammonia: >99%	N.A.	Feed temperature: 55°C Ammonia stripping solution: 0.1 M H_2SO_4
	Swine manure (Zarebska et al. 2014)	Ammonia	Direct contact MD	Ammonia: >99%	Organic fouling followed by pore wetting	Feed temperature: 40°C Ammonia stripping solution: 0.5 M H_2SO_4
	Swine manure (Thygesen et al. 2014)	Ammonia	Direct contact MD	Ammonia: >98%	Organic fouling	Feed temperature: 35°C Ammonia stripping solution: 0.5 M H_2SO_4
Electrically-driven	Urine (Pronk et al. 2006a)	Ammonium, phosphate, potassium	ED with ion exchange membrane	Concentration factors: ammonia (2.9), potassium (3.1), phosphate (2.7); Eliminating micropollutants	N.A.	Applied current density: 22.5 mA/cm^2 Current efficiency: 50%
	Municipal Wastewater (Zhang et al. 2013a)	Phosphate	ED with ion exchange membrane	Concentration factors: phosphate (6.5)	N.A.	Applied current density: 31.25 A/cm^2 Current efficiency: 72% Energy consumption: 16.7 kWh/(kg PO_4^{3-})

	Synthetic wastewater (Wang et al. 2013)	Phosphate	ED with ion exchange membrane	Concentration factors: phosphate (4.2)	N.A.	Applied current density: 71.5 mA/cm^2
	Synthetic wastewater (Wang et al. 2013)	Phosphate	ED with bipolar membrane	Concentration factors: phosphate (16); product phosphorus acid of 0.075 mol/L	N.A.	Applied current density: 50 mA/cm^2 Current efficiency: 75% Energy consumption: 29.3 kWh/(kg H_3PO_4)
	Swine manure (Mondor et al. 2008, Mondor et al. 2009)	Ammonium	ED with ion exchange membrane	Concentration factors: ammonium (5.3)	Calcium and colloidal particle deposition	Applied current density: 2.7 A/cm^2 Current efficiency: 77.9%

[*] not applicable