

Electrochemical Wastewater Refining: A Vision for Circular Chemical Manufacturing

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ABSTRACT: Wastewater is an underleveraged resource; it contains pollutants that can be transformed into valuable high-purity products. Innovations in chemistry and chemical engineering will play critical roles in valorizing wastewater to remediate environmental pollution, provide equitable access to chemical resources and services, and secure critical materials from diminishing feedstock availability. This perspective envisions **electrochemical wastewater refining**—the use of electrochemical processes to tune and recover specific products from wastewaters—as the necessary framework to accelerate wastewater-based electrochemistry to widespread practice. We define and prescribe a use-informed approach that simultaneously serves specific wastewater-pollutant-product triads and uncovers a mechanistic understanding generalizable to broad use cases. We use this approach to evaluate research needs in specific case studies of electrocatalysis, stoichiometric electrochemical conversions, and electrochemical separations. Finally, we provide rationale and guidance for intentionally expanding the electrochemical wastewater refining product portfolio. Wastewater refining will require a coordinated effort from multiple expertise areas to meet the urgent need of extracting maximal value from complex, variable, diverse, and abundant wastewater resources.

1. INTRODUCTION: WASTEWATERS—THE NEXT FRONTIER FOR CHEMICAL REFINING

1.1. Opportunities to Circularize Conventionally Linear Chemical Processes. The chemical sciences are responsible for providing commodities that support societal needs at a meaningful scale. From fermentation processes developed nearly ten thousand years ago to the discovery and production of medicines like penicillin, chemical processes have been iteratively developed to meet dynamic global demands. Modern chemical refining, which provides chemical commodities from readily available feedstocks, began in the 1850s when the first oil well was drilled in Pittsburgh, Pennsylvania.¹ The first century of refining focused primarily on crude oil distillation for lamp fuel and heat until the burgeoning 1940s automobile industry increased demand for complex petrochemical fuels. Hydrocarbon cracking, steam methane reforming, and catalytic reforming enabled an expanded petrochemical product portfolio, including lubricants, monomers, and solvents. These advances enabled improvements in quality of life that increased the volume and variety of commodity chemical manufacturing processes, including Haber-Bosch for ammonia, industrial fermentation for alcohols, and polymerization for plastics. Now centralized refineries and manufacturing facilities convert a few raw material inputs (crude oil, air, natural gas, water, biomass) into the countless chemicals that sustain modern life. Over the course of the 20th century, refineries achieved state-of-the-art integration, energy efficiency, flexibility toward variations in raw material, and economies of scale. Today's chemical manufacturing has generally prioritized high-volume production and distribution and ultimately established linear extract-react-emit economies. As these priorities expand today to

include climate change and the environmental and health effects of solid, gaseous, and waterborne anthropogenic pollutants, there is a renewed critical need for chemical manufacturing to fulfill its mandate of meeting humanity's current and future needs at scale. Twenty-first century state-of-the-art chemical manufacturing must enable circular economies by maximizing resource efficiency, minimizing environmental impacts, and sustaining quality of life amidst diminishing feedstock availability.

1.2. Wastewater Refining Can Address Multifaceted Modern Challenges. To meet global sustainability goals, circular chemical manufacturing converts discharges to products. Reaching net-zero manufacturing emissions by 2050² has motivated the reuse of solid and gaseous emissions via carbon capture and utilization (CCU),³ plastic recycling,⁴ and biomass refining.⁵ In contrast, liquid emissions (i.e., wastewaters) have been understudied as feedstocks for circular manufacturing.^{6,7} Wastewaters carry dissolved contaminants that, left untreated, disrupt aquatic ecosystem biodiversity, exacerbate food scarcity, threaten human water supplies, and contribute to greenhouse gas emissions.⁸ Instead of emitting or removing contaminants, refining wastewater contaminants into purified products could supply a myriad of chemical commodities (e.g., fertilizers, monomers, acids, bases, biomass). Potable water is one resource that is already recovered

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Table 1. Definitions (Alphabetical) of Wastewater Treatment, Chemical Manufacturing, and Electrochemical Wastewater Refining Terms

term	definition	reference
Circular manufacturing	Manufacturing that converts waste products, components, and materials into commodity products	10
Distributed manufacturing	Decentralized production of a commodity at a smaller scale relative to conventional, centralized production of the same commodity	11,12
Electrocatalysis	Electrochemical redox reactions mediated by the transfer of electrons through a catalyst active site	11
Electrochemical separations	Separation processes that involve the use of electrochemical driving forces	13
Potable reuse	The use of highly treated municipal wastewater to augment the raw water supply	14
Primary treatment	The first step of wastewater treatment when materials are removed by flotation or sedimentation	15
Reactive separations	An integration of reaction and separation imposed at the system, unit process, subunit process, or molecular scale	16
Resource recovery	Extraction/recovery of valuable entities from waste; in the case of wastewater, recoverable resources include energy, materials/chemicals, and water	6
Secondary treatment	The second step in most wastewater treatment systems when organic contaminants are removed by biological processes	15
Stoichiometric electrochemical conversions	Homogeneous phase reactions facilitated by electrogenerated reactants	17
Tertiary/advanced treatment	Further treatment of wastewater secondary treatment effluent to remove pollutants like nutrients, metals, or trace organics	15
Use-informed research	Scientific investigation driven by context-specific details of the applied problem area to (1) generate fundamental findings relevant to concrete global challenges and (2) generalize mechanistic understanding of applied technologies to diverse use cases	This work
Use-inspired research	Scientific investigation whose rationale, conceptualization, and research directions are motivated by potential use cases	18
Value proposition	A benefit of an approach to meet a stakeholder need	19
Wastewater(s)	Aqueous effluents from domestic, urban, industrial, or agricultural activities	20
Wastewater-based electrochemistry	The science and engineering of electrochemistry applied to wastewater treatment, resource recovery, or refining	This work
Wastewater refining	The use of chemical processes to tune and recover specific, desired products from wastewater resources	This work

from wastewater, and could support the 40% of the global population that experiences freshwater scarcity.⁹ **Wastewater refining**—the use of chemical transformations to convert wastewater pollutants into tunable manufactured chemical commodities—builds on resource recovery to expand the portfolio of products beyond species already present in wastewaters (Table 1). This approach can address several sustainability goals, including the United Nations Sustainable Development Goals (SDGs) designed “to end poverty, protect the planet, and ensure that by 2030 all people enjoy peace and prosperity.”⁹ Refining wastewater resources could enhance access to fertilizers (SDG 2), promote responsible resource consumption and production (SDG 12), reduce pollutant emissions (SDGs 13, 14), transform industry and infrastructure (SDG 9), and reduce freshwater scarcity (SDG 6). We therefore aim to tackle these circular, sustainable, and climate-adaptive goals by producing chemical products from complex unrefined wastewater streams.

By analogy to oil refining, “crude” wastewaters are promising manufacturing feedstocks because they are abundant, resource-rich, and underutilized. Wastewaters are abundant globally— 2.2×10^{15} L of wastewaters (54% of the volume of all freshwater withdrawals) are discharged annually from municipalities, agriculture, and industry.²⁰ One hundred moles of wastewater are emitted from anthropogenic practices for every mole of CO₂ emitted.²¹ Like oil, wastewaters are rich in chemicals that sustain modern society, including nutrients (N, P, and K), minerals (Ca, Mg, and S), and metals (Li, Co, and Ni) (see Table 2). However, 80% of wastewaters are not adequately treated before discharge.²⁰ Current wastewater management induces environmental damage, and discharges resources worth more than \$100 billion annually (Figure 1). Wastewaters are underutilized because we underestimate their

role in chemical manufacturing and because we lack the chemical processes to extract their value. The varied scales of wastewater (e.g., household, municipality, manufacturing site) could facilitate distributed manufacturing, especially if refining processes are colocated with processes that generate wastewater. In turn, distributed manufacturing (Table 1) can reduce transport-related costs and energy consumption.^{22,23} Establishing frameworks for valorizing pollutants in various scenarios, especially as wastewaters increase in volume with population, can drive innovation toward wastewater refining processes.

Wastewater refining will require a library of chemical unit processes that target, convert, and separate specific contaminants into purified products. We focus on electrochemical wastewater refining processes because: (1) they valorize pollutants to products; (2) they leverage renewable electricity as a driving force; and (3) they enable additional benefits, including process control and modularity. Conventional wastewater treatment tends to focus on meeting discharge regulations via pollutant removal. Wastewater resource recovery extracts valuable existing compounds, such as ammonium and phosphate,²⁴ and chemical mixtures, such as biogas.⁶ Wastewater refining builds on recovery by expanding the portfolio of possible products via tunable chemical transformations. Thermochemical driving forces are insufficient for refining wastewater resources because the high specific heat capacity of water induces prohibitive energy requirements for phase-change reactions and separations. Separations already account for 10–15% of the world’s energy consumption and are high priorities for decarbonization because 80% of existing separations are thermochemical (e.g., crude oil distillation).²⁵ Wastewater refining requires its own fit-for-purpose driving force to achieve circular resource economies.²⁶ **Electrochemical driving forces, powered by**

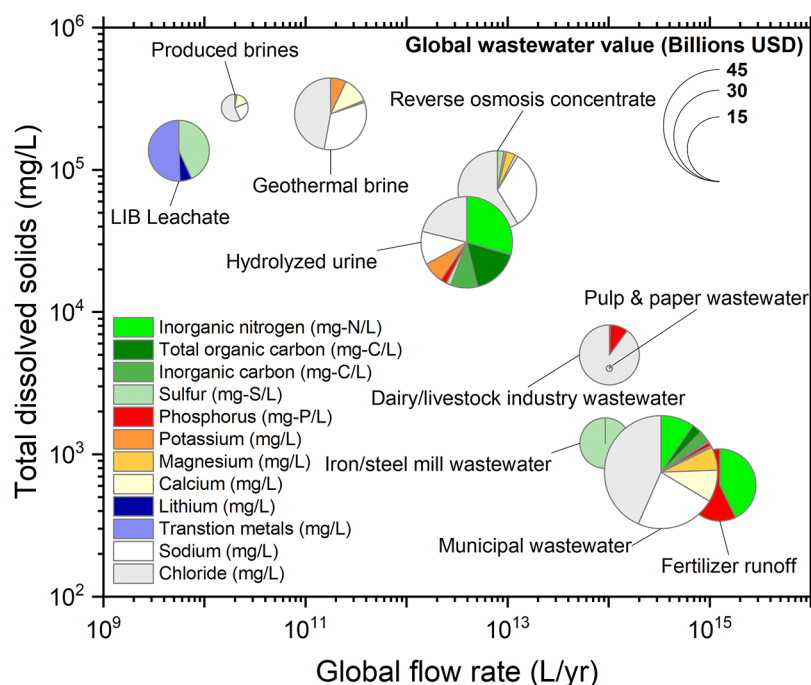


Figure 1. Pie charts of common wastewaters plotted as a function of global flow/generation rate (x-axis) and total dissolved solid concentration (y-axis). The size of each pie chart represents global annual value; the size of each slice represents solute mass fraction. Wastewater composition, volumetric flow rate, and chemical value data were compiled from available data in literature (Supporting Information Section S1). Value was calculated by multiplying the concentration of an element in each wastewater by the corresponding global flow rate and the consumer price of the most common product in conventional manufacturing (e.g., urea for inorganic nitrogen). Sodium and chloride were not included in value calculations, but mass fractions from available data are shown.

renewable electricity, are uniquely poised to valorize solutes through electrocatalysis, stoichiometric electrochemical conversions, and electrochemical separations. Electrochemistry also boasts facile process control (electrode free energy via potential and reaction rate via current), replacement of chemical oxidants and reductants with electrons, and a high degree of modularity. This modularity helps manage the varied composition of wastewaters, which requires tunable processes to convert various contaminants into products (Table 2). Fortunately, driving selective reactions and separations at solid–liquid interfaces is precisely where electrochemistry thrives. The vision of electrochemical wastewater refining is to leverage electrochemical driving forces to generate circular, decarbonized products that are indistinguishable from those produced in conventional linear processes.

1.3. Closing the Gap between Opportunity and Practice for Wastewater Refining. The central thesis of this Perspective is that electrochemical wastewater refining presents tractable challenges and impactful opportunities that require integrated fundamental and applied advances from chemical scientists. Ultimately, wastewater-based electrochemistry must address pervasive sustainability challenges and reach meaningful deployment in 27 years (by 2050), much less time than 20th century refining took to develop. Integrating one unit process into wastewater treatment using the traditional fundamental-to-applied research framework normally takes decades.²⁷ The urgency of achieving refining benefits necessitates coordination across fields as early as possible in technology development.⁶ Use-inspired research that acknowledges these pressing realities is necessary but insufficient to meet the challenge of revolutionizing chemical manufacturing. This perspective describes use-informed

research (Table 1) that addresses fundamental and applied questions in parallel (rather than in series) and ensures relevance to applications throughout process design while enabling tunability to diverse scenarios. Related to wastewater refining, carbon capture and utilization (CCU) is a rapidly maturing field investigated academically and pursued industrially; CCU feedstocks range from flue gas to direct air capture, and products include fuels, syngas, and organic commodities.^{28,29} Similar open challenges exist in electrochemical wastewater refining: selective reactions and separations must be improved on multiple scales. The breadth of wastewater contaminants and products requires contributions from fundamental chemical sciences to extract the full potential from wastewater contaminants, especially with selective recovery from complex mixtures. Even for existing water treatment processes, practitioners report one of their largest knowledge gaps as understanding underlying treatment mechanisms.²⁴

Thus, realizing electrochemical wastewater refining will require coordinated fundamental investigations and applied use cases, which have historically been viewed as disparate sequential thrusts. We will show that use-informed electrochemical wastewater refining is a prime example of the contrary: that (1) fundamental research can directly serve applications, and (2) applied research uncovers new fundamental phenomena. Applying approaches like systems thinking, quantitative sustainable design, and integrated reactive separations^{26,30} can facilitate answers to fundamental molecular scale questions at the same time as, or enabled entirely by, engineering the process itself. Using this integrated approach instead of siloed investigations for electrochemical wastewater refining will accelerate meaningful progress to

Table 2. Aqueous Wastewater Resources, Their Uses as Commodity Chemicals, and the Wastewaters That Contain Them

wastewater contaminant	uses	wastewaters
Ammonia/ammonium	Fertilizer, disinfectant, coolant, precursor to synthetic nitrogenous products	Municipal wastewater, hydrolyzed urine, agricultural/fertilizer runoff
Nitrate	Fertilizer, nitric acid	Agricultural/fertilizer runoff, livestock industry wastewater, postsecondary treatment municipal wastewater, nuclear power plant brine
Urea	Fertilizer, resin, personal care products	Fresh urine, agricultural/fertilizer runoff
Carbonate/bicarbonate	Buffer, cement	Agricultural/fertilizer runoff, industrial wastewater, municipal wastewater, urine, geothermal brine
Sulfate	Fertilizer, sulfuric acid	Municipal wastewater, urine, industrial wastewater, seawater reverse osmosis concentrate, oil and gas produced brine, geothermal brine
Sulfide	Precursor to organosulfur compounds	Postanaerobic treatment municipal wastewater
Potassium	Fertilizer, counterion to industrial salts/bases, medicine	Municipal wastewaters, urine, seawater reverse osmosis concentrate, geothermal brine, oil and gas produced brine
Magnesium	Fertilizer, structural metal, construction materials, medicine	Municipal wastewater, fresh urine, seawater reverse osmosis concentrate, geothermal brines, oil and gas produced brine
Calcium	Fertilizer, construction materials, personal care products, medicine	Municipal wastewater, fresh urine, seawater reverse osmosis concentrate, geothermal brine, oil and gas produced brine
Phosphate	Fertilizer, detergent, food additives	Municipal wastewater, urine, agricultural/fertilizer runoff, industrial brine
Lithium	Batteries, ceramics, lubricant, medicine	Geothermal brine, lithium-ion battery waste leachate, oil and gas produced brine, seawater reverse osmosis concentrate
Cobalt	Alloys, batteries, catalysts, pigments and dyes	Lithium-ion battery waste leachate
Nickel	Alloys, electroplating, batteries	Lithium-ion battery waste leachate
Copper	Wire and cable, electronics, architecture	Lithium-ion battery waste leachate
Organic matter	Fertilizer, biorefinery feedstocks	Municipal wastewater, urine, livestock industry wastewater, groundwater, landfill leachate
Dyes	Clothing and textiles, personal care products, food preparation, packaging	Industrial wastewater, municipal wastewater
Pharmaceuticals	Medicine	Municipal wastewater, urine, pharmaceutical industry wastewater, landfill leachate
Per- and polyfluoroalkyl substances (PFAS)	Cookware, clothing and textiles, foam, plastic, rubber, personal care products	Municipal wastewater
Arsenic	Lead alloys, car batteries, pesticide, animal feed additive, medicine	Municipal wastewater, polluted groundwater, industrial wastewater
Gold	Coinage, jewelry, electronics	Municipal wastewater
Silver	Coinage, jewelry, electronics	Municipal wastewater

match the scale and urgency of global resource imbalances and environmental perturbations.

We aim to encourage crosstalk among interdisciplinary chemical fields and to scaffold new discussions within the wastewater refining framework. This shift in focus underscores the need to standardize challenges around a coherent electrochemical wastewater refining vision, which includes three major thrusts: electrocatalysis, stoichiometric electrochemical conversion, and electrochemical separations. We also aim to systematically introduce readers to the scenario-dependent applications, opportunities, and objectives in wastewater using case studies of specific wastewater-pollutant-product combinations. In this perspective, we define the opportunities and associated metrics for fundamental electrochemical refining research (Section 2); highlight progress and challenges toward achieving the wastewater refining vision in electrocatalysis, stoichiometric electrochemical conversions, and electrochemical separations (Section 3); and enumerate specific tools chemical scientists can leverage to expand the wastewater refining product portfolio (Section 4). Together, these sections motivate a call to action for electrochemical researchers to elevate use-inspired research to use-informed research in the dynamic and critically important field of wastewater refining.

2. DEFINING THE OPPORTUNITIES AND TARGET METRICS FOR WASTEWATER REFINING FUNDAMENTAL RESEARCH

Because wastewaters vary widely across several categories, guiding frameworks are needed to prioritize underexplored opportunities for wastewater refining. Wastewaters are primarily characterized by the domestic, urban, industrial, and agricultural activities that generate them. They can be further classified as point or nonpoint sources, where point sources are aggregated at a single location (e.g., sewer municipal wastewater treatment plants), and nonpoint sources are released over a large area (e.g., stormwater or fertilizer runoff initiated by heavy rainfall). Diverse effluent compositions result from several factors, including the type of human activity (municipal, agricultural, or industrial discharges), biogeochemical location (source and destination of wastewater), and type of treatment (e.g., secondary effluent). Within any of these categories, wastewaters can vary spatiotemporally and will thus exhibit a range of concentrations of primary (N, P, K) and secondary (Mg, Ca, S) nutrients, metals (Li, Mn, Co, Ni, Cu, Zn), and organic and inorganic C (Figure 1).²⁰ This variability underscores the need for an informed framework to categorize, prioritize, and diversify valorization efforts.

In Figure 1, we propose four core wastewater properties to guide wastewater refining efforts: (1) global flow rate (*x*-axis), (2) total dissolved solids (*y*-axis, i.e., concentration of solutes), (3) theoretical monetary value of refinable resources (size of each circle), and (4) mass composition of refinable resources

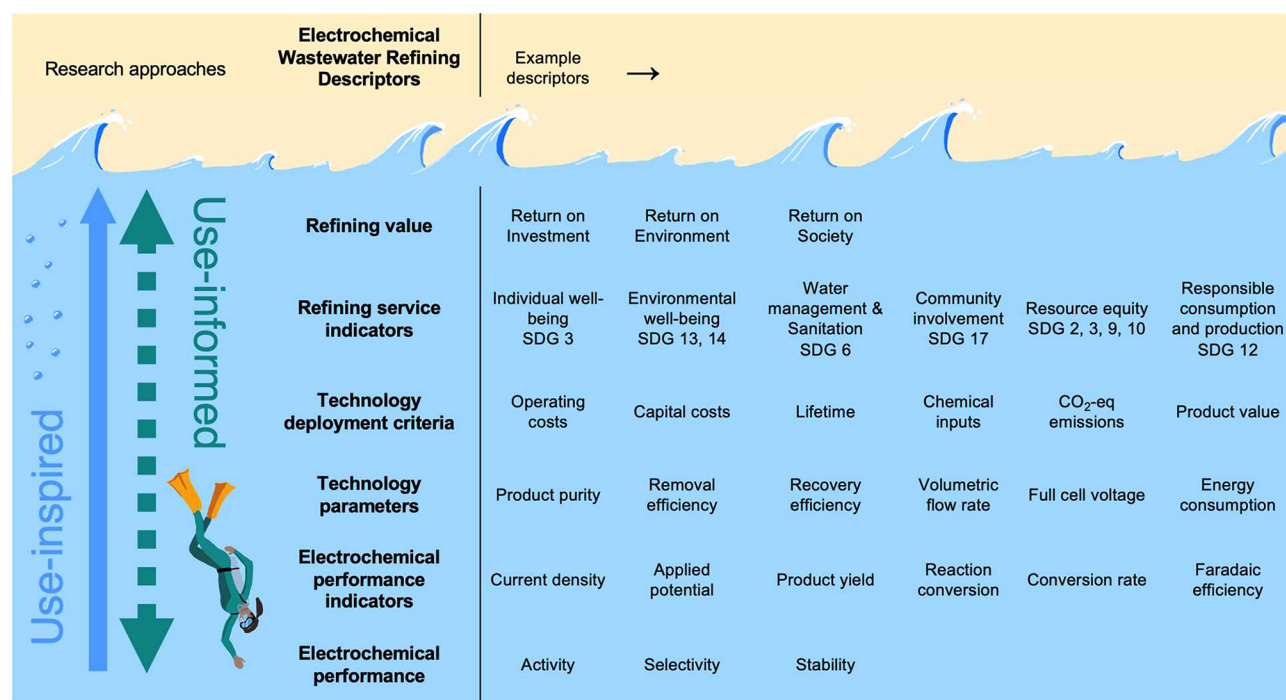


Figure 2. Refining-relevant descriptors (bold) that span from fundamental electrochemical performance and performance indicators (bottom), to applied technology parameters and deployment criteria, to refining service indicators and values of deployed systems (top). Example metrics for each characteristic level are provided on the right. Use-inspired research primarily moves unidirectionally from fundamental to applied, like bubbles rising in the ocean. Use-informed research moves bidirectionally, like a diver, between fundamental and applied considerations such that (1) fundamental findings remain relevant to concrete value propositions and (2) applied demonstrations are understood mechanistically, so they can be generalized to diverse use cases.

(subsections of each circle; details in [Supporting Information Section S1](#)). Several observations can be gleaned from this framework. **First**, the concentration and total volume of target resources vary by several orders of magnitude. For example, NH_3 -nitrogen in human urine is 100 to 1000 times more concentrated than NO_3^- -nitrogen in fertilizer runoff; however, because the global flow rate of urine is nearly 1000 times smaller than that of fertilizer runoff, the two wastewaters contain similar amounts of nitrogen (16–30 Tg-N in urine, 19–48 Tg-N in fertilizer runoff).^{20,31–36} **Second**, dissolved solid compositions vary drastically between wastewaters. Third, these variations present numerous value propositions for each feedstock, especially with breakthroughs in tunable reactions and separations. For municipal wastewater, several resources present in comparable concentrations enable production of commodity chemicals (e.g., NH_3 , HNO_3 , H_2SO_4 , NaOH), fertilizers (e.g., $(\text{NH}_4)_2\text{SO}_4$, $\text{NH}_4\text{H}_2\text{PO}_4/(\text{NH}_4)_2\text{HPO}_4$, NH_4NO_3 , KCl , $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$, $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$), building materials (e.g., $\text{Ca}(\text{OH})_2$), and metal smelting precursors (e.g., MgCl_2).^{34,37,38} In this perspective, we focus on the fundamental refining challenges for common inorganic constituents, which can be integrated with other circular manufacturing efforts such as biomass refining or plastic recycling.^{39–44} Note that estimates of the extractable value from any wastewater are limited by the state of aqueous characterization. Compared to municipal wastewater and urine, industrial and agricultural effluents are undercharacterized in terms of target compounds and nontarget competitors that may influence refining. To extract the maximum value from wastewater refining, accurate compositions that account for spatiotemporal variability are needed for all wastewater types.

Any value proposition for wastewater refining contains three parts: a wastewater, a pollutant, and a desired product. Prioritizing which wastewater-pollutant-product combination to pursue requires advancing basic research from use-inspired to use-informed ([Figure 2](#)). Use-inspired research, the predominant paradigm, aims to address a relatively distant problem area by generating fundamental knowledge that may lead to practical solutions (upward in [Figure 2](#)).¹⁸ In contrast, use-informed studies use context-specific details to prioritize and motivate fundamental questions that more immediately address problems encountered in practice (bidirectional, in [Figure 2](#)). A use-informed refining study would begin with a top-down approach to discern the economic, environmental, and societal **refining value** provided by scientific innovation. Economic services (ROI, return on investment) generate monetary value from technological investments, environmental services (ROE, return on environment) mitigate deleterious effects of pollutant emissions, and societal services (ROS, return on society) bolster community-level infrastructure capabilities for equitable access to critical resources. These use-informed services should be specific to each wastewater-pollutant-product combination, like refining nutrients in municipal wastewater to fertilizers. Economically, municipal wastewaters are low-cost chemical feedstocks ($\text{NH}_3/\text{NH}_4^+$, $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$) that could improve profit margins and introduce new revenue streams for manufacturers. We estimate that recovering nitrogen as NH_3 from existing, sewerage municipal wastewaters could yield USD 6.3 billion per year.^{31,45} The environmental benefits of circular fertilizer production are two-fold; resituating discharged aqueous nutrients (16.6 Tg-N, 3 Tg-P globally)³¹ mitigates surface

water ecosystem disruptions like algal blooms that over-consume oxygen,⁴⁶ and reduces reliance on conventional petrochemical-based industrial processes. Electrochemical wastewater refining can achieve a return on society via modular electrified installations that refine wastewaters at the point of generation. Distributed wastewater collection and refining enables communities to produce their own resources (independent of existing supply chains), promote sanitation access, and mitigate damage to their local ecosystems.^{20,47,48} While ROI is readily and quantitatively comparable to conventional processes, quantitative ROE and ROS require participation from local stakeholders invested in context-specific environmental justice and community-based implementation. Tools like life-cycle assessment (LCA) and quantitative sustainable design (QSD) can concretize ROE and ROS as **refining service indicators** for technology suitability and deployment assessments in diverse contexts.^{6,49,50} This relatively mature example of nitrogen and phosphorus fertilizers from municipal wastewater demonstrates the value of use-informed research. This top-down approach beginning with the refining values informs which research questions to pursue and how more fundamental findings are translated to practice.

Continuing with the example of use-informed municipal wastewater refining of nutrients, refining values are connected to research efforts by specific SDGs that serve as **refining service indicators**.⁵¹ The QSD framework supports the informed deployment of sustainability research using a shared lexicon across disciplines that delineates broad qualitative goals (e.g., SDG 6 Clean Water and Sanitation), quantitative indicators that assess progress toward goals (e.g., percentage of population with regular access to improved sanitation), and target values of indicators with endpoints and time tables (e.g., halve the number of people without access to improved sanitation by 2030).⁵⁰ Refining services will be provided by specific technologies; **technology deployment criteria** highlight the system performance metrics that govern deployment feasibility in specific scenarios. A survey of wastewater treatment engineers and technicians highlighted the most critical **technology parameters** used to assess process feasibility, including energy consumption (e.g., MJ/kg-N) and removal/recovery efficiency (e.g., normalized to influent concentration) in municipal wastewater systems.²⁴ Quantitative metrics like those in Section S2 must therefore be reported with clear definitions (e.g., product yield vs product recovery) to make unit process level decisions. As an example of a study that reports such practical parameters, electrochemical stripping (ECS), an electrodialysis-based NH_3 recovery process, was recently evaluated in terms of energy consumption per mass $\text{NH}_3\text{-N}$ recovered as a function of influent nitrogen concentration and device operating conditions.⁵² This study also reports **electrochemical indicators** (Section S2) in experimental nitrogen refining research (e.g., cell potential, current density, product yield rate) and identifies membrane transport as the limiting step for these parameters. Similar indicators have been compiled in related review articles for wastewater treatment processes^{32,53–55} and electrocatalytic reactions (e.g., CO_2 reduction).^{56–58} In addition to quantifying electrochemical performance and optimization opportunities with indicators relevant to the applied problem space, investigation of ECS in real urine also uncovered unexpected aqueous phenomena: naturally occurring organic radical scavengers in urine enhance performance by impeding

ammonia from reacting with active chlorine radical species formed at the anode.⁵⁹ Bridging fundamental and applied considerations will be paramount as the fields of electrocatalysis (e.g., NO_3^- reduction), stoichiometric electrochemical conversions (e.g., struvite precipitation), and electrochemical separations (e.g., NH_4^+ -selective electromigration) aim to refine more nitrogenous products from more wastewaters. These use-informed efforts that broaden the scope of wastewater refining will require investigating fundamental **electrochemical performance** (activity, selectivity, and stability) and phenomena under increasingly large-scale, refining-relevant conditions to deconvolute the effects of numerous wastewater constituents and operating conditions. While this discussion has focused on how applied use cases guide the relevance of fundamental studies (i.e., top-down in Figure 2), use-informed research communication should be bidirectional. The modular nature of electrochemical reactors (i.e., multiple cells constitute a stack) facilitates investigating practical reactor scales and operating conditions in the laboratory setting. Achieving feedback loops between applied performance and fundamental insights requires investigating processes with clearly articulated wastewater-pollutant-product combinations. In the remainder of this perspective, we highlight key advances in specific refining thrusts and identify nascent opportunities that electrochemical researchers can address.

3. ADVANCES MADE AND ADVANCES NEEDED IN USE-INFORMED ELECTROCHEMICAL WASTEWATER REFINING

Existing centralized municipal wastewater treatment processes primarily employ processes that remove pollutants to minimize ecosystem damage. Removal is accomplished in stages, each with distinct target molecules (e.g., dissolved organic carbon) and objectives (e.g., effluent concentration below 10 mg C/L). Primary treatment that separates solids from wastewater was invented in the 1860s to avoid sewer clogging.⁶⁰ Secondary treatment was invented in the 1910s to convert dissolved organic carbon into CO_2 using aerobic bacteria, thus avoiding oxygen depletion in aquatic ecosystems.⁶¹ Throughout the 20th century, advanced (i.e., tertiary) treatment was developed to target pollutants such as nitrogen (nitrification-denitrification), phosphorus (chemical precipitation), bacteria (chlorination/UV), dilute metals (coagulation), and trace organic contaminants (advanced oxidation processes).²⁴ Due to their high operational costs and chemical input needs, municipal wastewater treatment plants are still not universal.^{62–64} More recently, wastewater treatment plants evolved into water resource recovery facilities, targeting recovery of potable water and commodity chemicals.^{65,66} Whereas removal achieves pollutant mitigation and recovery achieves circular manufacturing in a limited nature (i.e., separation without conversion), wastewater refining will enable tunable generation of a diverse portfolio of commodity chemicals. As wastewater treatment plants in the U.S. face significant reinvestment requirements (\$271 billion nationwide) toward the end of their usable lifetime, there are timely opportunities to explore disruptive electrochemical technologies focused on upgrading wastewater pollutant removal to resource refining.⁶³

Two major technical advances are needed to realize use-informed electrochemical wastewater refining: (1) improved understanding and control of interfacial microenvironments and (2) strategic co-investigation of material properties and relevant operating conditions. In this section, we detail each of

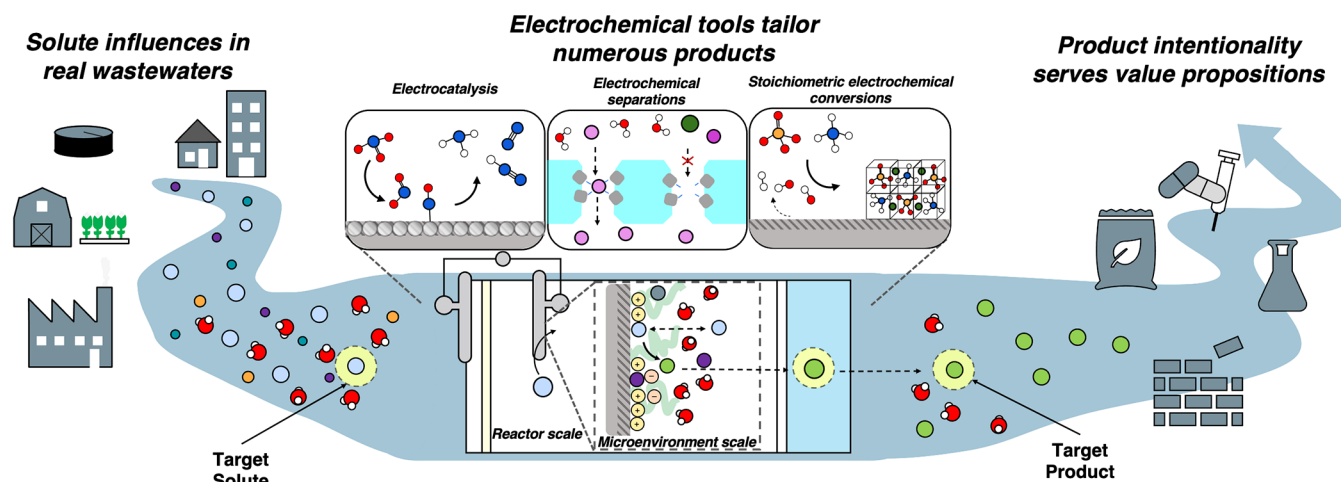


Figure 3. Conceptual figure showing the connection among wastewaters, pollutants, and products through electrochemical reactions and separations. Electrochemical tools facilitate a diverse product portfolio that serves various value propositions via three major approaches: electrocatalysis, stoichiometric electrochemical conversions, and electrochemical separations. Electrocatalysis utilizes an electrochemical potential to perform redox reactions at catalyst active sites (e.g., NO_3^- reduction). Stoichiometric electrochemical conversions are homogeneous phase reactions facilitated by electrogenerated reactants (e.g., struvite precipitation). Electrochemical separations leverage an electric field to drive ion sorption at an electrode surface or to drive ion migration across a membrane (e.g., lithium recovery). Molecular-scale phenomena can be controlled at the reactor scale and at the microenvironment scale, allowing for reactive separation engineering toward products of interest.

these advances across three representative electrochemical wastewater refining techniques: electrocatalysis, stoichiometric electrochemical conversions, and electrochemical separations (Figure 3). Electrocatalysis converts reactive pollutants such as NO_3^- into diverse products. Stoichiometric electrochemical conversions, in which electrogenerated species react with contaminants, capture and purify elements like phosphorus. Interfacing selective materials with electrochemistry, like selective membranes with electrodialysis, extracts critical materials like lithium from wastewaters. Iteratively and bidirectionally engineering catalysts, electrodes, electrolytes, and reactive separations at multiple scales (from microenvironment scale to practical reactor scale, and vice versa) will accelerate progress toward tunable wastewater valorization and enable informed decisions between available wastewater refining processes.

3.1. Wastewater-Based Electrocatalysis: Nitrate Reduction. Electrocatalysis can circularize global nitrogen flows, which have been skewed by reactive nitrogen discharges in fertilizer runoff and municipal wastewater generated by Haber-Bosch NH_3 manufacturing. The global rate of reactive nitrogen (e.g., NH_3 , NO_3^- , NO_x) generation by Haber-Bosch and N_2 -fixing organisms is now double the rate of removal by wastewater treatment and biological systems; the nitrogen cycle has been pushed so far past its planetary boundary that there are high risks of irreversible environmental changes.⁶⁷ The field of nitrogen electrocatalysis includes the N_2 reduction reaction (N_2RR) that produces NH_3 from air and the NH_3 oxidation reaction (AOR) that removes aqueous pollutants as N_2 ; we focus on the NO_3^- reduction reaction (NO_3RR) to NH_3 because it uniquely exemplifies electrochemical wastewater refining by converting an aqueous pollutant into a commodity chemical. In fact, NO_3^- is the most commonly reported drinking water pollutant violation,^{68,69} and NH_3 is the conventional precursor to all synthetic nitrogenous products.^{45,70}

To date, heterogeneous NO_3RR efforts focus primarily on designing catalysts, specifically single metals (e.g., Pt, Cu, Co,

Fe, Ti), alloys (e.g., CuNi, PtRu), and semiconductors (e.g., TiO_2 , MoS_2).^{71–75} Electrocatalyst composition and structure have been modified to understand and enhance performance (overpotential, activity, and selectivity). NO_3^- adsorption and reduction to NO_2^- are typically rate-determining for single metal surfaces.^{72,76} The overall eight-electron, nine-proton transfer reaction pathway diverges from adsorbed NO^* , and catalyst identity influences selectivity toward N_2 , N_2O , and NH_3 products.⁷⁷ Comprehensive discussions of intrinsic catalyst reactivity are covered in other reviews,^{71,78–80} but the sensitivity of NO_3RR product selectivity to catalyst identity is one avenue for tunable product distributions. Despite abundant fundamental work, few demonstrations of NO_3RR to NH_3 have compared catalytic performance in real or use-informed simulated wastewaters.^{81,82} These proofs-of-concept in wastewater environments enable comparison of novel electrochemical processes to existing wastewater treatment and thermochemical manufacturing. Additionally, bench-scale investigations should model practical-scale reactors conditions such that fundamental understanding of the electrolyte and electrocatalyst sides of the catalytic microenvironment remains relevant to applied use cases.^{83–86}

NO_3RR activity and selectivity depend on both electrocatalyst identity and electrolyte composition. Inhibitory, promoting, or neutral effects of wastewater environments guide the feasibility of direct treatment for specific wastewaters and inform needs for electrolyte engineering. Systematically increasing electrolyte complexity from ideal solution to real wastewater (a recent framework for aqueous separations research⁸⁷) can prioritize the effects of electrolyte properties on observed electrocatalytic mechanisms. Water hardness (Ca^{2+} and Mg^{2+}) and alkalinity ($\text{HCO}_3^-/\text{CO}_3^{2-}$) have been shown to significantly impact NO_3RR activity by forming inactive electrode deposits.⁸⁸ Although the first-order rate law of the NO_3RR incentivizes the use of highly concentrated wastewaters, the largest refining opportunities exist for dilute agricultural waste streams that contribute the majority of NO_3^- emissions. Differences in bulk electrolyte composition also

influence catalytic microenvironment properties (e.g., interfacial pH, ion concentrations), which in turn dictate product selectivity via interactions between electrocatalysts and reactants (both near-surface and adsorbed).⁶⁸ Freely diffusing NO₃RR intermediates (such as HNO₂) can react in the aqueous phase to produce NH₂OH, N₂O, or NH₃. The strong influence of the electrolyte on the NO₃RR motivates electrolyte engineering informed by fundamental understanding of the microenvironment with the same level of rigor as electrocatalyst engineering. Prior NO₃RR work has highlighted strong dependencies of activity and selectivity as a function of bulk NO₃⁻ concentration and pH at transition metal and alloy surfaces.^{80,89} There is a significant need to link observed electrolyte effects under analytical conditions to practical-scale reactor operation through a detailed understanding of the microenvironment. Leveraging electroanalysis (e.g., rotating disk electrode voltammetry, scanning electrochemical microscopy), spectroscopic characterization (e.g., ATR-SEIRAS, XRR), and computational simulation (e.g., continuum modeling, molecular dynamics) can improve molecular-scale understanding of the local electrolyte environment that advances experimental observations toward mechanistic insights.⁹⁰ Improved spatiotemporal resolution of the microenvironment in both model and practical systems will guide electrolyte engineering strategies at the macro- (e.g., flow rate, precatalysis separation) and microscales (e.g., ionomers to modulate interfacial pH, delivery of reactants, interfacial charge⁸⁶) to achieve desired product distributions from specific electrolyte compositions. Thus, sole use of catalyst benchmarks such as current density oversimplifies the NO₃RR problem space and should be supplemented with use-informed metrics related to energy consumption, volume-specific conversion, and longevity referenced to a specific wastewater composition.

Electrolyte and wastewater compositions can be differentiated via unit processes that combine electrochemical reactions and separations (i.e., reactive separations). Separations and catalysis are normally considered distinct areas of research, but can be integrated as reactive separations across multiple length scales to achieve electrochemical wastewater refining.⁹¹ At the microscale, separations can mediate reactant and product transport between bulk electrolytes and interfacial microenvironments.⁹² In turn, changes in microenvironments, such as basification observed during the NO₃RR, can influence catalytic activity and selectivity. At the macroscale, integrated reactive separation processes can leverage membrane-separated cell architectures to control electrolyte composition amidst variable influent wastewater compositions. Furthermore, the NO₃RR must be designed for selective product formation and reactive separation of those products from wastewaters. The paucity of separations work to extract dilute NO₃⁻ and recover NH₃^{81,93} represents a significant gap in NO₃RR research despite an abundance of work in NH₃ reactive separation from NH₄⁺/NH₃-laden wastewaters.^{52,59} Reactor components (e.g., catalysts, electrolytes, and membranes) should be analyzed individually and in lab-scale NO₃RR reactive separations to translate electrochemical performance indicators (e.g., current density, faradaic efficiency, and limiting turnover number) to technology deployment considerations (e.g., product yield, power consumption, and operating costs). By analogy to waste heat integration for oil refining, electrochemical process intensification could integrate cathodic and anodic reactions to maximize input energy efficiency, such as coupled NO₃RR and alcohol oxidation.^{94,95} Multiple cathodic processes could

be integrated, such as NO₃RR and struvite precipitation for simultaneous nitrogen and phosphorus recovery. Reactive separations present opportunities to broaden and deepen wastewater-based electrocatalysis research centered on circular manufacturing.

Beyond nitrate reduction, the principles of wastewater-based electrocatalysis apply to other elements (including carbon and sulfur) and to bidirectional redox reactions, especially those that traverse the same intermediates in forward and reverse reactions (e.g., AOR and NO₃RR). CO₂RR researchers have interrogated the effect of electrolyte composition, mass transport, electrocatalyst structure, and reactor design on activity and selectivity.⁹⁶ CO₂RR product diversification has motivated selective manufacturing of complex multicarbon products (beyond CO or CH₄) that should be mirrored in wastewater refining.^{97–100} S²⁻ oxidation and SO₄²⁻ reduction could also be explored, and integrated reactions for multiple elements could lead to organic products that contain C–N or C–S bonds, such as amines, ureas, and thioureas.¹⁰¹ Tailoring products with oxidation reactions may be of equal importance in wastewater refining, underscored by the roughly equal mass of nitrogen in NO₃⁻ and NH₄⁺-laden wastewaters (Section 2). Generally, understanding the effects of coupled macro- and microscale operating conditions (electrolyte, catalyst, potential, pH, mass transport) on intermediate and final product(s) formation remains a gap in refining research.

3.2. Stoichiometric Electrochemical Conversions: Struvite Precipitation.

Stoichiometric electrochemical conversion, or noncatalytic electrogeneration of reactants, can valorize phosphorus discharges that (like reactive nitrogen) exceed planetary boundaries and stimulate eutrophication.⁶⁷ Phosphorus is distinct because it is mined from the earth's crust; its finite nature is predicted to strain the cost and availability of agriculture.¹⁰² Conventional wastewater treatment employs chemical or biological treatments to remove phosphorus. Chemical addition of CaCO₃ causes phosphate mineral precipitation; addition of FeCl₃ or Al₂(SO₄)₃ cause coagulation and flocculation of insoluble metal hydroxyphosphates.¹⁰³ Enhanced biological phosphorus removal leverages heterotrophic bacteria to store phosphorus and release it after cells are separated from influent wastewater.¹⁰³ Upgrading removal processes toward recovery and reuse requires enhanced selectivity among possible products, including multicomponent fertilizers, such as ammonium struvite (NH₄MgPO₄·6H₂O) and potassium struvite (KMgPO₄·6H₂O), or other products, such as hydroxyapatite (Ca₅(PO₄)₃OH; ceramics) and iron phosphate (FePO₄; pesticide). These minerals require bulk basification and cation addition¹⁰⁴ that can preclude distributed installations due to prohibitive cost, supply chains, and downstream treatment to balance pH or remove surplus salts. Stoichiometric electrochemical precipitation can circumvent chemical additions to recover phosphorus minerals. Two major approaches can be leveraged: (1) electrochemical dosing of Mg²⁺ using sacrificial anodes¹⁰⁵ or (2) near-electrode basification using chemically inert cathodes.¹⁰⁶ In contrast to wastewater-based electrocatalysis, stoichiometric electrochemical phosphate precipitation has achieved significant process-focused engineering¹⁰⁷ and demonstration in real wastewater environments.¹⁰⁸ These advances have facilitated comparisons of electrochemical struvite precipitation to conventional phosphorus removal and nonelectrochemical phosphorus recovery.¹⁰⁹ However, critical knowledge gaps regarding the role of the electro-

chemical interface in determining product identity, purity, and uniformity present barriers to rationally engineering systems for generalizable application to various wastewater compositions, use cases, and process needs.

Electrochemical struvite precipitation could benefit from an improved fundamental understanding of the reaction microenvironment to inform device improvements in real wastewaters. To date, electrochemical struvite precipitation work has mapped the effects of macroscale parameters (current density, applied potential, bulk electrolyte composition) to macroscale performance (removal efficiency, product selectivity, energy consumption).¹⁰⁷ But precipitation reactions are inherently interfacial, especially when reactants are generated electrochemically and their production rate influences the purity and throughput of recovered products.¹¹⁰ Both interfacial pH basification¹⁰⁶ and Mg^{2+} dosing¹⁰⁵ are subject to microenvironment effects because the speciation of magnesium precipitates, passivating oxide layers, and dissolved Mg^{2+} in the wastewater depends on local electrolyte composition. The microenvironment composition during precipitation is inherently sensitive to local operating conditions such as hydrodynamics, electrode material and geometry, and electric field. Microenvironment chemical activities, acid dissociation constants, and solubility products govern the relative rates of competitive precipitation reactions and therefore selectivity. The kinetics of nucleation and growth under supersaturated local conditions can be controlled by modulating reactant concentrations at well-defined electrode–electrolyte interfaces.¹¹¹ Improved characterization can provide critical information about interfacial pH and ion concentrations. Electroanalytical tools like rotating disk electrode (RDE), rotating ring-disk electrode (RRDE), or scanning electrochemical microscopy (SECM) could be employed to directly measure interfacial pH during precipitation.¹¹² *Operando* infrared spectroscopy could identify transient precipitate speciation. Electrochemical quartz crystal microbalance (EQCM) could measure the product formation rate. To translate these interfacial insights to rational choice of operating conditions and cell architectures, multiphysics models (microkinetic, solution phase chemical equilibria, precipitation kinetics) could be used to generalize observations to different use cases.¹¹³

Phosphorus must be both precipitated and purified for wastewater refining, which motivates reactive separation unit processes. In addition to connecting interfacial phenomena to observed performance, reactive separations can improve process metrics, such as electrode lifetime, energy efficiency, and product selectivity and purity. Direct control over reactant concentrations has been demonstrated with peptide coatings to locally modulate the concentration and conformation of Mg^{2+} , lowering the overpotential of magnesium oxidation and significantly increasing removal efficiency.¹¹⁴ Similar methods could broaden the product portfolio by colocating reactants to overcome local pK_{sp} challenges that control product selectivity between $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ($\text{pK}_{\text{sp}} = 13.3$) and more soluble struvites like $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ ($\text{pK}_{\text{sp}} = 11.7$).^{115,116} Engineering microscale separations can control the reaction interface through hydrodynamics, stabilizing agents, or electrode modifications; it could also control product quality parameters like crystal size uniformity.¹¹⁷ For all products, passivation increases energy consumption and lowers activity, even when the cell is operated galvanically.¹¹⁰ Enhancing electrode lifetime will require strategies to either facilitate or avoid the

deposition of competing precipitates on the electrode. Replacing or regenerating passivated electrodes in a batch or semibatch process could be impractical and costly at scale. Fluidized bed reactors with inert beads (e.g., glass) could agitate and remove precipitated products from electrodes.¹¹⁸ This design achieves localized separation of the product from the interface, which will equilibrate by enhancing precipitation. Electrochemical precipitation research will need to focus on the purity and uniformity of the product formed and how separations will be achieved in scalable reactor systems.

In summary, the effects of fundamental reaction phenomena extend beyond catalysis to stoichiometric electrochemical conversions, such as electrochemical precipitation. For struvite, products not swept away from the interface influence reaction kinetics and thermodynamic solid and aqueous speciation. Product removal then readjusts the microenvironment in which complex interfacial phenomena present a challenge to product selectivity and uniformity and an opportunity for product tunability. Importantly, these considerations could build from advances in electrocoagulation,¹⁰⁹ although purity requirements may be more stringent for precipitation. The fundamental considerations in this section also extend to stoichiometric reactions like reductive amination where electrogenerated species (aldehydes or ketones generated by alcohol oxidation) react in the solution phase (with amines/ NH_3 and dissolved H_2) to produce higher molecular weight amines.

3.3. Interfacing Selective Materials with Electrochemistry: Lithium Recovery. Advances in selective separation materials are needed to meet chemical manufacturing product purity standards from impure wastewater sources. In many sectors, replacing traditional separation processes with electrochemically driven separations can reduce energy and chemical inputs. For example, there is urgent demand for critical materials (e.g., lithium, cobalt, and rare earth elements) to support the rapid growth of the energy storage sector.¹¹⁹ Lithium demand is rising rapidly with the growth of the electric vehicle market; conventional supplies (ores and salar brines) are projected to fall short of demand between 2023 and 2027.¹²⁰ Lithium-containing oil and gas produced water and geothermal brines (teralibers generated per day) could help close the projected lithium supply demand gap and introduce an additional wastewater-derived revenue source. Despite many brines containing 50–1000 ppm Li^+ ,^{121,122} the presence of other impurities (e.g., Na^+ , Ca^{2+} , Fe^{3+} , H_2S) at higher concentrations (e.g., >60,000 ppm of Na^+ , >30,000 ppm of Ca^{2+})¹²³ presents a challenge for high-purity lithium extraction. Conventional separation techniques such as evaporation, crystallization, ion exchange, and solvent extraction exhibit low productivity and high chemical inputs, water use, and waste generation. Electrochemical separations can overcome these barriers and handle large salinity variations across various wastewaters, including battery leachate, geothermal brines, and oil and gas produced water brines.¹²¹ In fact, the National Alliance for Water Innovation identifies electrified separation processes as one of six main research priorities in their 2021 resource extraction sector technology roadmap.¹²⁴ The continued development of selective materials, including membranes for selective electrodialysis (S-ED) and electrically switched ion-exchange (ESIX) electrodes, can advance the industrial-scale adoption of these processes. Electrified separation processes such as ESIX and S-ED systems could render lithium recovery from wastewaters feasible.^{125,126} Just as

improvements in activity, product selectivity, and stability are pursued for electrocatalysis, so are improvements in separation selectivity, “activity” (e.g., flux or adsorption capacity), and stability (e.g., fouling resistance, cyclic regenerability) of selective electrochemical separation materials. These improvements are especially needed for ion-selective separations, a fundamental challenge and emerging research frontier that requires molecular design and evaluation.^{127–129} This section highlights key research challenges and opportunities for interfacing selective materials with electrochemistry in the context of lithium recovery from brines and battery leachate.

Industrial implementation of ion-selective separations requires the development of selective materials (e.g., electrodes, membranes) informed by an improved understanding of interfacial microenvironments across various wastewaters. For ESIX intercalation electrodes, lithium-selective ion insertion materials have been studied, including lithium iron phosphate (LFP) and spinel lithium manganese oxide (LMO). While unamended LFP materials offer promising Li/Mg insertion selectivities (e.g., reducing brine $\text{Mg}^{2+}/\text{Li}^+$ molar ratio from 38.4 to 0.34),¹³⁰ Li^+/Na^+ monovalent separation improvements are still needed. Hydrophilic electrode coatings have been leveraged to improve intercalation selectivity by increasing electrode–electrolyte contact and acting as an additional diffusive barrier to Na^+ . TiO_2 and polydopamine have been coated onto LFP electrodes to lower the Li^+ insertion overpotential and enhance Li^+ insertion selectivity by factors of 2.1 to 16.4.^{131,132} Selective electrodialysis membranes under investigation include cation exchange membranes, ion-imprinted membranes, and mixed matrix membranes containing metal–organic or covalent–organic frameworks.¹³³ These membranes are generally less selective than ESIX electrodes, with Li^+/X selectivities ranging from 6.4 to 65 (compared to 1.8×10^4 for ESIX electrodes).¹³⁴ Most commercial membranes exhibit Li^+/Na^+ selectivity values near or below one due to the similar characteristics (e.g., size, valence) of Li^+ and Na^+ .¹³³ As with ESIX electrodes, improved understanding and control of the microenvironment (electrolyte–membrane interface) are required to enhance separation performance. Considerations of microenvironment thermodynamics and kinetics at the electrolyte–membrane interface are remarkably similar to electrocatalysis: competing cations at water–material interfaces influence near-surface electrolyte transport, transport of species from the solution–membrane interface to the membrane bulk influences near-surface electrolyte restructuring, and the potential drop across a membrane is a function of electrochemical driving force and Donnan potentials (arising from electrolyte and membrane composition). The impacts of these microenvironment features are nontrivial; complex electrolyte compositions and varying driving forces alter membrane separation performance, making material comparison and evaluation challenging.¹³⁵ Selectivity metrics are often measured under diffusive operation, where total ion flux is low and flux-coupling effects may impact selectivity.^{136,137} Use-informed assessment under high flux S-ED conditions could help evaluate the permeability–selectivity trade-off under regimes in which flux-coupling effects are avoided and the depleted diffusion layers at the membrane–solution interface impact kinetic control of ion transport.^{138,139} Continued development of ion transport theory and related transport models would support membrane design efforts. Models accounting for the complex architecture of functionalized membranes (e.g., fractional free volume, ion exchange

capacity, ion–membrane interactions), the added complexity of multicomponent electrolytes, solution-phase hydrated ion migration, and electrodriven permeation would guide membrane design for enhanced performance in various wastewater compositions and operating conditions.

Maximizing electrochemical separation performance requires an integrated design of both material properties and operating parameters. Performance includes selectivity, “activity,” and stability that influence product purity, component lifetime, and energy consumption. In S-ED, an inherent trade-off exists between membrane selectivity and permeability; in ESIX, electrode stability is closely tied to selectivity and the degradation that occurs due to competing ion intercalation. Thus, both materials design and electrochemical process optimization (e.g., reactor design, current density profiles, fouling control) applied to complex, realistic electrolyte compositions are required for a more complete understanding of a technology’s translational potential. With ESIX, pulsed-rest and pulse-rest-reverse intercalation methods over 10 cycles can lower intercalation overpotentials and limit Na^+ intercalation that could compromise structural stability by expanding electrode lattices.¹³¹ However, deployment requires validated stability lasting hundreds to thousands of electrochemical cycles. Process-level studies of S-ED permeability and selectivity are also needed to unite fundamental selectivity studies with informed process engineering.¹²⁵ In both S-ED and ESIX, a shift beyond fundamental batch selectivity studies to flow-through investigations would accelerate translation, enable tuning of operational parameters (e.g., electrochemical driving force and electrolyte composition), and guide the design of next-generation separation materials and processes.

Interfacing selective materials with electrochemistry shows great potential for reduced capital costs,¹⁴⁰ chemical inputs,¹⁴¹ and emissions¹⁴² compared to conventional separation techniques.¹⁴³ While we recommend future directions for electrified separations research in the context of lithium recovery, the insights apply broadly to other ion–ion separations, such as metal recovery from acid mine drainage.^{144,145} From a molecular perspective, use-informed design of selective materials can be facilitated by a more complete understanding of ion transport mechanisms and by more standardized selectivity metrics.¹²⁵ Moving from the molecular scale to the process scale, the integration of selective materials into electrochemical processes also necessitates future work in engineering reactor design, process optimization, and fouling control to bring bench-scale studies to the pilot scale and beyond.

4. EXPANDING THE WASTEWATER REFINING PORTFOLIO

One of the hallmark achievements of chemical sciences in the 20th century is the breadth and volume of chemically manufactured products. The electrochemical wastewater refining product portfolio must expand to meet the existing and emerging resource needs that are conventionally supplied by centralized refining processes. Figure 4a, presents an analysis of progress in academic electrochemical research for producing chemical products from common wastewater contaminants represented qualitatively as the shaded area in each radar plot. Compared to conventional manufacturing, the current electrochemical wastewater refining portfolio spans fewer chemical products; target products are not chosen with sufficient rationale to maximize shaded areas and meet the full

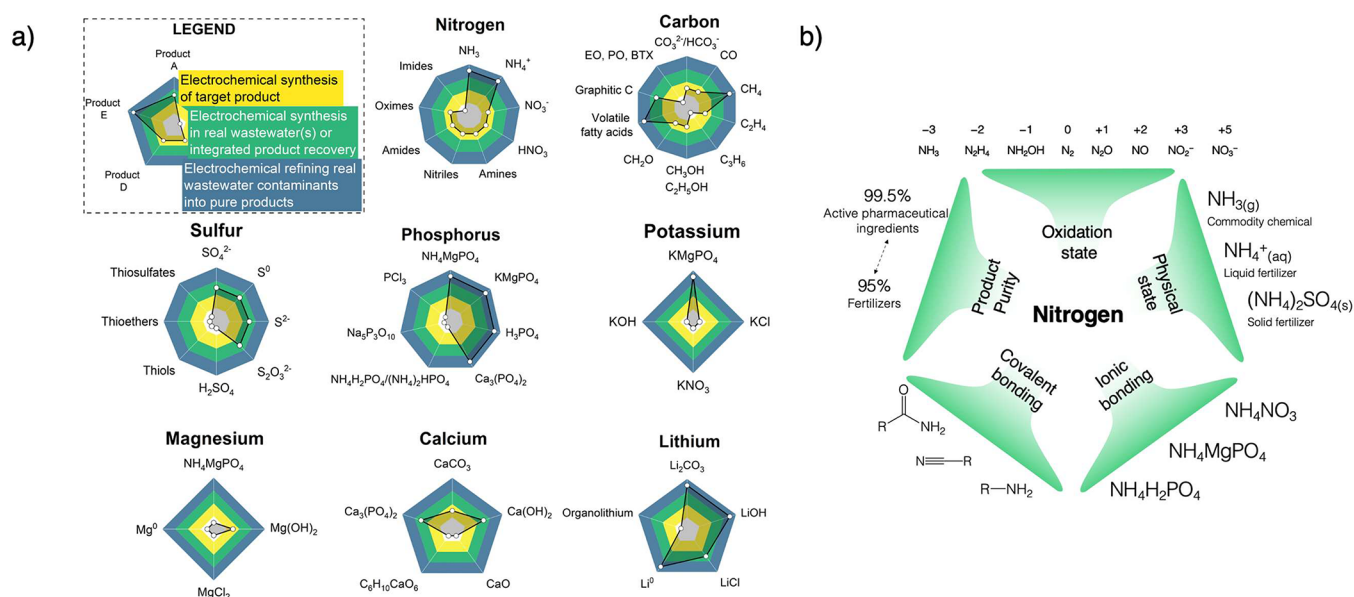


Figure 4. (a) Comparison of the “state-of-the-art” product portfolios for conventional manufacturing and electrochemical methods. The shape of each radar plot is set by the number of common conventional products containing each element. From innermost to outermost, the colored levels indicate maturity level in refining capabilities, from no electrochemical processes targeting the specified product (white), to at least one electrochemical process achieves the specified product from a common wastewater contaminant (yellow), to either electrochemical synthesis using a real wastewater or integrated electrochemical product recovery (green), and finally integrated recovery of a pure product from a real wastewater (blue). The third level indicates electrochemical research has demonstrated mature refining technology of a real wastewater contaminant and may be prepared for pilot-scale testing and analysis (cost, rate, efficiency, etc.). Qualitatively, the vision of electrochemical refining is to maximize the area of the shaded region for each element. For carbon, we include ethylene oxide (EO), propylene oxide (PO), and benzene, toluene, and xylene (BTX) as a single product category. References can be found in Section S3. Panel (b) provides five axes that electrochemical processes can leverage to diversify products from a wastewater contaminant, with nitrogen as an example. Not all five axes apply to every element.

potential of circular manufacturing from aqueous waste. Other circular manufacturing fields have defined the same challenge of expanding future product portfolios, including CCU,⁹⁸ biorefineries,¹⁴⁶ plastic recycling,¹⁴⁷ and oil refining beyond gasoline production.¹⁴⁸ Use-informed approaches are needed to define the potential of electrochemical wastewater refining to decarbonize and circularize the production of a wide array of compounds from aqueous contaminants (e.g., N, P, Li). Broadening the wastewater refining portfolio with use-informed approaches can expand the associated refining values (Section 2) and help reach the SDGs, net-zero emissions targets, and increasingly stringent water quality regulations. The rationale for target products must be guided by these refining values, and product requirements must be clearly and explicitly defined based on demands of the specific refining context. To achieve these requirements, electrochemical processes can expand the product portfolio along five distinct axes (Figure 4b): **oxidation state, physical state, purity, ionic bonding, and covalent bonding**. To maximize product utility, each axis for each element should be use-informed by the broader challenges in wastewater treatment and circular resource manufacturing.

The **oxidation state** of elements such as nitrogen determines the utility of refined products. Inorganic nitrogen oxidation state determines product utility between fertilizers (NH₃/NH₄⁺ and NO₃⁻), basic chemicals (NH₃, N₂, N₂O, NO, and HNO₃), and specialty chemicals (N₂H₄, NH₂OH). Although NH₃ (fully reduced nitrogen) tends to be the most common product targeted, its primary role is as a chemical precursor for other commercial nitrogenous products.⁷⁰ Fertilizer uses 80–90% of produced nitrogen but only represents 40% of the total market value of nitrogen.⁴⁵ Making diverse products in the

nitrogen portfolio requires basic and specialty chemicals that serve as on-site process chemical inputs. For example, selective electrocatalysis processes might reactively separate NH₂OH or HNO₃ as precursors to adiponitrile (nylon).⁶⁸ Additionally, process acids like HNO₃ (70 million metric tons globally⁴⁵) and H₂SO₄ (220 million metric tons globally¹⁴⁹) are ubiquitously used to produce a wide portfolio of fertilizers ((NH₄)₂SO₄, NH₄H₂PO₄/(NH₄)₂HPO₄, NH₄NO₃), petrochemicals, polymers, and batteries.¹⁵⁰ Beyond these conventional needs, refining unit processes will also require acids and bases as absorbents (e.g., gas stripping processes), regenerants (e.g., ion exchange), and electrolytes. Electrifying and localizing chemical production will reduce refining technology reliance on existing supply chains and offset emissions from high temperature thermochemical processes (e.g., wet contact process for H₂SO₄, Ostwald Process for HNO₃).¹⁵¹

Most conventional “finished” nitrogenous products contain nitrogen in the −3 oxidation state but are not ammonia; they require **covalent bonding** with heteroatom C–N bond formation. Heteroatom bonds like C–N and C–S are crucial functional groups in polymers, solvents, amino acids, and pharmaceuticals.¹⁰¹ Wastewater refining could produce amine, amide, carbamate, thioester, and nitrile precursors for these organic commodities. For example, acrylonitrile is used to make polyacrylonitrile (rubbers), acrylonitrile-butadiene-styrene (plastics), and adiponitrile. Decarbonization efforts have already incentivized aqueous electrochemical production of traditionally petrochemical products via CO₂RR from waste carbon feedstocks.⁹⁸ CO₂RR now targets complex C₂₊ products like ethylene by designing catalytic interfaces and processes for C–C coupling. Truly negative emissions chemical manufacturing must use emissionless nitrogen and

sulfur feedstocks to make heteroatom bonds. Wastewaters are abundant sources of aqueous carbon, nitrogen, and sulfur—a promising combined feedstock for circular organic synthesis instead of conventional siloed reactant sources.

Ionic bonding describes inorganic fertilizers that provide nutrient mixtures to plants. Large- and small-scale growers use a breadth of fertilizer blends to address variable (e.g., rainfall events), region-specific (e.g., soil type, pH, water and nutrient retention), and crop-specific (e.g., nutrient utilization rate) parameters.¹⁵² Consequently, refining products will need to meet flexible farming demands. While electrochemical refining has primarily targeted nitrogen and phosphorus, potassium (the third plant micronutrient) is underexplored but strained in sub-Saharan Africa because mineable potash is scarce.^{32,153} Selectively extracting ionic components such as potassium could complement nitrogen and phosphorus recovery for complete macronutrient refining of fertilizers and other commodity chemicals, like KOH.

Product purity is linked to the utility of manufactured chemicals, including lithium. Basic chemical-grade lithium products used in the glass, ceramics, and grease manufacturing industries typically require 95–99% purity, while specialty battery-grade lithium products (anticipated to account for over 90% of 2040 global lithium production) require purities exceeding 99.5%.¹²² Lithium products are traditionally high-purity crystalline Li_2CO_3 or $\text{LiOH}\cdot\text{H}_2\text{O}$. Selective electrochemical separations must account for product value based on purity when developing new materials and establishing benchmarks for selectivity and production rate.

Physical state influences how chemicals are transported, stored, and used. Aqueous fertilizers are more useful at the point of generation with on-site fertigation systems, while liquid NH_3 , solid urea, and crystalline salt products are more nutrient-dense and amenable to transport. Liquid fertilizers provide plants immediate access to nutrients while solid fertilizers like pelletized urea dissolve slowly into the soil. Reactive separations could be developed with more intention to match the product physical state to specific use case. New physical states introduce new interfacial phenomena to investigate, exemplifying a use-informed approach that avoids optimizing systems that provide suboptimal solutions.¹⁵⁴

Target products in electrochemical wastewater refining must be sufficiently tunable and scalable to leverage the distributed nature of wastewater generation. While global production volumes are useful, use-informed local demands and values influence the potential of wastewater-pollutant-product combinations in practice. With narrow product portfolios, refined products would need to be shipped back to centralized plants for conversion, which could impose transport costs, energy demand, and environmental impacts that nullify the equity, economic, and environmental benefits of point-of-generation wastewater refining. In short, the scale of refining values cannot be divorced from the scale of wastewater generation.¹⁵⁵ Electrochemical wastewater refining could also create entirely new process pathways that do not exist in conventional manufacturing:

1. In conventional lithium refining, sequential processes are used to transform solutions into Li_2CO_3 and subsequently $\text{LiOH}\cdot\text{H}_2\text{O}$, requiring chemical additions and generating solid waste.¹²² In contrast, integrating membrane electrolysis with electrochemical separation

technologies could produce $\text{LiOH}\cdot\text{H}_2\text{O}$ directly from Li^+ -laden wastewaters.

2. Stoichiometric electrochemical precipitations can be used to extract products beyond fertilizers, such as CaO or $\text{Ca}(\text{OH})_2$ —key components of concrete, mortar, and plaster—that are normally produced by mining calcium carbonate from large quarries and calcining at 900 °C.¹⁵⁶

Electrocatalysis, stoichiometric electrochemical conversions, and electrochemical separations could enable integrated and distributed manufacturing for numerous products through controlled electron transfers that mimic industrial or biological pathways to common commodities.¹⁵⁷ Tunable electrocatalysis for refining may require producing, stabilizing, and separating intermediates and controlling their delivery to distinct active sites.^{158,159} For example, NO_2^- (formed by NO_3RR at Ti)⁶⁹ could be isolated and directed in cascading reduction reactions toward inorganic products like NH_4^+ , N_2O , or NO at MoS_2 .^{160,161} Electrocatalytic coreduction of NO_3^- and CO_2 to form amines and amides is promising for heteroatom bond formation, which could be achieved in complex wastewater electrolytes.^{160,162,163} Thus, engineering electrocatalytic micro-environments (catalyst active sites, interfacial pH, aqueous species transport, intermediate stabilization, pulsed electrolysis¹⁶⁴) could promote more tunable inorganic and organic product formation. A complete electrocatalytic nitrogen refining system might employ multiple catalysts, electrolytes, operating conditions, or reactors for cascading reduction reactions to make a range of nitrogenous products.

Designing active sites for catalytic reactions, intermediate stabilization, and product separation can expand beyond heterogeneous interfaces, which are abundant but not universal in conventional chemical manufacturing. Enzymes have transition metal centers that exchange electrons with electroactive mediators, and active sites with high reactant and product selectivity that can enable complex chemical synthesis or serve as blueprints for the rational design of molecular catalysts.¹⁶⁵ However, molecular catalysts are typically understudied for wastewater applications because they most readily operate in the same phase as reactants and products, making catalyst recovery and reuse difficult. Membrane-separated cells, insoluble catalyst supports, and catalyst immobilization (which could be co-developed with catalysts) serve as viable options for translating homogeneous catalysis into practice.^{166–168} Analogous approaches for heteroatom bond formation in stoichiometric electrochemical conversions have also been underexplored. For example, reductive amination to produce amines from ammonia and alcohols or aldehydes is prominent in biomass upgrading, but not for ammonia-rich wastewaters.^{169,170} Synthesizing higher molecular weight molecules in the wastewater environment can also minimize needs for dedicated separation steps of reaction intermediates.¹⁰⁰ The concept of biomimicry also applies to selective electrochemical separations.¹⁷¹ Nature's highly selective separations are achieved by complexation of solutes with enzymes and membrane transporter proteins.^{172,173} These proteins may be purified, extracted, and incorporated into membrane materials or redox-tunable adsorption sites or otherwise copied through synthetic chemistry.

The nonexhaustive examples provided are feasible tools to expand the wastewater refining product portfolio with systematic, use-informed rationale. The reactants and waste-

waters from which these products are derived will also need to expand. For instance, there is pressing need to develop oxidation processes to refine prominent (yet under-researched) reduced contaminants like NH_3 or S^{2-} that may be produced during reductive wastewater treatment. Electrochemical wastewater refining should be developed with sufficient flexibility and modularity to close the circular manufacturing loop for emerging waste streams and pollutants. Additionally, interrogating the full portfolio of feasible products in a process may be useful because even conventionally undervalued products may be intermediates in electrochemical manufacturing. We propose there are countless reactions and separations in chemical refining that electrochemistry may be poised to address and that electrochemical wastewater refining is a useful framework to pursue exploratory fundamental research toward critically needed applied solutions.

5. CONCLUDING REMARKS

The future of chemical refining must achieve economic, environmental, and societal value propositions at multiple scales to address the urgency of 21st century imperatives. Climate change, water scarcity, ecosystem health, and equitable resource access are intimately connected to aqueous pollution, highlighting the need and opportunity for circular, electrified chemical manufacturing from wastewaters. Wastewater refining must do more than supplant the 20th century linear, centralized chemical refining paradigms. It must adapt to growing and changing complex chemical resource needs and wastewater compositions. The sheer number of pollutants, resources, and wastewaters requires systematic, coordinated investigations to make measurable progress in the time scale needed. Solutions must be designed to target value propositions for specific use cases. Use case context is critical, especially because wastewater treatment interfaces with chemical manufacturing, public health, and environmental protection.^{62,174} While we focus here on the technological aspects of wastewater refining, dedicated reviews beyond this perspective are needed to serve under-resourced communities. Studies should draw a clear connection to how they might fit into a process flow diagram within the electrochemical wastewater refining framework. Use-informed studies that translate value propositions to measures of technology performance will ensure relevance to applications throughout the design process.

Electrochemistry is a powerful tool to refine the numerous pollutants in complex wastewater electrolytes through electrocatalysis, stoichiometric electrochemical conversions, and electrochemical separations. We assert that the research questions underlying burgeoning wastewater-based electrochemical processes are simultaneously fundamental and applied. Fundamental research cannot be siloed as a linear predecessor to applied research; the circular feedback between the two will facilitate richer scientific insights and more optimal technologies. To this end, we provide use-informed recommendations for electrochemists and electrochemical engineers:

- **Maintain refining relevance:** Wastewater-based electrochemical studies should investigate and report fundamental electrochemical performance and process-level technology parameters, even if the unit process is not fully developed, to track technology progress for specific wastewater-pollutant-product value propositions.

- **Iteratively engineer reactive separations across multiple length scales:** Microenvironment insights should mechanistically explain the performance of the reactor in representative wastewater conditions, while controlled perturbations at the reactor scale help identify and investigate the impact of microenvironment conditions.
- **Expand the wastewater, pollutant, and product portfolios:** Develop electrochemical tools that tune chemical pollutants to numerous value-added products to accommodate diverse wastewater compositions.

Electrochemical refining research will rely on broadening participation of traditionally non-wastewater-focused fields to realize a diversified product portfolio. Novel reactions and separations will require downselecting permutations of catalysts, materials, and reactors in use-informed operational frameworks. We hope to galvanize cross-disciplinary participation around an understanding of the opportunities and knowledge gaps in wastewater refining. Ultimately, this coordination has the potential to reframe unwanted, underutilized, nonideal, aqueous pollution as chemical feedstocks to support a modern circular, sustainable, equitable human society.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.3c01142>.

Supporting equations for quantitative technology parameters and electrochemical indicators, and tables for wastewater compositions and flow rates, chemical product monetary values, and representative instances of wastewater-relevant electrochemistry (PDF)

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Notes

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