Critical Raw Materials (CRM) Recovery – Significance and Impact on Circular Economy

In the present world, raw materials are in greater demand but are becoming ever scarcer. To imply the sign of criticality, knowing that there is a high risk of supply shortage and economic impact, the European Commission formally adopted a list of specific raw materials designated as ‘critical raw materials’ (CRMs) as represented in Fig. 1. Regulatory policies are being implemented to bring down the extraction/mining trend for ultimately extending the lifetime of CRMs. On the other hand, advanced recycling systems are being practiced to promote and establish a core circular economy context by recycling, recovering, and separating CRMs. These recycling approaches are mostly aimed at the recovery of various metals such as palladium, gallium, germanium, copper, which are critical raw materials for the technology sector. There are also a specific group of CRMs including Phosphorus (P), natural phosphate rock and Magnesium (Mg) representing major primary, and secondary resources for industrial applications of high economic value (Loganathan et al., 2017; Yan et al., 2018). Crucially only P and Mg are deemed suitable candidate CRM’s for...
recovery from waste streams through effective separation and recycling strategies. Further, its supply-demand status and substitutability risks have driven the requisites for resource supplementing technology through effective recovery and recycling strategies.

The core focus of this article is to review the most effective sustainable technologies to recover CRMs. Specifically for P and Mg recovery, it is essential to balance the depletion of its primary reserves, whilst mitigating the disposal issues with a view to remediate industrial brine/waste sludge rich in Mg and P nutrients respectively. Hence, special emphasis has been given to recovering CRMs from waste streams, currently a source of both high potential and environmental, and health concerns. Long-time benefits would be possible by the recovery of P and Mg as a secondary resource to ameliorate the CRMs supply risk in countries deprived of natural mineral reserve. Perhaps, natural lifecycle of phosphate could be balanced by maintaining its sustainable supply to plants while controlling eutrophication, a phenomenon leading to excessive oxygen depletion in water bodies owing to disproportionate phosphate discharge. In a viewpoint to achieve dual advantage of discharging pollutant-free waste sludge and to allow efficient recovery of P/Mg in different forms useful to mankind and environment, robust recycling/recovery strategies are consolidated and discussed in the following sections.

Overview on Conventional Approaches of P and Mg Recovery

As the levels of CRMs in the natural sources are limited, their recovery from non-conventional secondary sources such as end-of-life products and waste generated through industrial activities is essential to meet the global demand. Various conventional methodologies are reported in literature based on physical, chemical and biotechnological principle for the critical raw material recovery for magnesium and phosphorus. General summary on the widely adopted spectrum of methodologies for the P and Mg recovery is discussed in this section.

Since P is an essential component of fertilizer composition, the waste water produced from fertilizer industry is considered as an important secondary source for the recovery of P. Other sources utilised for P recovery include effluent from waste water treatment plants, household activities, municipal waste and industrial organic solid waste. While sea water is considered as a largest source of Mg, exhausted waste brine solutions from industry is also Mg rich.

The widely used methodologies for the recovery of divalent Mg and P mainly involve chemical precipitation, adsorption and membrane separation. Chemical precipitation is considered as a most popular method which involves leaching of Ca/Mg using acidic or alkaline conditions followed by their precipitation by adding metal hydroxide such as calcium hydroxide. The precipitation of P is achieved in the form of struvite (magnesium ammonium salt) and hydroxyapatite. Further, manipulation of Ca/P ratio and calcium phosphate concentration in solution, leads to fast precipitation and recrystallization of phosphate (Vasenko and Qu, 2018). In addition a hybrid methodology involving both oxidation and ultra-sonication assisted pre-treatment, was found to improve P recovery. In recent reports, electrolytic system in combination with ion-exchange membrane was demonstrated where OH⁻ ions released from water breakdown help in the precipitation of Mg (Sano et al., 2018).

Adsorption methodology is considered a relatively simple process for the recovery of metal ions from aqueous waste. Activated charcoal and metal oxides such as ferric oxide/hydroxide, activated aluminium oxide and lanthanum oxide are well explored for their ability to adsorb metals from aqueous solutions. Ion-exchange resins are also used for metal ion recovery. The use of Anion exchange resin and cation exchange resins was studied for the recovery of P and Mg respectively. Further, application of magnetic ion-exchange (MIEx) resin is demonstrated for the recovery of Mg and P (Kim, 2015; Lehmann et al., 2014). MIEx are adsorptive resins where iron oxide particles, with magnetic properties, are incorporated into a polymeric matrix. MIEx assisted adsorption can be combined with membrane separation, and precipitation methods, to improve the recovery of metal ions. Recently Lanthanum based nanoparticles and nano-composites receiving greater attention for the recovery of Phosphate from aqueous solutions (Wu et al., 2017). Membrane separation is another popular method for the concentration and recovery of metal ions. Microfiltration, ultra-filtration, nanofiltration and dia-filtration have largely been demonstrated for the recovery P and Mg. Further, membrane separation is used in combination with ion-exchange resin and precipitation methodologies to improve the process recovery.

Advanced Technologies for CRM Recovery

Status of Phosphorus

Stimulated by the fact that phosphate rock resources have started depleting, the P recovery from any phosphorus-rich residue has drawn extensive attention to meet the industrial demand for P. The elevated phosphate concentration in wastewater/waste sludge presents significant opportunities for P recovery techniques to be readily integrated into current wastewater treatment infrastructure. Phosphate rock is the major natural source of phosphates used in fertilisers but the P extraction rate far exceeds the regeneration, thus estimating its depletion in the next 40–100 years. In contrast, 90% of the phosphate in wastewater is trapped in the sludge solids and also present as soluble PO₄ in the reject wastewater (>80% of total P) (Yan et al., 2018). Fig. 2 illustrates the simplified scheme of natural P cycle and its flows and distributions in global food chain. However the challenge remains to directly recover P/PO₄ from municipal wastewater which redirects the focus to recover P as secondary resources for its significance in various industrial applications (Fig. 3).
Struvite is one of the widely attracted secondary raw material rich in both P and Mg. It is interesting to note that resources constituting Mg is crucial to maximize the P separation based on either conventional precipitation or novel osmotic membrane separation methods. Calcium phosphate is yet another promising P based raw material, allowing recovery directly from the liquid phase (as dissolved P), which is not otherwise possible using conventional biological based wastewater treatment. If P can be
removed and recovered at the very beginning of the wastewater treatment, then steps related to downstream processing of P-rich sludge could be avoided.

Status of Magnesium

The economic gains obtained by extracting minerals depend mainly on the concentration of minerals and their market price. In this respect, Na, Ca, Mg, K, Li, Sr, Br, B and U are potentially attractive for extraction, provided economically feasible extraction methods can be found to avoid direct land mining. There is a great demand for the group of minerals that can be profitably extracted from seawater, or effluent brine to benefit agriculture, industry, environmental remediation, and medicine. Mg is identified to be one of the key CRMs posing a huge demand, owing to its application in wide spectrum of industries including chemicals, construction materials, aluminium, steel and fertilizers. With magnesite being a prime source for Mg recovery, the growing demand and faster depletion of naturally occurring mines has led to the exploration of other Mg sources including dolomite, forsterite and brucite deposits. Mg and P are rather different class of CRMs that does not fall into the categories of precious metals like gold, silver and palladium; and selected set of critical metals (S-CRMs) like gallium, indium, rare earth elements (REEs), tantalum, and cobalt. Moreover, such different classes of CRMs, except Mg and P, could be readily recovered by recycling the WEEs. The world production of Mg is around 12 million ton per year (2012), but only 14% is produced in EU area. If the Mg recovery from waste brine of European saltworks are highly efficient, then the production from the EU zone could increase by 5% (Nakoa et al., 2016).

Membrane Based Approaches for P and Mg Recovery

Combining P recovery with domestic/industrial wastewater treatment systems

To overcome the limitations related to lower P recovery and high cost required (e.g., the addition of inorganic salts like Mg) for conventional precipitation, it is rather important to focus on advanced separation technologies like membrane processes for improving the P recovery. Research interests on P recovery using forward osmosis, selective electrodialysis, and osmotic membrane bioreactor as an integrated process have recently been increased (Qiu et al., 2016). Table 1 summarizes some of the feasible combination of membrane processes for recovery of P and Mg based raw materials from different waste resources. Thermally driven membrane processes like membrane distillation (MD) and membrane crystallization (MCr) have been widely used for desalination with simultaneous recovery of MgSO₄·7H₂O, owing to its well-controlled and easy tuneable precipitation at low energy requirements, which are difficult to obtain from normal crystallization processes. However, MCr/MD for P recovery is also feasible to produce both solid struvite precipitate, and ammonia rich liquid stream, while also being operated using waste heat to ensure a lean cost process.

In most of the osmotic membrane bioreactors, FO membrane helps to reject P to one side of a collection tank, while the MF/UF membrane permeates it for final recovery of P without the need for any addition of calcium or magnesium ions. Further, other rejected solutes in the FO system are transported into the bioreactor for final extraction using MF, which also enables lowering the salt accumulation in the bioreactor. Electroosmosis (ED) is one of the versatile methods which have had its prime role in heavy metals remediation of pollutant streams including industrial effluents and sewage sludge. Recently studies are investigating ED for direct P recovery, while being integrated with biological reactors to ensure both P availability and to make use of great fertilizer value of final sludge solids. The present challenges of ED including membrane fouling and increased electrical resistance (translating into higher operating/maintenance costs) could be effectively met by combining ED with anaerobic biological process, which stimulates the P release. Ion exchange membranes are known for its synergistic mechanism of membrane separation with selective ion-exchange capacity. Extensive potential of the ED has been utilised to separate phosphate from waste/sewage sludge.

Combining Mg recovery with desalination systems

In order to maximize the production of Mg, membrane technology is considered a leading viable option, due its established popularity in the field of desalination. Wide spectrum of CRMs are found in sea water, yet commercial scale recovery remains a major barrier due to its low concentrations upon recovery. Whereas, industrially processed effluents are considered as one of the richest sources of inorganic salts/minerals, thus shifting the need for CRMs recovery towards effluents coming from desalination and wastewater treatment units. The paradox in combining minerals recovery with desalination, is that water is both a human necessity, but also a waste product in the mining industry. Likewise the desalination industry have seen their mineral-rich stream as waste, during the production of clean water. By combining these two industries in ‘mining from the sea’, many synergies can be obtained. The interesting objective of recovering minerals from the sea might actually partly aim to reduce the problem of brine disposal in desalination. Moreover, as an intriguing, positive side effect, it can contribute to the conventional mining industry, thus reducing mineral depletion. Several methods are emerging for mining valuable minerals on both individual and combined basis among which majorly employed methods include solar evaporation, electrodialysis (ED), and membrane distillation (MD)/membrane distillation crystallization (MDC) (Loganathan et al., 2017). Schematic of the process flow diagram employing ED and MD with crystallizer systems for Mg recovery is shown in Fig. 4.
Membrane distillation

Growing research interest in zero liquid discharge (ZLD) technologies have driven the importance of treating RO concentrate, as it is considered as one of the waste resources to recover magnesium salts (Chung et al., 2017). Research studies dealing with the treatment of emerging RO concentrate are to develop cost-effective methods to minimize the potential impacts on the environment. This will also offer alternative strategies to viably extract available salts, and to recover purified water. Several strategies have been adopted for the treatment technologies of RO brines and multiple review papers have also been published in the last decade (Subramani and Jacangelo, 2014; Jensen et al., 2019).

Second major component of RO brine is magnesium and mostly the elements remain in the form of sulphates than carbonates. Major obstacle lies on the presence of calcium, either as CaCO₃ or CaSO₄, both of which affects the membrane performance due to its poor solubility. Despite having no direct influence of Ca²⁺ present in seawater on Mg recovery, its impact is indirect on the efficiency of struvite recovery due to calcium phosphate formation. However, association of calcium carbonate (CaCO₃) with Mg results on the production of Dolomite (CaMg (CO₃)₂), which represent one of the primary natural sources of magnesium production.

Membrane crystallization

In a typical reactive crystallization, magnesium salts can be precipitated by means of hydroxyl radicals. Cationic form Mg²⁺ form can further be obtained based on electrodialysis mechanism. In the reactive hybrid process, integration of ion exchange membranes enables the development of Membrane Crystallizer Reactor (MCR) wherein IEMs are in selective contact with the alkaline reagents. In MCR, precipitation reaction occurs between brine and alkaline solution with no direct contact which is in contrast to conventional reactive crystallization. Moreover, indirect contact of IEMs with two different electrolyte solutions reduces the risk of co-precipitation of by-products thus enhancing the recovery efficiency. MCr was applied in an integrated system working on NF.
and RO brine for the recovery of sodium and magnesium. Introduction of NF is required to separate bivalent and monovalent ions, thus providing that magnesium can be recovered from the NF retentate and sodium from the RO retentate, since it highlights that MCs can control/tune the polymorph selection, thus increasing the product value and minimizing the post-treatment.

**Electrodialysis**

In contrast to P, only scarce Mg sources are available from struvite or municipal wastewater, thus driving the need for fractionating Mg$^{2+}$ from seawater. Hence, ED takes its role by combining the standard cation-exchange membranes, and monovalent selective cation-exchange membranes, for selective fractionation of Mg$^{2+}$ from various side-streams rich in divalent ions (not limited to bittem, sea water, brucite, RO brine, and NF retentate). Seawater, containing substantial Mg$^{2+}$, is regarded as one of the leading potential resources offering the combination of desalination for product water treatment along with Mg$^{2+}$ recovery.

**Strategies to Maximize Mg and P Recovery**

**Integration of Mg and P Recovery Process- Closing the Loop Approaches**

An integrated approach of bringing together various membrane processes having lower footprint may be significant to extract one or more valuable minerals, in particular Mg and P from seawater/brine effluent, and sewage wastewater respectively. Struvite, one of the potential secondary raw materials for both soluble P and Mg, can be recovered from wastewater based on various strategies. Membrane technologies employing advanced osmotic membrane reactors (OMR) as a stand-alone process (or integrated with other filtration processes like microfiltration/ultrafiltration) are now viewed as viable options for both P recovery and the production of clean water.

Design of a continuous and closed loop system for the recovery of valuable minerals like P and Mg from waste and renewable resources would be the challenging implementation steps for waste treatment or desalination. Process intensification is gaining more focus to mitigate against the issues related to CRMs depletion, water shortage, global warming, and waste recycling. Membrane processes closely match the current requirements of process intensification, for its energy-efficient separation routes when compared with conventional separation technologies. Membrane separation processes are already recognized as the best available technologies, allowing easy retro-fitting to most of the available processes to contribute to sustainable development.

For instance, current products such as membrane bioreactors (MBRs), primarily use for wastewater treatments, membrane-assisted crystallization, condensation and distillation, are based on the concept of facile redesigning of conventional energy-intensive separation methods. The interesting results achieved with these new technologies could overcome the limitations in recycling strategies. A relatively high P concentration combined with relative low organic matter content can be achieved by stimulating release of P from secondary sludge using volatile fatty acids (VFAs) under anaerobic conditions. Extracting P from the resulting liquid phase of the sludge will result in less fouling of the membranes and subsequently higher efficiency of P extraction.

By judicious selection of the draw solute for the operation of OMR, it is quite feasible to integrate hybrid MF/UF-OMR system into the tertiary wastewater treatment phase, wherein retentate stream of nanofiltration (NF) permeate or reverse osmosis (RO) retentate system containing MgCl$_2$ helps to enhance ionic strength and precipitation potential for P recovery (Ashley et al., 2016). With pH adjustment greater than 8, P could be precipitated directly recovered from NF permeate without requiring any inorganic salts. With pH adjustment greater than 8, P could be precipitated, directly recovered from MF permeate, without requiring any inorganic salts. The feasibility of using sea water as a draw solute for P recovery using hybrid MF-OMR, followed by separation of Mg by electrodialysis would be gaining greater potential in terms of economics and process integration (Joo and Tansel, 2015). A typical process flowchart illustrating the concept of simultaneous recovery of both P and Mg and the integration potential of sea water RO (SWRO) brine, a concentrated stream of concern from desalination systems being used as a draw solute for operating FO as shown in Fig. 5.

**Pre-Treatment Approaches**

For integrated process design of advanced technologies for CRM recovery, pre-treatment strategies play a crucial role as most of the CRM recovery is aimed from secondary waste resources/ raw materials. Specifically to recover P and Mg, several methods including acid, alkaline, electrodialytic and ultrasonic, incineration have been studied, yet it is challenging to choose appropriate pre-treatment to best exploit the efficacy of entire recovery system. Despite many methods can significantly accelerate the phosphorus release during the sludge disintegration process, it is indispensable to choose cost-effective and efficient methodology. Most of the conventional stand-alone methods are cost intensive due to high energy inputs and/or substantial chemical requirements which might limit its largescale application. Furthermore, those methods certainly pose negative consequences on environment. Therefore, a cost-effective, efficient and environmentally friendly treatment method to enhance phosphorus release from wastewater is needed. For instance, mineralization of struvite or whey (dairy by-product) is quite complex due to the presence of various inorganic minerals/materials. Within, implementation of simple and efficient pre-treatment steps could play a major role in removing the valuable minerals which would rather hinder the efficiency of further downstream processing. In lactic acid production process from dairy by-product streams, Ca(OH)$_2$ precipitation has proven as an efficient pre-treatment step in recovering CaPO$_4$ while enhancing the production efficiency of lactic acid from whey permeate (O’Brien et al., 2018). Fig. 6 summarizes the
series of advanced pre-treatment, intermediate and final steps being adopted to enhance P release from wastewater and Mg recovery from seawater/brine.

**Biotechnological Approaches**

Phosphorous can be recovered by biotechnological approaches based on two strategies. The first being microbial cell lysis for release of intracellular phosphate accumulated during biological nutrient removal process and the other is to induce the precipitation of phosphorous by influencing the pH conditions of the wastewater through metabolic pathways. In general, wastewater generated by domestic activities contains 5–20 g of phosphorous per cubic metre. The domestic wastewater is mostly treated using activated sludge processes. During the activated sludge process, the phosphates available in the wastewater are taken up by the microbial consortia present in the sludge to meet the metabolic needs of the cell. The excess phosphate taken up by the cell is stored as polyphosphate with in polyphosphate accumulating organisms. These organisms can be enriched by recirculating the
activated sludge for accumulation of significant amount of phosphorous (up to 90%) (Wang et al., 2017). Hence, waste activated sludge (WAS), a by-product of biological wastewater treatment process is gaining attention for recovery of phosphate due to its availability and affordability. However, several challenges are need to be addressed such as low phosphorous release, economics of the entire process etc. Though the substrate is cheaply available, low recovery of phosphorous pose a serious challenge in recovery of phosphorous from sludge.

The first step in recovery of phosphorous from WAS is the release of phosphorous from intracellular and extracellular of the microbial cell. This step is typically done by microbial cell disintegration, yet efficient means of cell disintegration are required to meet the desirability. Various methods such as acid/ alkali hydrolysis, incineration, electro dialysis, ultrasonication have been investigated (Xu et al., 2018). Though these methods can substantially increase the rate of release by disintegrating the cell wall and extra cellular polymeric substances, requirements of huge amounts of chemicals (acid/alkali), energy requirements affects the commercial viability and eco-friendly nature of these processes. Hence, identification of eco-friendly, energy efficient and affordable technologies to promote the recovery of phosphorous from waste activated sludge is need of hour. Few processes such as free ammonia treatment have been investigated for its biocidal activity and its application in sludge disintegration at lower concentrations. In this context, insights into energy efficient technologies need to be developed for enhanced recovery of phosphorous from microbial sludge produced during biological treatment processes.

On the other side, phosphorus can be precipitated/crystallized as hydroxyl apatite via changing the pH conditions and chemical dosing in wastewater (Baur et al., 2008). However, this phenomenon could lead to clogging of the pipes if not properly controlled and can lead to economic loss. Therefore alternate strategies need to be explored for precipitation of phosphorous. Aerobic granular sludge process is one process that could be investigated as economically viable option for phosphorous recovery. The aerobic granular sludge process is recognized as a promising technology for treatment of wastewater at high organic loading rates. In addition to the removal of organics simultaneous nitrification and denitrification, phosphorous accumulation could be achieved. Precipitation of P has also been reported during activated sludge systems, however more insights into the process need to be developed. Calcium phosphate precipitation is a key contribution for P removal during Enhanced Biological Phosphorous Removal Processes (EBPR) and it is believed to increase the efficiency of biological phosphorous removal.

**Future Perspectives and Technology Challenges on Sustainability**

Globally securing sustainable access to CRMs is of high importance to meet the demands of industrialisation. However, with varying substitutability indices across the CRM spectrum, certain countries hold a monopoly on future, finite supplies. Currently the processing, recycling, reuse and recovery technologies of CRM are very complex, costly, and with very low yields. It is essential that new innovative technologies are implemented to provide efficient and scalable solutions to recover CRMs such as P and Mg from various complex resources. However, the biggest challenge to industry is to scale the innovative recovery technologies to produce commercially viable CRM’s in a sustainable manner. A recent report highlighted that the use of CRM’s in the EU economy is far from the ideal closed loop, circular economy (Mathieux et al., 2017). That report also suggests a multi-component approach to tackle this global issue:

1. The need for a legislative framework governing processes to facilitate the extraction of CRMs from input flows.
2. Implement a sustainable policy on product life cycle - recycling, re-use, product lifetime extension, and new business models.
3. Ensuring up-to-date data is produced tracking CRM’s across the life cycle (e.g., via The Raw Material Information System).

In order make these technologies industrially adoptable, it is essential to integrate traditional recovery processes with novel separation processes, such as membrane based technologies. The main advantage of membrane separation processes is that can offer relatively high yield CRM recovery, at low temperatures which minimises energy consumption. However to overcome other existing limitations of traditional membranes, more advanced membranes such as surface functionalised ion exchange membranes and electrospun membranes may offer a sustainable solution (Saranya et al., 2018). These separation processes can further coupled with pre-treatment and bioremediation processes, resulting in relatively high yield and purity products. Clearly it is of critical importance that new processes that are developed are environmentally friendly with high energy efficiencies to create a global sustainable solution to this immediate issue.

Adoption of integrated process to catalyse a switch in the recycling and production transformation for CRMs and fossil-energy based materials could essentially help in building circular material flows on par with United Nations Sustainability development Goals. Promotion of sustainable technologies for sewage waste management and desalination enable P and Mg recycling respectively to ensure several sustainable aspects, however not limiting to depollution, renewability, demand-supply balance, food/environmental safety, macronutrient balance. It is also worth mentioning that one best solution does not preferably be suited for either P or Mg recovery as the process selection and integration depends on various factors including the geographical context, feed wastewater properties and so on. For example, membrane bioreactor combined with struvite precipitation is effective in terms of biosolids management, energy and P recovery. Further research and monitoring are strongly needed, including into improving organic contaminants removal in biosolids treatment, optimisation of energy recovery, and development and implementation of nutrient recovery processes. While focusing particular methodology for sewage/brine management and P/Mg recycling, the merits of various approaches specific to each stand-alone process must be brought together in the context of zero
waste, quality control, transparency and effective product recovery. The European Commission has also estimated that P recycling methods could preferably replace 30% of Europe’s P import for producing mineral based fertilizers. In the context of sustainability and renewability of Mg, it is worth considering the findings from a recent publication which highlighted that for every litre of freshwater output, desalination plants produce approximately 1.5 litre of brine (Jones et al., 2018). On the global level this equates to 142 million cubic meters of hypersaline brine discharged every day, as a magnesium rich waste stream. Unfortunately to date, the high economic costs and energy demands of brine treatment for the recovery of magnesium remains a significant barrier to more widespread application. The role of research and innovation is critical to realise a closed loop solution to this immediate issue, and membrane separation technical developments now offer a viable future path. Indeed, future vision on committing to ‘sustainability’ and ‘zero waste’ are focused greatly on CRM recovery from waste to stay well ahead of strict regulations on waste management and circular economy.

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