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Development of Separation Techniques for Magnesium Recovery: A Mini-Review

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The rapid rise of industrialization prompts an increase in wastewater discharge, which worsens water pollution conditions worldwide. Although a naturally occurring metal in water, magnesium can cause environmental problems when discharged with concentrated amounts in exhaust brine and wastewater. Aside from its environmental impact, the recovery of magnesium also presents excellent economic value since it is considered one of the 30 Critical Raw Materials cited by the European Union. The demand for magnesium is also continuously rising in the automobile, fertilizer production, paper and pulp, and wastewater treatment industries. With the environmental and economic favor of extracting magnesium, this review seeks to explore and discuss separation techniques developed and studied throughout the years. For magnesium extraction, separation techniques vary from conventional precipitation-crystallization methods to alternative and integrated methods such as adsorption, solvent extraction, and membrane separation. With this, the advantages and disadvantages of each method will be analyzed through their metal removal efficiency, optimal extraction parameters utilized, and other external conditions presented.

1. Introduction

In the 21st century, rapid industrialization results in increased wastewater discharge that often contains levels of soluble heavy metals with harmful properties. Among the various heavy metals in wastewater, magnesium (Mg) is one of the most harmless pollutants, indicated by its lack of limiting regulations in drinking water and effluents. Although Mg is not necessarily an adverse water pollutant, elevated levels of Mg in industries can cause permanent hardness on water and subsequent problems in recycling (Wang et al., 2019).

Mg is listed as one of the 30 critical raw materials (CRM) by the European Union (Vassallo et al., 2021). In recent years, Mg has also seen rising demand in the automobile, fertilizer production, paper and pulp, and wastewater treatment industries (Le et al., 2021). Conventional methods of obtaining Mg include mineral mining and seawater extraction. Interest in alternative sources such as industrial wastewater and brines have been increasing as it provides sustainable means of obtaining the said metal (Vassallo et al., 2021). With everything considered, the extraction of Mg from industrial wastewater can have both environmental advantages through sustainable effects and corresponding significant economic benefits.

Increasing interest in obtaining heavy metals, such as Mg, through wastewater has realized the study and development of several separation techniques. Researchers continually search for more sustainable, efficient, and cost-effective wastewater treatment technology (Rathour et al., 2019). Current techniques ranging from conventional methods to alternative and integrated methods can be classified into five categories: (1) chemical-based, (2) electric-based, (3) membrane-based, (4) adsorption-based, and (5) photocatalytic-based (Qasem et al., 2021).

The objective of this mini-review is to consolidate and examine the existing literature concerning the various techniques employed for Mg extraction and recovery. By compiling both older and recent studies, the methodologies employed in the selected approaches can be adequately evaluated and compared. Through this process, the paper aims to identify the existing research gaps and potential future avenues for Mg extraction and recovery, thereby providing the novelty of this work. To be specific, the paper caters to a more selective list of separation techniques for Mg extraction, namely chemical precipitation and crystallization, adsorption, solvent extraction, electrocoagulation, and integrated methods.

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2. Separation Technologies for Magnesium Recovery

The following section describes the separation technologies for Mg recovery from industrial wastewater or brine. With it, the description of each separation technology, their qualities and gaps, and their significant results in extracting Mg are enumerated.

2.1 Chemical Precipitation and Crystallization

Chemical precipitation is a conventional method utilized in treating wastewater and is most widely implemented for its simple operation and low-cost removal of heavy metals from inorganic effluents. It utilizes a deposition mechanism of converting metal ions into insoluble compounds via a precipitating agent. Subsequent sedimentation and filtration are then used to separate agglomerated precipitates from the aqueous phase (Zhou et al., 2018). Crystallization, on the other hand, is a similar process with a distinction in its solid products of crystalline structures (Ma et al., 2020).

Studies on hydroxide precipitation to extract magnesium hydroxide ($Mg(OH)_2$) take precedence with the implementation of precipitating agents, such as sodium hydroxide (NaOH), ammonium hydroxide (NH_4OH), and calcium hydroxide ($Ca(OH)_2$). A study by Ahmad et al. (2019) investigated the three mentioned inorganic precipitants and concluded that, at the same operating conditions, NaOH is best suited to treat seawater brine due to its faster reaction time and crystal growth of materials, including Mg precipitants. Cipollina et al. (2015) also observed that the purity of Mg precipitates all range across 98-100 % when NaOH is used as the alkaline source when performed in varying operating conditions.

Other precipitation agents have also been explored, including the use of carbonates (Caulfield et al., 2022), phosphates (Sorour et al., 2014), oxalic acid (Wang et al., 2019), organic alkyl phenoxy acetic acid derivatives (Wang et al., 2019), and the simultaneous addition of aluminum and fluorine (Mahrou et al., 2021). These methods present opportunities in heavy metal recovery with a variety of metal removal efficiency, metal selectivity, and process speed.

Different precipitating agents used for chemical precipitation and crystallization of Mg, along with their optimal parameters and optimal recovery and removal percentage, are summarized in Table 1.

Table 1: Different precipitants and their respective optimal parameters and magnesium extraction percentage

Precipitant	Treated Medium	Optimal Parameters	Percentage Mg Recovery/Removal	Ref
NaOH	Exhausted Brines	NaOH flow rate = 14 ml/min C_{NaOH} = 4 M; C_{Mg} = 1 M	99–100 %	Cipollina et al. (2015)
	Desalination plant reject brine	NaOH to Mg^{2+} molar ratio = 2	94–99 %	Dong et al. (2018)
	Desalination plant reject brine	pH = 10 Temperature = 90 °C	98 %	Ahmad et al. (2019)
	Steelmaking Slag Leach Liquor	pH = 9.57 Stabilization time = 5 min Temperature = 80 °C	100 %	Kim and Azimi (2022)
NH_4OH	Desalination plant reject brine	NH_4OH to Mg^{2+} molar ratio = 6	>90 %	Dong et al. (2017)
	Desalination plant reject brine	Temperature = 14.9 °C Brine salinity = 85.4 g/L NH_3 to Mg molar ratio = 4.4	99 %	Mohammad et al. (2019)
Na_2CO_3	Synthetic Brine	pH > 11	85.6–91.3 %	Sorour et al. (2014)
Na_3PO_4	Synthetic Brine	pH = 8.1–8.4	24–47 %	Sorour et al. (2014)
Oxalic Acid	Rare earth industry wastewater	N/A (not optimized)	58.1 %	Wang et al. (2019)
Alkyl phenoxy acetic acid derivatives	Rare earth industry wastewater	Use of 4-tertoctyl phenoxy acetic acid (O-POAA)	95 %	Wang et al. (2019)
Aluminum & Fluorine	Phosphoric Acid	Temperature = 80 °C Metallic Al to Mg ratio = 1 NaF to Mg ratio = 16	70 %	Mahrou et al. (2021)

Precipitation methods often possess limitations on high sludge production with toxic properties, which may incur additional costs when further treated or secondary pollution concerns when improperly addressed (Abidli et al., 2022).

Bioprecipitation is an alteration to the conventional process through substituting chemical precipitants with microorganisms. The study of Sun et al. (2020) explored the bioprecipitation of mineral carbonate and phosphate using *Citrobacter freundii* ZW123 bacterium, which showed success in precipitating calcite, Mg-rich calcite, and struvite from an Mg and Ca-rich laboratory simulated water. The authors noted how the bacterium promoted pH increase and drove supersaturation by providing carbonic anhydrase (CA), alkaline phosphatase, and ammonium. CA is an enzyme that has been found to greatly enhance the precipitation of carbonates. Caulfield et al. (2022) used the enzyme both directly through bovine CA and indirectly through microalgae and found that it promoted magnesium carbonate precipitation at relatively low temperatures and pressures.

Another solution to conventional precipitation is the novel technology of fluidized bed reactors (FBRs), which can extract target compounds in wastewater with minimal moisture content (Seckler, 2022).

A study by Le et al. (2021) is one of the few studies on utilizing FBR technology to extract Mg. Their study employed the fluidized bed homogeneous granulation (FBHG) process using sodium carbonate as the precipitating agent to extract magnesium carbonate from raw Mg-rich wastewater. Carbon capture and storage implications were explored through the recovered product of nesquehonite ($MgCO_3 \cdot 3H_2O$).

2.2 Alternative Methods

Besides the conventional chemical precipitation method, other separation techniques have also been used to address, remove, or recover Mg in wastewater and industrial brines. This study explores the more common processes of adsorption, solvent extraction, and electrocoagulation.

2.2.1 Adsorption

The adsorption process involves the accumulation of target substances at the surface of the adsorbent, where an interface of two phases is formed (De Gisi et al., 2016). Adsorption, in general, is a practical, cost-effective, and versatile method for heavy metal removal as it offers a wide variety of adsorbent materials and a flexible design and operation for the treatment of wastewater (Abidli et al., 2022). It also presents an economic advantage regarding the reversible nature of some adsorption processes, where adsorbents can undergo desorption to be regenerated and reused (Fu and Wang, 2011). Disadvantages of the process include poor compound selectivity and excess waste products from adsorbents (Saleh et al., 2022).

Related studies commonly fall along treating water hardness in the form of Ca^{2+} and Mg^{2+} ions in addressing Mg using adsorption. An earlier study by Mubarak et al. (2016) utilized rice husk-based magnetic biochar in extracting Mg from a simulated solution with varying parameters of pH, adsorbent dosage, agitation speed, and contact time. A more recent and novel study in adsorbing Ca^{2+} and Mg^{2+} ions involves using alginate/citrate composite aerogel (CA-SC) adsorbents (Wang et al., 2021). The CA-SC adsorbents combine with the target ions through coordination effects and have been found to have a maximum capacity of 36.23 mg/g.

The use of biological specimens through biosorption has also been implemented in magnesium extraction. The native bacteria specimens from Djebel Onk have been studied and found to have great magnesium sorption abilities (Rabia et al., 2021). The study involves the purification of phosphate ores and has found that *Bacillus sp.* HK4 strain performed the best with a biosorption capacity of 8000 µg Mg/g at a pH of 7. For aqueous medium studies, a recent study by Sharma and Devi (2023) utilized *Bellamya bengalensis* shell dust to treat industrial wastewater. Results indicated a decrease in magnesium concentration and total hardness of treated waters.

2.2.2 Solvent Extraction

Solvent extraction is a liquid-liquid extraction process that utilizes the selective distribution of target metal ions between two immiscible phases, typically between an aqueous and organic phase (Nicol et al., 2022). Solvent extraction technology presents industrial advantages through its straightforward process design, implementation, and large-scale production. It also provides high metal recovery efficiency, remarkable selectivity, and low energy consumption. The effectiveness of solvent extraction does come with the price of utilizing highly toxic solvents (Abidli et al., 2022).

A sustainable extraction method recently utilized a three-liquid-phase-extraction (TLPE) system with green solvents. In the study of (Kurtulus et al., 2022), an aqueous sample containing zinc, copper, and Mg was treated with deep-eutectic solvent (DES)-based TLPE process to separate and extract the three metals in an acid-rich top phase, a DES-rich middle phase, and a salt-rich bottom phase, respectively. Besides treating water samples with Mg, common studies on Mg extraction involve its separation from industrial brines and solutions. Mainly, the presence of Mg was separated from lithium-rich brines using Versatic Acid 10 [V10] and Aliquat 336 [A336] (Li et al., 2019), and β-diketone and Cyanex 923 (Li and Binnemans, 2020), with high removal efficiencies.

2.2.3 Electrocoagulation

Electrocoagulation utilizes principles of electrochemistry to produce metal ion coagulants on the anode, destabilizing target substances to form complex anions capable of producing aggregates. Following the formation of flocs, these can subsequently be collected by the flotation process initiated by hydrogen gas produced in the cathode (Saleh et al., 2022). Compared to typical chemical coagulation, electrocoagulation-flotation is more cost-effective and environmentally friendly due to using electrodes instead of chemicals to drive the separation process (Butler et al., 2011). Electrochemical treatment methods such as electrocoagulation does require high capital investment to run and operate (Fu and Wang, 2011).

In line with the mentioned adsorption studies, most studies on the electrocoagulation separation of Mg from water coincide with the treatment of hard water with high Ca and Mg impurities. A study on the electrocoagulation technique in removing water hardness conducted by Helmy et al. (2017) utilized a square aluminum (Al) plate as the cathode and four arrays of Al cylinders as the anode. Another study experimented on three different electrodes, namely stainless steel, Al, and iron (Fe), to perform electrocoagulation on hard water (Hamada et al., 2018). Both studies explored several parameters, including initial pH, current density, and operation time to optimize the electrocoagulation of magnesium. Overall, significant removal percentages were observed for the process.

A summary of the varying alternative method in extracting Mg, along with their optimal parameters and optimal recovery and removal percentage, is listed in Table 2.

Table 2: Alternative methods and their optimal parameters in extracting magnesium (A: adsorption, S: solvent extraction, E: electrocoagulation)

Treating Substance	Treated Medium	Optimal Parameters	Percentage Mg Recovery/Removal	Ref
A: Rice husk-based magnetic biochar	Simulated Mg solution	pH = 4.0 Adsorbent dosage = 0.5 g Agitation speed = 150 rpm Contact time = 180 min	95 %	Mubarak et al. (2016)
A: CA-SC	Deionized water	3.0 w/v% sodium alginate & 5.0 w/v% ethylenediamine pH = 5.0–9.5 Adsorption time = 6 h	96.8 %	Wang et al. (2021)
S: [V10] [A336]	Synthetic Mg-Li brine	[V10] [A336] = 1.0 M, 64 vol %	>98 %	Li et al. (2019)
S: β-diketones and Cyanex 923	Synthetic Mg-Li brine	Use of HPMBP β-diketone pH = 4.5		Li and Binnemans (2020)
S: DES-based TLPE	Filtered Meriç river water samples	D2EHPA (acid phase)/hexane = 20 % (v/v) DES loading = 1.72 g K_2HPO_4 (salt phase) = 3.12 g	98.1 %	Kurtulus et al. (2022)
E: Al electrode	Hard water solution	Operation time = 60 min Current density = 50.56 mA/cm^2 pH = 10	100 %	Helmy et al. (2017)
	Treatment plant wastewater	Inter-electrode spacing = 1 cm Operating time = 40 min Current density = 3.18 mA/cm^2 pH = 7.45	95.2 %	Hamada et al. (2018)
E: Stainless steel electrode	Treatment plant wastewater	Same parameters from one reference	92.30 %	Hamada et al. (2018)
E: Fe electrode	Treatment plant wastewater		87.64 %	Hamada et al. (2018)

2.3 Integrated Methods

Separation techniques usually have disadvantages that hinder great qualities in treatment and practical application in the large-scale industry. Therefore, implementing subsequent or concurrent methods may be needed to optimize the quality and ability of specific methods into integrated methods (Zhou et al., 2018).
A recent development is the novel ion exchange membrane crystallizer (CrIEM) developed by La Corte et al. (2020), which integrates reactive crystallization and membrane separation to recover high-purity magnesium. The method implemented an anion exchange membrane separating an alkaline and saline compartment. It utilizes the membrane to prevent the mixing between solutions and directs the crystallization of magnesium hydroxide, thoroughly avoiding the risk of co-precipitation of contaminated crystals. The process recovered magnesium with efficiencies above 89 % and purity grade above 94 %. This novel method was reinforced by a simulation tool study by Vassallo et al. (2021). In the study, experimental data, laboratory tests, and literature studies were conducted and compiled to provide a suitable model for the said system.

3. Conclusions

The various separation techniques for magnesium extraction, from conventional to alternative and integrated methods, have shown unique properties and abilities that merit their operation. The presented pros and cons of each method can be used to gauge the opportunities and gaps in the varying chemicals, materials, and technology in previous studies. The review has also noted gaps in the collated works of literature by its applicability in industrial operations as the limited assessment has been done on large-scale processes and process systems. In developing a feasible and effective process for extracting magnesium from wastewater, more studies should be conducted on the up-scaling, economic analysis, and environmental impact assessment of the methods applied at an industrial level. The continual development of separation processes can see to realize the demand for magnesium resources through wastewater and reject brines. The development of alternative and integrated methods also presents a great opportunity for practical decisions for succeeding magnesium resource supply. The future direction of the study in terms of analysis of the use of varying magnesium precipitates as products can be explored. Economic studies on its profitability and environmental studies on its sustainability can then be evaluated.

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