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A Review on Lithium Removal Techniques in Aqueous Environment

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Abstract: The growing demand for lithium in renewable energy technologies, such as batteries for electric vehicles and energy storage systems, has led to an increase in its extraction and processing activities, resulting in elevated levels of lithium in industrial wastewater. The effective removal of lithium from wastewater is crucial to mitigate its environmental impact and recover this valuable resource. This review provides a comprehensive overview of the current methods for lithium removal from industrial effluents, including chemical precipitation, ion exchange, adsorption, membrane technologies, and electrochemical processes. It evaluates these methods in terms of efficiency, cost, environmental impact, and scalability. Additionally, emerging approaches such as bio-remediation and hybrid techniques are discussed, highlighting their potential for enhanced lithium recovery. The review also identifies knowledge gaps and future research directions to optimize lithium removal and recovery processes. By consolidating current advancements and challenges, this work aims to guide researchers and industry stakeholders in developing sustainable solutions for lithium management in industrial wastewater.

Keywords: *Lithium, Wastewater, Bio-Remediation, Industrial, Energy.*

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I. INTRODUCTION

The name lithium originates from the Greek word *lithos* (stone), its most naturally abundant source Spodumene ($LiAlSi_2O_6$) has diminished so lithium is now commonly obtained from brines as lithium carbonate [1]. Lithium (Li, Atomic No 3) is a soft, silvery-white metal that can be easily cut with a knife and it is a very reactive alkali metal. It is the lightest metal and the least dense solid element known, making it highly hunted for countless industrial and commercial applications. Lithium is highly reactive, especially with water. It also readily forms compounds with other elements [2] .

Lithium's low density and high electrochemical potential makes it valuable in lightweight applications and battery production respectively. Lithium parades good thermal conductivity, which makes it suitable in heat transfer applications. One of the most significant applications of lithium is in rechargeable lithium-ion batteries, which are widely used in portable electronic devices such as smartphones, laptops, tablets, and electric vehicles (EVs). Lithium-ion batteries offer high energy density and long cycle life.[3, 4]. In the health sector lithium compounds have used in the treatment of bipolar disorder and depression and salts such as lithium carbonate and lithium citrate are prescribed as mood stabilizers. Lithium compounds are used as thickening agents in greases and lubricants due to their capacity to provide high viscosity and good adhesion properties.

Lithium compounds are also used in the manufacture of ceramics and glass, where they act as fluxes to lower the melting point and improve the properties of these materials.

Lithium is mostly alloyed with aluminium, copper, and magnesium to improve their strength, hardness, and conductivity. These alloys find applications in aerospace and automotive industries. This valuable metal has also found use in nuclear fusion reactions as a fusion fuel and as a coolant in some types of nuclear reactors.

Lithium chloride is used in air conditioning systems and industrial drying processes as a desiccant to absorb moisture from the air. Lithium compounds are used as reagents in organic synthesis reactions, particularly in the production of pharmaceuticals and fine chemicals. Lithium boasts the highest electrochemical potential among metals, making it an ideal choice for battery applications. Pursuant to its unique intrinsic properties lithium and its derivatives have been utilized in a plethora of application as shown in figure 1.

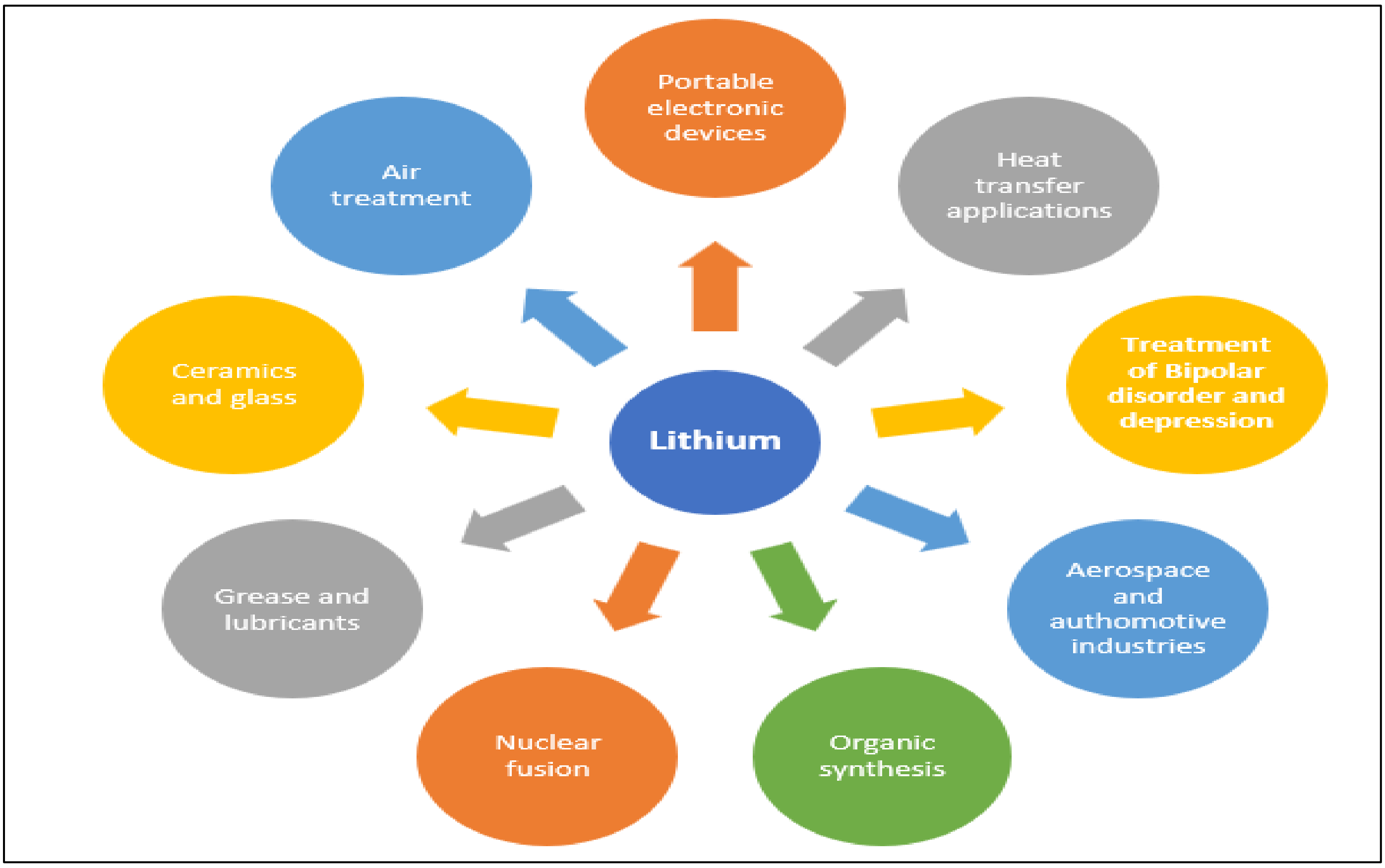

Fig 1 Applications of Lithium

With a wide vista of applications lithium systematically seeps into the environment unnoticed because of its minute size.

II. LITHIUM EXTRACTION PROCESSES

Lithium sequestration is a critical process, especially with the rising demand for lithium in the production of batteries for electric vehicles, portable electronics, and renewable energy storage. Several methods have been developed for extracting and sequestering lithium, each with its own merits and demerits. The most prominent methods include solar evaporation, extraction from spodumene ores, and direct lithium extraction (DLE) from brines.

➢ *Solar Evaporation*

Solar evaporation is a traditional method used to extract lithium from brine sources. This process involves pumping lithium-rich brine into large ponds, where it is left to evaporate under the sun. Over time, the lithium concentration increases, and the concentrated brine is further processed to extract lithium.

- *Advantages:*

✓ *Low Energy Requirement*: The process relies primarily on solar energy, making it energy-efficient and cost-effective in regions with high solar insolation.
✓ *Simplicity*: It is a well-established and simple process that has been used for decades.
✓ *Scalability*: Solar evaporation can be easily scaled up by increasing the number and size of evaporation ponds.

- *Disadvantages:*

✓ *Time-Consuming*: The process can take several months to years to complete, which is a significant drawback in meeting the rapidly growing demand for lithium.
✓ *Environmental Impact*: The process requires vast areas of land and can lead to habitat disruption. Additionally, it is highly water-intensive, which is problematic in arid regions.
✓ *Low Efficiency*: The lithium recovery rate is relatively low, leading to the loss of significant amounts of lithium in the residual brine [4].

➢ *Extraction from Spodumene Ores*

Lithium can also be extracted from hard rock minerals, particularly spodumene. The extraction process involves crushing the ore, followed by high-temperature processing to convert spodumene to a form that can be leached with acid to recover lithium.

- *Advantages:*

✓ *High Lithium Concentration*: Spodumene ores typically contain higher concentrations of lithium compared to brines, making the extraction process more efficient.
✓ *Shorter Extraction Time*: Unlike solar evaporation, the process can be completed in a much shorter time frame.

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- ✓ *Controlled Environment:* Extraction from ores allows for better control over the process and quality of the final product.

- Disadvantages:
- ✓ *Energy-Intensive:* The process requires significant energy inputs, particularly in the high-temperature conversion of spodumene.
- ✓ *Environmental Concerns:* Mining activities associated with spodumene extraction can have adverse environmental impacts, including habitat destruction, soil erosion, and pollution from tailings.
- ✓ *Higher Costs:* The overall cost of extraction from ores is higher compared to brine extraction, particularly when energy and environmental mitigation costs are considered [5].

➢ *Direct Lithium Extraction (DLE)*

DLE is an emerging technology that aims to extract lithium directly from brine using a variety of methods, including ion exchange, solvent extraction, and membrane separation. This process is designed to be more efficient and environmentally friendly than traditional methods.

- *Advantages:*

- ✓ *High Efficiency*: DLE processes can achieve higher lithium recovery rates compared to solar evaporation, potentially extracting over 90% of the lithium present in brines.
- ✓ *Lower Environmental Impact*: DLE processes can be less water-intensive and require less land, reducing their environmental footprint.
- ✓ *Faster Processing*: The process can be completed in a matter of hours or days, making it much faster than solar evaporation.

- *Disadvantages:*

- ✓ *Complexity*: DLE processes are more complex and require advanced technology and expertise, which can limit their widespread adoption.
- ✓ *High Initial Costs:* The initial capital investment for DLE facilities is higher compared to traditional methods, although operational costs may be lower in the long term.
- ✓ *Technological Maturity*: Many DLE technologies are still in the development or early commercialization stages, meaning their long-term viability and scalability are yet to be fully proven [6].

Each lithium sequestration process has its own merits and demerits. Solar evaporation is cost-effective but slow and environmentally taxing, extraction from spodumene is efficient but energy-intensive, and DLE offers high efficiency and lower environmental impact but is technologically complex and costly. The choice of method depends on various factors, including the source of lithium, environmental considerations, and economic viability.

III. KEY PARAMETERS THAT AID THE EASY REMOVAL OF LITHIUM FROM AQUEOUS SYSTEMS

The easy removal of lithium and its derivatives from wastewater depends on several key parameters namely:

➢ *pH of the Wastewater*

Lithium removal is highly pH-dependent primarily because pH influences lithium speciation, solubility, and interaction with removal agents. Accordingly, Precipitation methods work best at alkaline pH (e.g., using phosphate or carbonate). Adsorption and ion-exchange processes may require neutral to slightly acidic conditions[7]

- *Precipitation Reactions Are pH-Sensitive*

Lithium does not easily form insoluble hydroxides like other metals (e.g., $Fe(OH)_3$, $Al(OH)_3$). However, it can be removed by precipitation with phosphate (Li_3PO_4), carbonate (Li_2CO_3), or aluminum hydroxides, which depend on pH:

- *Ion-Exchange and Adsorption Efficiency Varies with pH*

Lithium removal by ion-exchange resins and adsorbents (e.g., MnO_2, Al_2O_3, zeolites, bio-adsorbents) depends on pH because at low pH, competing H^+ ions reduce lithium adsorption.

While at high pH, adsorbent surface charges may repel Li^+ or change structure. Generally, optimal adsorption is often at neutral to slightly alkaline pH (~7–9).

- *Solubility and Speciation of Lithium Derivatives*

Lithium is mostly present as free Li^+ ions in wastewater, which do not precipitate easily. However, some lithium compounds such as LiF, Li_2CO_3 and Li_3PO_4 become less soluble at higher pH values thereby enabling removal. At extreme pH values, lithium may form soluble complexes such as LiOH at very high pH and this reduces removal efficiency.

- *Electrochemical Removal Efficiency*

In electrochemical lithium recovery, pH affects the reaction kinetics at the electrode surface. Therefore, Lithium intercalation into selective materials (e.g., $LiMn_2O_4$) is optimal at a specific pH range.

➢ *Presence of Coexisting Ions*

High concentrations of competing cations such as Na^+, K^+, Ca^{2+}, Mg^{2+} can interfere with ion-exchange and adsorption efficiency. Meanwhile, anionic species such as SO_4^{2-} and Cl^- can influence lithium speciation and precipitation.

➢ *Temperature*

Some removal processes, such as evaporation and membrane separation, work more efficiently at elevated temperatures. Therefore, adsorption capacity of certain materials such as zeolites and manganese oxides may increase with temperature.

➢ *Lithium Concentration*

Low lithium concentrations (< 10 mg/L) make recovery more challenging and require selective adsorbents or advanced membrane technologies. High concentrations allow for direct precipitation and chemical recovery.

➢ *Organic and Inorganic Contaminants*

The presence of organics (e.g., surfactants, oils) can foul membranes and adsorbents. Aqueous systems with high turbidity and suspended solids may require pre-treatment (e.g., coagulation and filtration processes) [8].

Table 1 Summary of Best Method Based for Lithium Removal

Method	Best for	Pre-treatment Needed (Surfactants, pH, etc.)	Challenges
Precipitation (Li_2CO_3, Li_3PO_4)	High Li concentration (>100 mg/L)	Requires pH increase (to >10)	Surfactants interfere, pH control needed
Adsorption (MnO_2, Ion-sieves, Zeolites)	Moderate Li concentration (10–100 mg/L)	pH adjustment (7–9), surfactant removal	Adsorbent fouling, lower efficiency at acidic pH
Ion Exchange (Lithium-selective resins)	Moderate Li concentration (10–100 mg/L)	Pre-filtration needed (carbon treatment)	Expensive, affected by competing ions
Membrane Filtration (RO/NF)	High TDS, Lithium separation	Surfactant removal needed	High energy cost, membrane fouling
Electrochemical Recovery (CDI, Intercalation)	High-purity Lithium recovery	Surfactant removal, voltage control	High initial cost

Table 2 Selectivity of Methodsused for Lithium Removal

Method	Best for	Pre-treatment Needed?	Advantages	Challenges
Chemical Precipitation	High Li concentration (>100 mg/L)	Yes (pH increases surfactant removal)	Simple, cost-effective	High sludge production, pH control
Adsorption (MnO_2, Ion-sieves)	Moderate Li concentration (10–100 mg/L)	Yes (pH 7–9, surfactant removal)	Selective, reusable adsorbents	Adsorbent fouling, regeneration required
Ion Exchange (Lithium-selective resins)	Moderate Li concentration (10–100 mg/L)	Yes (pH 6–8, surfactant removal)	High selectivity for lithium	Expensive, affected by competing ions
Membrane Filtration	Lithium concentration & TDS removal	Yes (surfactant removal)	Efficient for lithium recovery	High energy cost, membrane fouling
Electrochemical Removal	High-purity lithium recovery	Yes (surfactant removal)	Lithium extraction for reuse	High capital cost, requires fine control

IV. EFFECTIVE MANAGEMENT OF LITHIUM WASTE

The increasing demand for lithium-ion batteries, driven by the proliferation of electric vehicles and portable electronics, has resulted in a significant rise in lithium waste. Effective management of this waste is crucial to mitigate environmental impacts and recover valuable resources. This article explores key strategies for the effective management of lithium waste, emphasizing recycling, resource recovery, and policy frameworks.

➢ *Recycling and Resource Recovery*

Recycling is a critical component of lithium waste management. Lithium-ion batteries contain valuable metals like lithium, cobalt, nickel, and manganese, which can be recovered and reused. The recycling process generally involves several stages, including collection, sorting, dismantling, and material recovery through hydrometallurgical or pyrometallurgical methods [9](Gaines, 2018). Hydrometallurgy, which uses aqueous solutions to extract metals, is often preferred due to its lower energy consumption and higher recovery rates [10](Zeng et al., 2014).

One challenge in recycling lithium-ion batteries is the diverse range of battery chemistries and formats, which complicates the recycling process. To address this, some companies are developing advanced technologies that can handle mixed battery streams and recover a broader range of materials [11](Harper et al., 2019). Additionally, improving battery design to facilitate easier disassembly and recycling can further enhance the efficiency of resource recovery [9](Gaines, 2018).

➢ *Safe Disposal and Environmental Protection*

When recycling is not feasible, safe disposal of lithium waste is essential to prevent environmental contamination. Lithium-ion batteries contain hazardous materials that can leach into the soil and water if not properly managed [10] (Zeng et al., 2014). Therefore, it is crucial to establish guidelines for the safe collection, storage, and disposal of lithium waste.

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Landfilling of lithium waste is discouraged due to the potential for environmental harm. Instead, thermal treatment or stabilization methods can be used to neutralize hazardous components before disposal. Moreover, developing closed-loop recycling systems, where waste is processed to produce new batteries or other products, can reduce the need for disposal altogether [9] (Gaines, 2018).

➢ *Regulatory and Policy Frameworks*

Effective management of lithium waste also requires robust regulatory and policy frameworks. Governments play a key role in setting standards for waste management, recycling, and environmental protection. Extended Producer Responsibility (EPR) policies, which make manufacturers responsible for the end-of-life management of their products, can drive improvements in recycling and waste reduction [11] (Harper et al., 2019).

In addition to EPR, regulations that mandate minimum recycling rates and prohibit the disposal of lithium batteries in landfills can further promote sustainable waste management practices. Incentives for research and development of new recycling technologies, as well as public awareness campaigns, are also important components of a comprehensive policy approach [10] (Zeng et al., 2014).

➢ *Future Directions and Challenges*

Despite progress in lithium waste management, several challenges remain. The growing volume of lithium-ion batteries reaching end-of-life, combined with the complexity of recycling processes, poses significant logistical and technical challenges. Moreover, the economic viability of recycling depends on the fluctuating prices of recovered materials and the cost of recycling operations [12].

To overcome these challenges, continued innovation in recycling technologies and battery design is necessary. Collaborative efforts between industry, government, and research institutions can drive the development of more efficient and sustainable waste management solutions. Additionally, international cooperation is needed to address the global nature of lithium waste, as batteries are often produced in one country, used in another, and discarded in yet another.

Effective management of lithium waste is essential to mitigate environmental impacts and recover valuable resources. Recycling and resource recovery, safe disposal practices, and robust regulatory frameworks are key components of a sustainable waste management strategy. As the demand for lithium-ion batteries continues to grow, ongoing innovation and collaboration will be crucial to ensuring that lithium waste is managed in an environmentally responsible and economically viable manner.

V. EFFECTIVE REMOVAL OF LITHIUM FROM AQUEOUS SYSTEMS: PROCESSES AND EMERGING CHALLENGES

The increasing use of lithium in various industries, particularly in the production of lithium-ion batteries, has led to the contamination of aqueous systems with lithium. Effective removal of lithium from water is crucial to prevent environmental pollution and to recover lithium for reuse. This article discusses the various processes used for lithium removal from aqueous systems and highlights emerging challenges associated with these methods.

Several processes have been developed for the removal of lithium from aqueous systems. These include ion exchange, membrane filtration, adsorption, precipitation, and electrochemical methods. Each process has its advantages and limitations, which are discussed below.

➢ *Ion Exchange*

Ion exchange is one of the most widely used methods for lithium removal. It involves the use of ion exchange resins that selectively capture lithium ions from water while releasing other ions, such as sodium or hydrogen, in exchange. Ion exchange resins, particularly those with high selectivity for lithium, have been developed to improve the efficiency of this process [13] (Xie et al., 2019). However, the regeneration of resins and the handling of the waste generated during the process are significant challenges.

➢ *Membrane Filtration*

Membrane filtration techniques, such as nanofiltration and reverse osmosis, have been used to remove lithium from aqueous systems. These processes rely on the size exclusion and charge repulsion mechanisms to separate lithium ions from water [14] (Zhao et al., 2018). Membrane filtration is effective in removing low concentrations of lithium, but the high energy consumption and membrane fouling are major drawbacks.

➢ *Adsorption*

Adsorption is another effective method for lithium removal, particularly when using materials with a high affinity for lithium ions. Various adsorbents, such as activated carbon, clay minerals, and metal-organic frameworks (MOFs), have been studied for this purpose [15] (Kim et al., 2020). Adsorption is a cost-effective process, but the selectivity of adsorbents and the challenges associated with adsorbent regeneration limit its widespread application.

➢ *Precipitation*

Chemical precipitation involves the addition of reagents that react with lithium to form insoluble compounds, which can then be removed from the water. This method is effective in treating high concentrations of lithium, but the disposal of the precipitated sludge and the need for precise control of pH and reagent dosage are significant challenges [16] (Li et al., 2017).

➢ *Electrochemical Methods*

Electrochemical methods, such as electrodialysis and electrocoagulation, have been explored for lithium removal from aqueous systems. These methods use electrical energy to drive the separation of lithium ions from water [17] (Su et al., 2019). While electrochemical methods offer high efficiency and the potential for lithium recovery, their high

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energy requirements and the complexity of the systems are notable challenges.

➢ *Bioremediation*

Bioremediation, a sustainable and environmentally friendly approach, has emerged as a potential method for recovering lithium from industrial wastewater. This method leverages the ability of biological systems, such as microorganisms, algae, and plants, to adsorb, accumulate, or transform lithium ions, offering a low-energy alternative to conventional physicochemical processes.

➢ *Mechanisms of Lithium Bioremediation*

- *Biosorption*

Biosorption involves the passive binding of lithium ions onto the surface of biological materials, including dead biomass or cell walls of microorganisms. Functional groups such as carboxyl, hydroxyl, and phosphate present in biomass contribute to the binding of lithium. Certain bacteria and fungi, such as *Bacillus subtilis* and *Saccharomyces cerevisiae*, have shown potential for lithium biosorption due to their high surface area and active sites [18] (Wang et al., 2021).

- *Bioaccumulation*

In contrast to biosorption, bioaccumulation refers to the active uptake and intracellular storage of lithium by living cells. Microalgae, such as *Chlorella vulgaris* and *Scenedesmus obliquus*, have demonstrated the ability to bioaccumulate lithium through ion transport mechanisms [19](Liu et al., 2022). These systems rely on specific or non-specific transport proteins, allowing for selective lithium uptake even in the presence of competing ions.

- *Phytoextraction*

Certain hyperaccumulating plant species can absorb lithium from contaminated water and concentrate it within their tissues. Although still in the exploratory phase, phytoextraction offers a promising route for large-scale remediation, especially for low-concentration lithium wastes [20] (Kumar et al., 2020).

- *Advantages of Bioremediation*

✓ Sustainability: Bioremediation processes rely on renewable biological agents, minimizing energy consumption and environmental harm.
✓ Selectivity: Certain organisms exhibit selective uptake of lithium, even in the presence of other alkali and alkaline earth metals.
✓ Cost-Effectiveness: Compared to conventional methods like ion exchange or membrane separation, bioremediation can reduce operational costs, especially when utilizing waste biomass.

- *Challenges and Future Directions*

Despite its promise, bioremediation faces challenges such as:

✓ Limited capacity for lithium uptake compared to conventional methods.
✓ The need for genetic or metabolic engineering to enhance specificity and efficiency.
✓ Difficulty in recovering lithium from the biomass after accumulation.
✓ Future research should focus on:
✓ Exploring extremophiles and genetically modified organisms tailored for lithium recovery.
✓ Investigating synergistic approaches combining bioremediation with other technologies, such as adsorption or electrochemical methods.
✓ Developing scalable systems that integrate bioremediation into existing industrial processes.

Bioremediation offers a green and innovative solution for lithium recovery from industrial wastewater. While still in its infancy, advancements in microbial and plant biotechnology hold the potential to transform this approach into a commercially viable and sustainable alternative. Continued interdisciplinary research will be key to overcoming existing challenges and optimizing this method for industrial applications.

➢ *Emerging Challenges*

Despite the availability of various processes for lithium removal, several challenges remain in ensuring their effectiveness and sustainability.

➢ *Selectivity and Efficiency*

One of the major challenges in lithium removal is achieving high selectivity and efficiency, especially in the presence of competing ions such as sodium, magnesium, and calcium. Developing materials and processes that can selectively target lithium ions without being affected by other ions is crucial for improving the efficiency of lithium removal [21] (Xie et al., 2019).

➢ *Environmental Impact*

The environmental impact of lithium removal processes, particularly in terms of waste generation and energy consumption, is a significant concern. For example, ion exchange and chemical precipitation generate waste streams that require proper disposal, while membrane filtration and electrochemical methods are energy-intensive [14] (Zhao et al., 2018). Minimizing the environmental footprint of these processes is essential for their sustainable application.

➢ *Cost and Scalability*

The cost and scalability of lithium removal processes are also major challenges, particularly for large-scale applications. While some methods, such as adsorption, are relatively low-cost, others, like membrane filtration and electrochemical methods, require significant capital and operational expenses [15] (Kim et al., 2020). Developing cost-effective and scalable solutions is key to the widespread adoption of lithium removal technologies.

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➢ *Recovery and Reuse*

Another emerging challenge is the recovery and reuse of lithium after its removal from aqueous systems. The economic viability of lithium recovery depends on the concentration of lithium in the water and the efficiency of the recovery process. Additionally, the purity of the recovered lithium is crucial for its reuse in industrial applications [22].

VI. CONCLUSION

The removal of lithium from wastewater is pH-dependent largely because pH influences lithium speciation, solubility, and interaction with removal agents. Lithium removal is pH-dependent because pH controls Precipitation reactions (carbonate, phosphate), adsorption and ion-exchange selectivity, Lithium solubility / speciation and electrochemical recovery efficiency. Studies have shown that for optimal lithium removal, neutral to alkaline pH (~7–10) is preferred, depending on the method used. The effective removal of lithium from aqueous systems is essential to protect the environment and recover valuable resources. While various processes, including ion exchange, membrane filtration, adsorption, precipitation, and electrochemical methods, are available for lithium removal, each has its own set of challenges. Improving selectivity and efficiency, minimizing environmental impact, reducing costs, and enhancing recovery and reuse are key areas of focus for future research and development in this field.

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