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 uncover 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.

Introduction: Wastewaters: the next frontier for chemical refining

Modern resource sustainability challenges present timely opportunities to circularize conventionally linear chemical processes.

The chemical sciences are responsible for providing commodities that support and advance societal needs at meaningful scale. From fermentation processes developed nearly ten thousand years ago to the discovery and production of medicines like penicillin in the 20th century, 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 bourgeoning 1940s automobile industry increased demand for complex and pure petrochemical fuels. Hydrocarbon cracking, steam methane reforming, and catalytic reforming enabled an expanded petrochemical product portfolio including fuels, lubricants, monomers, and solvents. These advances enabled improvements in quality of life that in turn increased the volume and variety of manufacturing processes that produce commodity chemicals, including Haber-Bosch for ammonia, industrial fermentation for alcohols, and polymerization for synthetic rubbers and 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, flexibility towards variations in raw material, energy efficiency, and above all economies of scale. Generally, today's chemical manufacturing has 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, sustaining quality of life amidst growing pollution, and diminishing feedstock availability.

Wastewater refining can address multifaceted modern challenges.

To meet global sustainability goals, circular chemical manufacturing mines and converts discharges to products and process inputs. Reaching net-zero manufacturing emissions by 2050[2] has primarily motivated the reuse of solid and gaseous emissions via carbon capture & utilization (CCU),[3] plastic recycling,[4] and refining biomass.[5] In contrast, liquid emissions (i.e., wastewaters) have been understudied, although they can also help achieve circular manufacturing.[6,7] Wastewaters carry dissolved contaminants that, left untreated, disrupt coastal and river 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 myriad chemical commodities (e.g., fertilizers, monomers, acids, bases, biomass). Potable water is one resource that is already recovered from wastewater, and could address 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. This approach can address several sustainability goals, including the United Nations Sustainable Development Goals (SDGs)[9] designed "to end poverty, protect the planet, and ensure that by 2030 all people enjoy peace and prosperity." Refining all the resources present in diverse, abundant wastewaters 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.

Table 1. Definitions (alphabetical) of terms relevant to wastewater treatment, chemical manufacturing, and electrochemical wastewater refining.

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	Separations 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, sub-unit 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

To draw an 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 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 CO_2 emitted.[21] Like oil, wastewaters are rich in chemicals that sustain modern society: nutrients (N, P, K), minerals (Ca, Mg, S), metals (Li, Co, Ni), and fine chemicals (pharmaceuticals) (Table 2). However, 80% of wastewaters are not adequately treated before discharge.[20] Current wastewater management simultaneously induces environmental damage and discharges resources worth over USD 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 co-located 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 and chemical manufacturing, can drive innovation towards 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 here on electrochemical wastewater refining processes for three reasons: (1) they valorize pollutants to products, unlike conventional wastewater treatment; (2) they can directly 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. Recent efforts have aimed to recover existing compounds in wastewater, such as ammonium and phosphate,[24] but have not achieved the potential of wastewater refining, which expands the portfolio of possible products via chemical transformations. Thermochemical driving forces are insufficient for refining wastewater resources because of prohibitive energy requirements for phase-change reactions and separations associated with the high specific heat capacity of water. Because 80% of existing separations are thermochemical (e.g., crude oil distillation), separations already account for 10-15% of the world's energy consumption and are high priorities for decarbonization.[25] Wastewater refining requires its own fit-for-purpose driving force to achieve 21st century circular resource economies.[26] **Electrochemical driving forces, powered by 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 control via current), replacement of chemical oxidants and reductants with electrons, and a high degree of modularity. This modularity is needed to manage the varied composition of wastewaters, which requires tunable processes to convert contaminants into products with varying uses (Table 2). Fortunately, driving selective reactions and separations at solid-liquid interfaces (instead of the bulk solution) is precisely where electrochemistry thrives. The vision of electrochemical wastewater refining is to leverage electrochemical driving forces to circularize and decarbonize manufacturing of chemical products that are indistinguishable at point of consumption from those produced in conventional linear processes.

Table 2. Aqueous wastewater resources, their uses in as commodity chemicals, and the biogeochemically-relevant 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 counterion	Agricultural/fertilizer runoff, livestock industry wastewater, post-secondary treatment municipal wastewater, nuclear powerplant brine
Urea	Fertilizer, resin, personal care products	Fresh urine, agricultural/fertilizer runoff
Carbonate/bicarbonate	Buffer, cement	Agricultural/fertilizer runoff, industrial brines, municipal wastewater, urine, geothermal brine
Sulfate	Fertilizer, sulfuric acid counterion	Municipal wastewater, urine, industrial brine, seawater reverse osmosis concentrate, oil & gas produced brine, geothermal brine
Sulfide	Precursor to organosulfur compounds	Post-anaerobic treatment municipal wastewater
Potassium	Fertilizer, counterion to industrial salts/bases, medicine	Municipal wastewaters, urine, seawater reverse osmosis concentrate, geothermal brine, oil & gas produced brine
Magnesium	Fertilizer, structural metal, construction materials, medicine	Municipal wastewater, fresh urine, seawater reverse osmosis concentrate, geothermal brines, oil & gas produced brine
Calcium	Fertilizer, construction materials, personal care products, medicine	Municipal wastewater, fresh urine, seawater reverse osmosis concentrate, geothermal brine, oil & 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 & gas produced brine, seawater reverse osmosis concentrate
Cobalt	Alloys, batteries, catalysts, pigments & dyes	Lithium-ion battery waste leachate
Nickel	Alloys, electroplating, batteries	Lithium-ion battery waste leachate
Copper	Wire & cable, electronics, architecture	Lithium-ion battery waste leachate
Organic matter	Fertilizer, biorefinery feedstocks	Municipal wastewater, urine, livestock industry wastewater, groundwater, landfill leachate

Dyes	Clothing & 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 & textiles, foam, plastic, rubber, personal care products	Municipal wastewater
Arsenic	Lead alloys, car batteries, pesticide, animal feed additive, medicine	Municipal wastewaters groundwater, industrial wastewater
Gold	Coinage, jewelry, electronics	Municipal wastewaters
Silver	Coinage, jewelry, electronics	Municipal wastewaters

Closing the gap between opportunity and practice for wastewater refining

The central thesis of this article 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 (60 years). Integrating one unit process into wastewater treatment using the traditional fundamental-to-applied research framework normally take decades;[27] the urgent need for refining to achieve the benefits of implementation necessitates coordination across fields and across unit processes 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, applied, and even policy questions in parallel (rather than in series) and ensures relevance to applications throughout process design while enabling tunability to diverse scenarios. By analogy to wastewater refining, carbon capture & utilization (CCU) is a rapidly maturing field that is 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 at multiple scales through sorption, catalysis, transport, separations, and reactor engineering. The breadth of wastewater contaminants and products requires contributions from the 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 electrochemical research in fundamental investigations and applied use cases, which have historically been viewed as disparate or 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 match the scale and urgency required to address global resource imbalances and environmental perturbations.

We aim not only to encourage crosstalk among interdisciplinary chemical fields, but to scaffold new discussions within the wastewater refining framework. This shift in focus underscores a need to standardize challenges and metrics 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 1); highlight progress and challenges toward achieving the wastewater refining vision in electrocatalysis, stoichiometric electrochemical conversions, and electrochemical separations (Section 2); and enumerate specific resource needs and tools we can leverage to achieve the future wastewater refining product portfolio (Section 3). 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.

Section 1: Defining the opportunities and target metrics for wastewater refining fundamental research

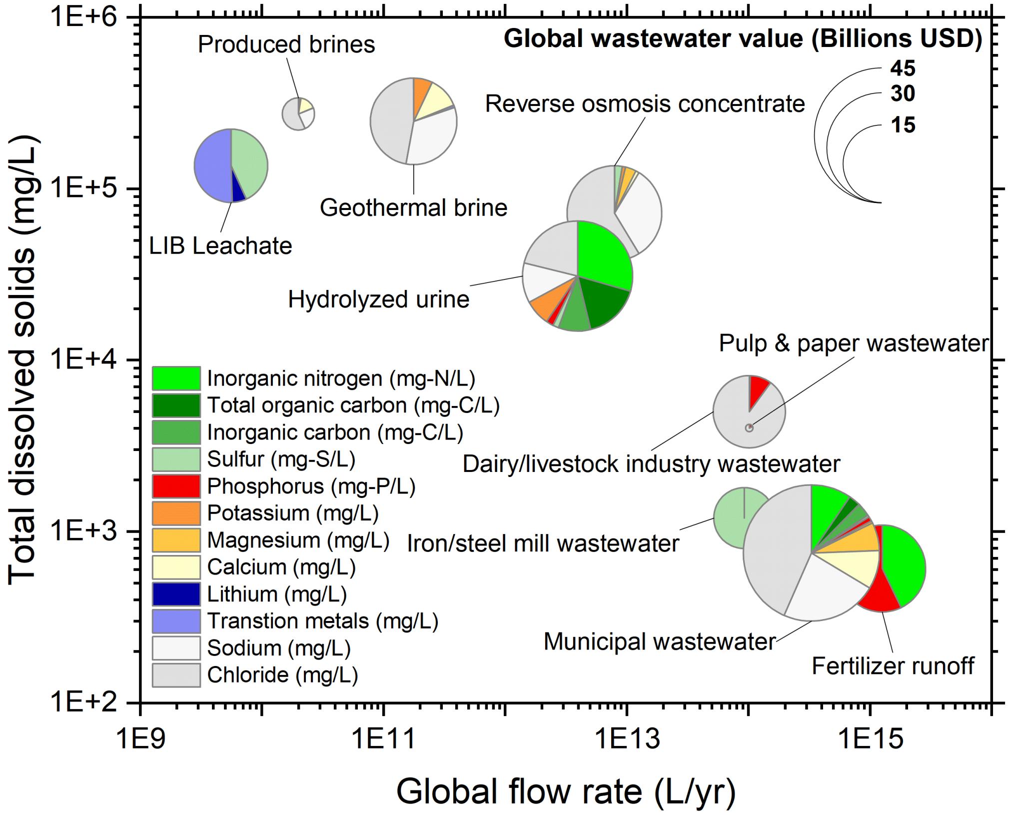

Figure 1. Pie charts of common wastewaters plotted as a function of global flow/generation rate (x-axis) and total dissolved solids concentration (y-axis). The size of each slice represents solute mass fraction and the size of each pie chart represents global annual value. Value was calculated by multiplying 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 for that element (e.g., urea for inorganic nitrogen). Sodium and chloride were not included in the value calculations, but we show their mass fractions from available data. Wastewater composition, volumetric flow rate, and chemical value data was compiled from available data in literature (Supporting Information).

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 non-point source, where point sources are aggregated at a single location (e.g., sewered municipal wastewater treatment plants), and non-point 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 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) macronutrients, 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) total dissolved solids (y-axis, i.e., concentration of solutes), (2) global flow rate (x-axis), (3) theoretical monetary value of refinable resources (size of each circle), and (4) mass composition of refinable resources (subsections of each circle; calculation details in Supporting Information). Several observations can be gleaned from this wastewater refining framework. **First**, the concentration and total volume of target resources vary by several orders of magnitude. For example, ammonia-nitrogen in human urine is two to three orders of magnitude more concentrated than nitrate-nitrogen in fertilizer runoff; however, because the global flow rate of urine is nearly three orders of magnitude 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 solids compositions vary drastically between wastewaters. **Third,** these variations present numerous value propositions for each feedstock, especially with fundamental breakthroughs in selective reactions and separations. For municipal wastewater, several resources are present in comparable concentrations and enable production of commodity chemicals (e.g., ammonia, nitric acid, sulfuric acid, sodium hydroxide), fertilizers (e.g., ammonium sulfate, ammonium phosphate, ammonium nitrate, potassium chloride, struvite), building materials (e.g., calcium hydroxide), and metal smelting precursors (e.g., magnesium chloride).[34,37,38] In this perspective we focus on the fundamental refining challenges for commonly detected inorganic constituents, which will likely be integrated with other circular manufacturing efforts such as biomass refining or plastic recycling.[39–44] Note that estimates of extractable value from any wastewater are limited by the state of aqueous characterization. Compared to municipal wastewater and urine, industrial and agricultural effluents are under-characterized in terms of both target compounds and non-target competitors that may influence refining. To extract maximum value from wastewater refining, accurate compositions that account for spatiotemporal variability are needed for all wastewater types.

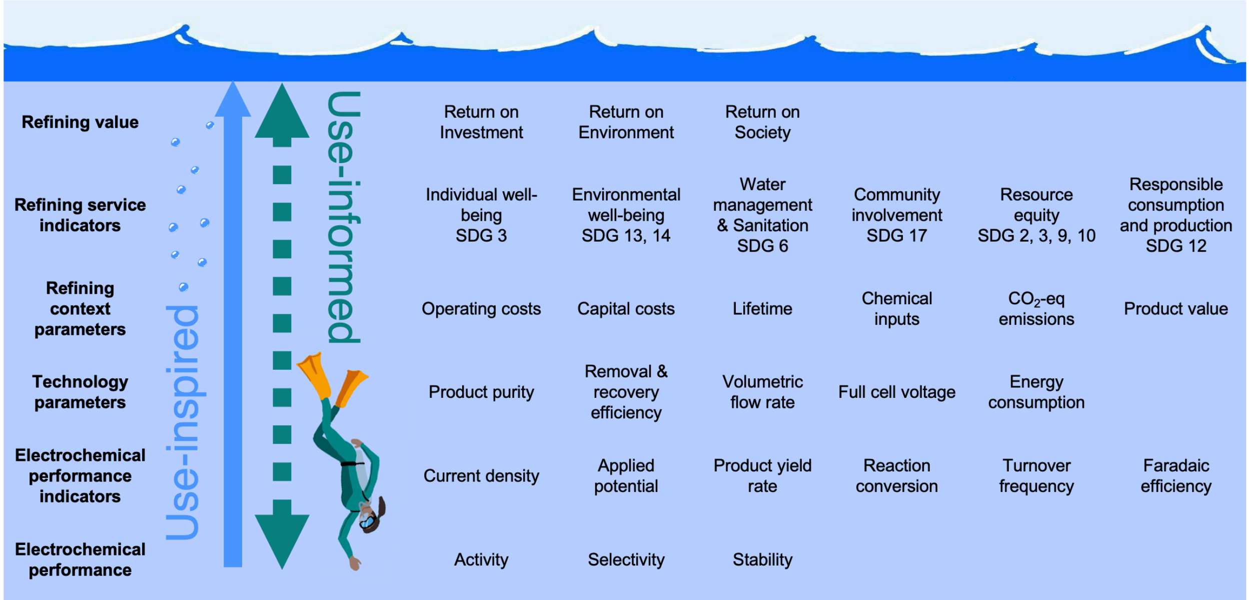

Figure 2. A ladder of refining-relevant descriptors (left) that span from fundamental electrochemical performance and performance indicators (bottom), to applied technologies and associated context parameters, to value and value indicators of deployed systems (top). Examples of the metrics for each characteristic level are provided to the right. Examples of refining value indicators are motivated by the Sustainable Development Goals (SDGs) listed. Use-inspired research primarily moves unidirectionally from fundamental to applied, much like bubbles rising in the ocean. Use-informed research moves bidirectionally 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.

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). 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 infrastructural capabilities for equitable access to critical resources. These use-informed services should be specific to each wastewater-pollutant-product combination; for example, refining nutrients in municipal wastewater to fertilizers poses substantial ROI, ROE, and ROS. Economically, municipal wastewaters are low-cost chemical feedstocks (NH_3/NH_4^+, $H_2PO_4^-/HPO_4^{2-}$) that could improve profit margins and introduce new revenue streams for manufacturers. We estimate that recovering nitrogen as ammonia from existing, sewered municipal wastewaters could yield USD 6.3 billion per year.[31,45] The environmental benefits of circular fertilizer production are twofold; resituating discharged aqueous nutrients (16.6 Tg-N, 3 Tg-P globally)[31] mitigates surface water ecosystem disruptions like algal blooms that overconsume oxygen,[46] and reduces reliance on conventional fossil-fuel powered industrial processes. Electrochemical wastewater refining can achieve a return on society via modular electrified installations that proactively refine wastewaters at their point of generation. Distributed wastewater collection and refining also 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 requires 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**.[49,50] This relatively mature example of nitrogen and phosphorus fertilizers from municipal wastewater demonstrates the value of use-informed research. Adding the 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 towards 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).[49] Refining services will be provided by specific technologies; **refining context parameters** highlight the system performance metrics that govern deployment feasibility in specific scenarios. Use-informed research must pursue practical knowledge gaps in these refining context parameters for a specific wastewater-pollutant-product triad to cross the "valley of death" in both directions between fundamental and applied electrochemistry research.[52] For electrochemical wastewater refining, 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 as a percentage) in municipal wastewater systems.[24] As an example of a study that reports such practical parameters, electrochemical stripping (ECS), an electrodialysis-based ammonia recovery process, was recently evaluated in terms of energy consumption per mass ammonia recovered (compared to a suite of conventional nitrogen removal processes) as a function of influent nitrogen concentration and device operating conditions.[53] This study also reports **electrochemical indicators** 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. 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 consumption by active chlorine radical species formed at the anode interface.[54] Bridging fundamental and applied considerations in wastewater nitrogen refining will be paramount as the fields of electrocatalysis (e.g., nitrate reduction), stoichiometric electrochemical conversions (e.g., struvite precipitation), and electrochemical separations (e.g., ammonium-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 in 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. Achieving feedback loops between applied performance and fundamental insights requires investigating processes with clearly articulated wastewater, pollutant, and 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.

Section 2: Advances made and advances needed in use-informed electrochemical wastewater refining

Existing centralized municipal wastewater treatment primarily employs 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.[55] The Industrial Revolution accelerated increases in urban wastewater volume due to population growth, which discharged dissolved organic carbon that stimulated aerobic bacterial activity and depleted oxygen in aquatic ecosystems. Secondary treatment was invented in the 1910s to convert this dissolved organic carbon into carbon dioxide using aerobic bacteria in aeration tanks.[56] Throughout the 20th century, advanced (i.e., tertiary) treatment was developed to target other deleterious 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.[57–59] More recently, wastewater treatment plants have taken on new roles as water resource recovery facilities, targeting recovery of potable water and commodity chemicals.[60,61] 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 from wastewaters. As several wastewater treatment plants in the U.S. face significant reinvestment requirements ($271 billion nationwide) towards the end of their usable lifetime, there are timely opportunities to explore disruptive, integrated electrocatalytic technologies focused on upgrading wastewater pollutant removal to resource refining.[58]

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 fundamental material properties and relevant operating conditions. In this section, we detail each of these advances across case studies that represent categories of electrochemical wastewater refining techniques: electrocatalysis, stoichiometric electrochemical conversions, and electrochemical separations (Figure 3). Electrocatalysis converts reactive pollutants like nitrate into diverse products. Stoichiometric electrochemical conversions, in which electrogenerated species react with contaminants, captures and purifies elements like phosphorus. Finally, interfacing selective materials with electrochemistry, like selective membranes with electrodialysis, extracts critical materials like lithium from wastewaters. Iteratively engineering catalysts, electrodes, electrolytes, and reactive separations at multiple scales (from microenvironment to full reactor) will accelerate progress towards tunable wastewater valorization and enable informed decisions between available wastewater refining processes.

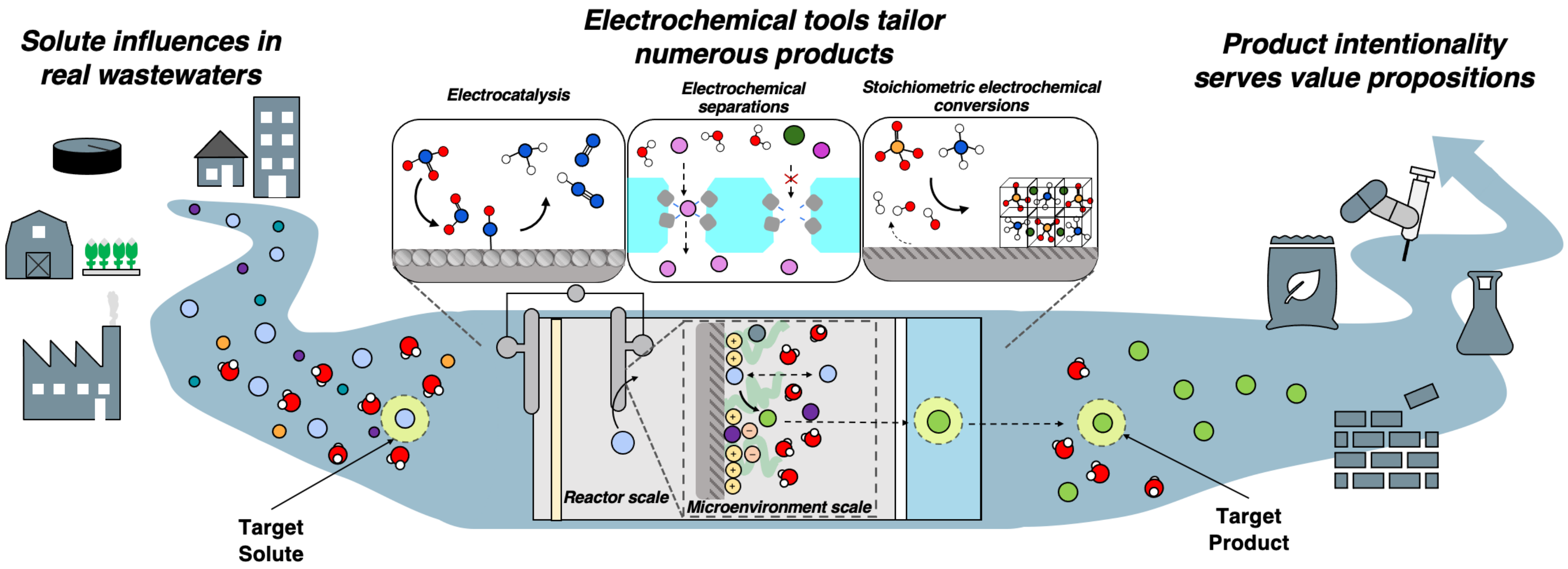

Figure 3. Conceptual figure showing the connection between wastewaters, pollutants, and products through electrochemical reactions and separations. Real wastewaters influence target solute delivery to reactive sites that form diverse products that serve various value propositions. Electrochemical tools facilitate this diverse product portfolio, and include three major approaches: electrocatalysis, stoichiometric electrochemical conversions, and electrochemical separations. Molecular-scale phenomena can be controlled at the reactor scale and at the microenvironment scale, allowing for engineering of reactive separations toward products of interest.

Subsection 2A: 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 ammonia manufacturing. The global rate of reactive nitrogen (NH_3, NO_3^-) generation by Haber-Bosch and N_2-fixing plants and bacteria 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.[62] The field of nitrogen electrocatalysis includes the dinitrogen reduction reaction (N_2RR) that produces ammonia from air, and the ammonia oxidation reaction (AOR) that removes aqueous pollutants as inert dinitrogen; we focus on the nitrate reduction reaction (NO_3RR) to ammonia because it uniquely exemplifies electrochemical wastewater refining by converting an aqueous pollutant into a commodity chemical. In fact, nitrate is the most commonly reported drinking water pollutant violation,[63,64] and ammonia is the conventional precursor to all synthetic nitrogenous products.[45,65]

To date, heterogeneous NO_3RR electrocatalysis has focused 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).[66–70] Modified electrocatalyst composition and structure have been investigated to understand and enhance catalytic performance (overpotential, activity, and selectivity). Nitrate adsorption and reduction to nitrite are typically rate-determining for single metal surfaces.[71,72] The overall eight-electron, ten-proton transfer reaction pathway diverges from adsorbed NO*, and catalyst identity influences NO_3RR selectivity toward N_2, N_2O, and NH_3 as products.[73] Catalysts that do not bind strongly to nitrate or nitrogenous intermediates (e.g., Ti) can form nitrite in significant quantities that may be subject to cascading reduction reactions at the catalyst surface.[64] Comprehensive discussions of intrinsic catalyst reactivity are covered in other reviews,[66,74–76] 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 ammonia have employed real or use-informed simulated wastewaters for comparative catalytic performance.[77,78] These proof-of-concept developments in wastewater environments enable comparison of novel electrochemical processes to existing wastewater treatment and thermochemical manufacturing. The applied nature of performance in relevant conditions is both informed by and informative for fundamental understanding of the electrolyte and electrocatalyst sides of the catalytic microenvironment.[79–82]

Activity and selectivity of NO_3RR is as much a function of electrolyte composition as of electrocatalyst identity. Inhibitory, promoting, or neutral effects of wastewater environments guide feasibility of direct treatment for specific wastewaters and inform needs for electrolyte engineering. Systematically increasing electrolyte complexity from ideal solution to real wastewater can prioritize the effects of electrolyte properties on observed electrocatalytic mechanisms. A recent framework for aqueous solution complexity in separations research[83] can apply to wastewater-based electrocatalysis. Although the first-order rate law of NO_3RR incentivizes the use of highly concentrated wastewaters, the largest refining opportunities exist for dilute agricultural waste streams that contribute the majority of nitrate emissions. Because nitrate and co-existing contaminants vary across wastewaters, insights from studies that mimic highly concentrated wastewaters may not apply to more relevant dilute streams. These 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).[63] Freely diffusing NO_3RR intermediates (like HNO_2) can further react in the aqueous phase to produce NH_2OH, N_2O, or NH_3. The strong influence of the electrolyte on NO_3RR motivates electrolyte engineering informed by fundamental understanding of the microenvironment with the same level of rigor as in electrocatalyst engineering. Prior NO_3RR work has highlighted strong dependencies of activity and selectivity as a function of bulk nitrate concentration and pH at transition metal and alloy surfaces.[76,84] 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 to mechanistic insights.[85] Improved spatiotemporal resolution of the microenvironment will guide electrolyte engineering strategies at the macro- (e.g., flow rate, pre-catalysis contaminant separation) and micro-scales (e.g., ionomers to modulate interfacial pH, delivery of reactants, interfacial charge[82]) to achieve desired product distributions from specific electrolyte compositions. Thus, sole use of catalyst benchmarks such as current density oversimplifies the NO_3RR problem space; supplemental use-informed metrics related to energy consumption, volume-specific conversion, and longevity referenced to a specific wastewater composition are more relevant.

Electrolyte and wastewater composition can be differentiated via integrated 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. At the microscale, separations can mediate reactant and product transport between bulk electrolytes and interfacial microenvironments.[86] In turn, changes in microenvironments, such as basification observed during NO_3RR, 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, NO_3RR must be designed for selective product formation and reactive separation of those products from wastewaters. The paucity of separations work to capture dilute nitrate and recover ammonia[77,87] represents a significant gap in NO_3RR research despite an abundance of work in ammonia recovery from ammonium/ammonia-laden wastewaters using reactive separations architectures.[53,54] By analogy to highly integrated oil refining, in which waste heat is often reused, electrochemical process intensification could involve integrating cathodic and anodic reactions to maximize input energy efficiency, such as coupled carbon dioxide reduction (CO_2RR) and alcohol oxidation.[88,89] Multiple refining processes could be integrated, like NO_3RR and struvite precipitation for simultaneous nitrogen and phosphorus recovery. Enhancing refining capabilities can incentivize collection of decentralized wastewaters (e.g., fertilizer runoff) that are seldom collected. 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 can 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 NO_3RR). The CO_2RR field has recently interrogated the effect of electrolyte composition, mass transport, electrocatalyst structure, and reactor design on activity and selectivity.[90] A desire to diversify the CO_2RR product portfolio has motivated selective manufacturing of complex multicarbon products (beyond CO or CH_4) that should be mirrored for wastewater refining.[91–94] Sulfide oxidation and sulfate reduction could be explored depending on the contaminant, wastewater, and desired product. In both cases, integrated reactions for multiple elements could lead to organic products that contain C-N or C-S bonds, such as amines, ureas, and thioureas.[95] Tailoring products with oxidation reactions may be of equal importance in wastewater refining, underscored by the roughly equal mass of nitrogen in nitrate- and ammonium-laden wastewaters (Section 1). Generally, understanding the effects of coupled macro- and micro-scale operating conditions (electrolyte, catalyst, potential, pH, mass transport) on intermediate and final product(s) formation remains a gap in refining research.

Subsection 2B: 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.[62] 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.[96] Conventional wastewater treatment employs chemical or biological treatment to remove phosphorus. Chemical addition of calcium carbonate causes precipitation of phosphate minerals; addition of iron (III) chloride or aluminum (III) sulfate cause coagulation and flocculation of insoluble metal hydroxyphosphates.[97] Enhanced biological phosphorus removal leverages heterotrophic bacteria to store phosphorus and release it after cells are separated from mainstream wastewater.[97] Upgrading removal processes toward recovery and reuse requires enhanced selectivity among possible products, including multicomponent fertilizers such as ammonium struvite ($NH_4MgPO_4{\cdot}6H_2O$) and potassium struvite ($KMgPO_4{\cdot}6H_2O$), or other products such as hydroxyapatite ($Ca_5(PO_4)_3OH$; ceramics) and iron phosphate ($FePO_4$; pesticide). All of these minerals require bulk basification and cation addition[98] that can preclude distributed installations due to prohibitive cost, supply chains, and downstream treatment to balance pH or remove surplus salts. Stoichiometric electrochemical precipitation (a subset of stoichiometric electrochemical conversions) can circumvent chemical additions to recover phosphorus minerals. Two major approaches can be leveraged: (1) electrochemical dosing of Mg using sacrificial anodes[99] or (2) near-electrode basification using chemically inert cathodes.[100] In contrast to wastewater-based electrocatalysis, stoichiometric electrochemical phosphate precipitation has achieved significant process-focused engineering[101] and demonstration in real wastewater environments.[102] These advances have facilitated comparisons of electrochemical struvite precipitation to conventional phosphorus removal and non-electrochemical phosphorus recovery.[103] However, critical knowledge gaps regarding the role of the electrochemical interface in determining product identity, purity, and uniformity present barriers to rationally engineering operating conditions and cell architectures for generalizable application to various wastewater compositions, use cases, and process needs.

Electrochemical struvite precipitation could benefit from improved fundamental understanding of the reaction microenvironment to inform rational improvements for devices 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).[101] But precipitation reactions are inherently interfacial, especially when reactants are generated electrochemically and their production rate influences the purity and throughput of recovered products.[104] Both interfacial pH basification[100] and magnesium dosing[99] are subject to microenvironment effects because the speciation of magnesium precipitates, passivating oxide layers, and dissolved magnesium in the wastewater depends on local electrolyte composition. The microenvironment composition during precipitation is inherently sensitive to local operating conditions like 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.[105] Improved characterization can provide critical information on 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.[106] *Operando* infrared spectroscopy could identify transient precipitate speciation. Electrochemical quartz crystal microbalance (EQCM) could measure 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 developed.[107] With experimentally validated models, fundamental microenvironment research can build on existing observations to make findings generalizable and actionable to different use cases.

Phosphorus must be both precipitated and purified for wastewater refining, which motivates reactive separation unit processes with rationally designed operating conditions and reactor architectures. 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 magnesium ions, lowering the overpotential of magnesium oxidation and significantly increasing removal efficiency.[108] Similar methods could co-locate reactants to broaden product selectivity, such as potassium struvite instead of ammonium struvite,[109] by overcoming local K_{sp} challenges. Potassium precipitation presents unique challenges, such as the lower pK_{sp} of potassium struvite (11.7) compared to ammonium struvite (13.26), making supersaturation less favorable.[110] Engineering separations at the microscale can overcome this barrier by controlling the reaction interface through hydrodynamics, stabilizing agents, or electrode modifications; it could also control important product quality parameters like crystal size uniformity.[111] For all products, passivation remains a challenge because it increases energy consumption and lowers activity, even when the cell is operated galvanically (i.e., no electrochemical bias applied).[104] Enhancing electrode lifetime will require strategies to either facilitate or avoid deposition of competing precipitates on the electrode. Replacing or regenerating passivated electrodes in a batch or semi-batch 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.[112] 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 a scalable reactor system.

In summary, the effects of fundamental electrochemical reaction phenomena extend beyond catalysis to stoichiometric electrochemical conversions like electrochemical precipitation. In the case of struvite, products not swept away from the interface impart influence reaction kinetics and thermodynamic solid and aqueous speciation. Product removal then readjusts the microenvironment, affecting product speciation and reaction kinetics. Complex interfacial phenomena present a challenge to product selectivity and uniformity, but also an opportunity for product tunability. Importantly, these considerations could build from advances in electrocoagulation,[103] although purity requirements may be more stringent for precipitation. The fundamental considerations in this section could also extend to stoichiometric reactions like reductive amination where electrogenerated species (aldehydes or ketones generated by alcohol oxidation) react in solution phase (with amines/ammonia and dissolved H_2) to produce higher molecular weight amines.

Subsection 2C: 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 and complex solute mixtures. In many sectors, traditional separations processes can be replaced with electrochemically-driven separations to 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.[113] 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.[114] Lithium-containing oil and gas produced water and geothermal brines (teraliters 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 lithium,[115,116] the co-existence of other impurities (e.g., Na^+, Ca^{2+}, Fe^{3+}, H_2S) at drastically higher concentrations (e.g., >60,000 ppm Na^+, >30,000 ppm Ca^{2+})[117] presents a challenge for high-purity lithium extraction. Conventional separation techniques such as evaporation, crystallization, ion exchange, and solvent extraction exhibit low productivity, high chemical inputs, high water use, and waste generation. Electrochemical separations can overcome these barriers and handle large salinity variations across various relevant wastewaters, including battery leachate, geothermal brines, and oil and gas produced water brines.[115,118] 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.[118] The continued development of selective materials, including membranes for selective electrodialysis (S-ED) and electrodes for electrically switched ion-exchange (ESIX), is a critical factor in the advancement and industrial-scale adoption of these processes. Electrified separation processes such as ESIX and S-ED systems could render lithium recovery from wastewaters feasible.[119,120] 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.[121,122,123] Thus, this section highlights key research challenges and opportunities remaining 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 (electrodes for ESIX, membranes for S-ED) informed by improved understanding of interfacial microenvironments across various wastewaters. For ESIX (where electrochemical biases drive ion separations at the electrode-electrolyte interface), 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 Mg/Li molar ratio from 38.4 to 0.34)[124], improvements in the more challenging Li/Na monovalent separation are still needed. Electrode coatings have been leveraged to improve intercalation selectivity, including TiO_2 and polydopamine as coatings on LFP electrodes that enhance Li/Na selectivity by factors of 2.1 to 16.4.[125,126] These hydrophilic coatings were specifically designed to control the interfacial microenvironment by increasing electrode-electrolyte contact and acting as an additional diffusive barrier to Na. This barrier lowers the Li insertion overpotential and enhances Li insertion selectivity. Selective electrodialysis membranes under investigation include cation exchange membranes, ion-imprinted membranes, and mixed matrix membranes containing metal-organic or covalent-organic frameworks.[127] 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).[128] In the most challenging case of Li/Na separation, 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.[127] As with ESIX electrodes, improved understanding and control of the microenvironment (electrolyte-membrane interface) is required to enhance membrane separation performance. Considerations of microenvironment thermodynamics and kinetics at the bulk 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 influence 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 non-trivial; complex electrolyte compositions and varying driving forces are known to alter membrane separation performance, making material comparison and evaluation challenging.[129] Selectivity metrics are often measured under diffusive operation, where total ion flux is low and flux-coupling effects may impact selectivity.[130,131] 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.[132,133] Continued development of ion transport theory and related transport models would greatly support membrane design efforts; for example, models accounting for the complex architecture of functionalized membranes (e.g., fractional free volume, ion exchange capacity, ion-membrane interactions), the added complexity of multi-component electrolytes, solution-phase hydrated ion migration, and electro-driven permeation would help guide further enhancements in membrane design for enhanced performance in various wastewater compositions and operating conditions.

As in electrocatalysis and stoichiometric electrochemical conversions, maximizing electrochemical separation performance requires integrated design of both material properties and operating parameters. Performance includes selectivity, 'activity,' and stability that influence metrics such as product purity, component lifetime, and energy consumption. In membrane-based S-ED, an inherent trade-off exists between 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 electrochemical intercalation methods have been used to lower intercalation overpotentials and limit Na intercalation that could compromise structural stability by expanding electrode lattices.[125] These advances demonstrate how the combined tuning of selective electrode materials and electrochemical methods can improve selectivity and prolong electrode lifetime (over 10 cycles).[125] However, deployment requites validated stability lasting hundreds to thousands of electrochemical cycles. Because S-ED membrane separation performance depends strongly on operating conditions (electrochemical driving force, electrolyte composition), process-level studies of S-ED permeability and selectivity are also sorely needed to unite fundamental selectivity studies with informed process engineering.[119] 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, and guide the design of next-generation separation materials and processes.

Interfacing selective materials with electrochemistry shows great potential for reduced capital costs,[134] chemical inputs,[135] and emissions[136] compared to conventional separation techniques.[137] Recommendations of future directions for electrified separations research are provided in the context of lithium recovery; however, these recommendations apply broadly to ion-ion separations at large, such as metal recovery from acid mine drainage.[138,139] From a molecular perspective, use-informed design of selective materials can be facilitated by a more well-developed understanding of ion transport mechanisms and the reporting of more standardized selectivity metrics.[119] 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.

Section 3: Expanding the wastewater refining portfolio

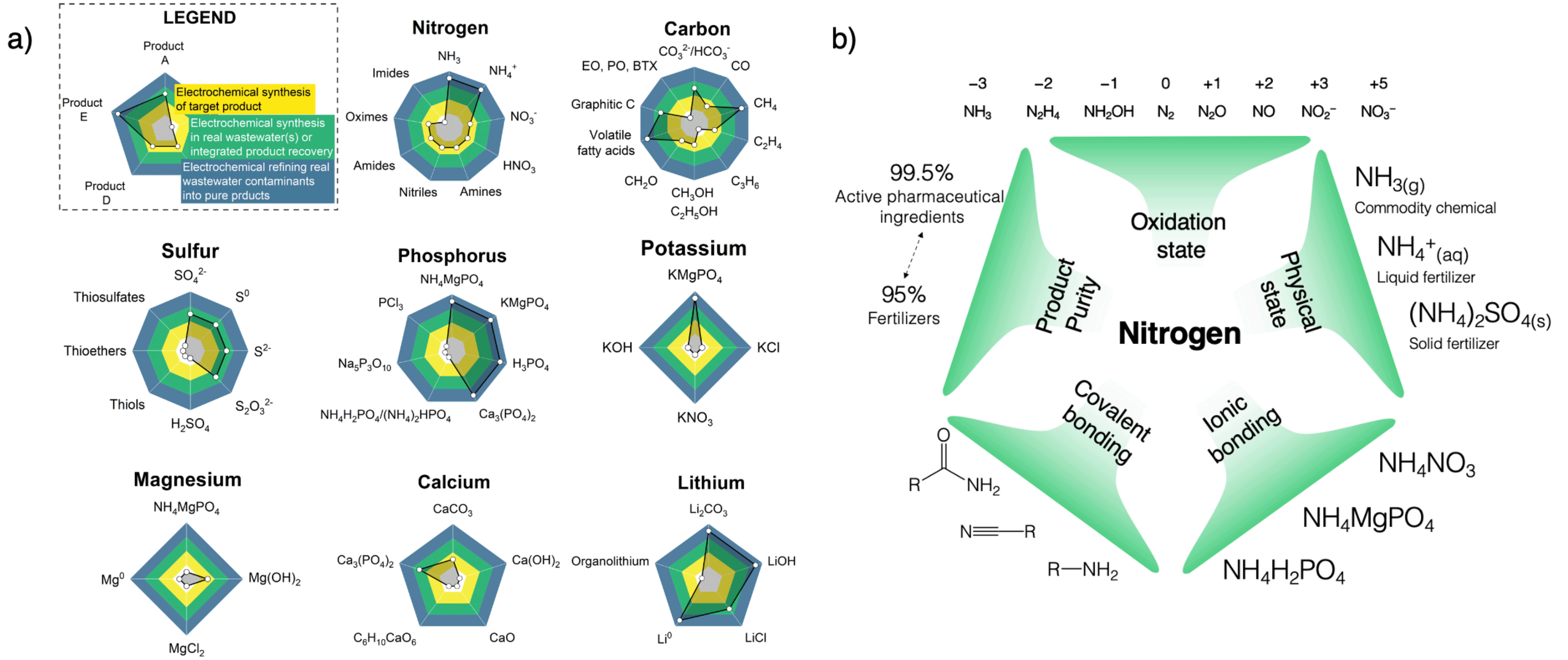

Figure 4. (a) A comparison of the "state-of-the-art" product portfolios for conventional manufacturing and electrochemical methods. The shape of each radar plot is set by the number of common conventional products containing each element. The colored levels of (a) indicate three levels of maturity in refining capabilities. The white innermost level indicates no electrochemical processes targeting the specified product. The yellow first level indicates an electrochemical process achieves the specified product from a common wastewater contaminant; the green second level indicates growing maturity, either by electrochemical synthesis using a real wastewater or by integrated product recovery; the blue third level of electrochemical refining is achieved when integrated recovery of a pure product is achieved in a real wastewater. The third level is not indicating that electrochemical processes are competitive with conventional manufacturing in terms of cost, rate, efficiency, etc., but that electrochemical research has demonstrated significantly mature refining technology of a real wastewater contaminant and may be prepared for pilot-scale and field testing. 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 for brevity. References can be found in the Supporting Information. Panel (b) provides five axes that electrochemical processes can leverage to diversify products from a wastewater contaminant with nitrogen as an example. Note that not all five axes apply to every element.

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 existing and emerging resource needs that are conventionally supplied by centralized refining processes. In Figure 4a, we show progress by element 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 the shaded areas and meet the full potential of circular manufacturing from aqueous waste. Figure 4a presents a framework to analyze the state-of-the-art and future needs of selective target molecule formation from real wastewaters with integrated product recovery. Other circular manufacturing fields have defined the same challenge of expanding future product portfolios, including CCU,[92] biorefineries,[140] plastic recycling,[141] and oil refining beyond gasoline production.[142] Use-informed approaches are needed to define the potential of electrochemical wastewater refining to decarbonize and circularize production of a wide array of compounds from aqueous contaminants (e.g., P, Li, reactive N). In addition, the distributed nature of electrochemical processes can reduce transport emissions, enhance equitable resource distribution, and minimize disposal costs. Broadening the wastewater refining portfolio with use-informed approaches can expand the associated refining values (Section 1) and help reach urgent aspirations including the SDGs, net-zero emissions targets, and increasingly stringent water quality regulations. The rationale for choosing 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**. Each axis for each element should be use-informed by the broader challenges in wastewater treatment and circular resource manufacturing. In the following paragraphs, we provide examples of how each axis influences product utility.

The **oxidation state** of elements like nitrogen determines the utility of refined products. Inorganic nitrogen oxidation state determines product utility between fertilizers (NH_3/NH_4^+, NO_3^-), basic chemicals (NH_3, N_2, N_2O, NO, HNO_3), and specialty chemicals (N_2H_4, NH_2OH). Although ammonia (fully reduced nitrogen) tends to be the most common product targeted in literature, its primary role is as a basic chemical precursor for other commercial nitrogenous products.[65] Although fertilizer uses 80-90% of produced nitrogen, it only represents 40% of the total market value of nitrogen.[45] Making the 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 hydroxylamine or nitric acid as precursors to adiponitrile (nylon).[63] Additionally, process acids like nitric acid (70 million metric tons globally[45]) and sulfuric acid (220 million metric tons globally[143]) are ubiquitously used to produce a wide portfolio of fertilizers (mono/diammonium phosphate, ammonium sulfate, ammonium nitrate), petrochemicals, polymers, and batteries.[144] 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 sulfuric acid, Ostwald Process for nitric acid).[145]

Most conventional "finished" nitrogenous products contain nitrogen in the –3 oxidation state but are themselves 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.[95] Wastewater refining could produce the 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. Efforts to decarbonize organic production have already incentivized aqueous electrochemical production of traditionally petrochemical products via CO_2RR from waste carbon feedstocks.[92] CO_2RR now targets complex C_{2+} products like ethylene by designing catalytic interfaces and processes for C–C coupling. Truly negative emissions chemical manufacturing must use emission-less 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 nutrients to plants in various salt mixtures. Large- and small-scale growers use a breadth of fertilizer blends to address variable (e.g., rainfall events), region-specific (e.g., soil consistency/type, soil pH, water and nutrient retention, mineralized N), and crop-specific (e.g., nutrient utilization rate) parameters.[146] Consequently, refining products will need to match flexible farming demands. While electrochemical refining has primarily targeted nitrogen and phosphorus, potassium (the third plant micronutrient) is under explored but strained in sub-Saharan Africa because mineable potash is scarce.[32,147] Selectively extracting ionic components like potassium could complement nitrogen and phosphorus recovery for complete macronutrient refining of fertilizers and other commodity chemicals, like potassium hydroxide.

Product purity is inextricably 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 end-use) require purities exceeding 99.5%.[116] Lithium products are traditionally high-purity crystalline Li_2CO_3 or $LiOH \cdot H_2O$, which may be derived from intermediate lithium products such as concentrated LiCl or Li_2SO_4 solutions. Selective electrochemical separations must account for product value based on purity when developing and assessing new materials, and establishing and reporting benchmarks for selectivity and production rate.

Physical state influences how chemicals will be transported, stored, and used. Aqueous fertilizers are more useful at the point of generation with on-site fertigation systems, while liquid ammonia, solid urea, or crystalline salt products are more amenable to transport because they are more nutrient-dense. Liquid fertilizers provide plants immediate access to nutrients while solid fertilizers like pelletized urea must first dissolve into the soil. Reactive separations could be developed with more intention to match the product physical state to a specific use case. New reactive separations introduce new interfacial phenomena to investigate, exemplifying a use-informed approach that avoids optimizing systems that provide suboptimal solutions.[148]

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 thermochemical 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.[149] 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 $LiOH \cdot H_2O$, requiring chemical additions and generating significant quantities of solid waste.[116] Integration of membrane electrolysis with electrochemical separation technologies could produce $LiOH \cdot H_2O$ directly from Li-laden wastewaters, avoiding inefficiencies in conventional processes.
(2) Stoichiometric electrochemical precipitations can be used to extract products beyond fertilizers, such as calcium oxide or hydroxide—key components of concrete, mortar, and plaster—that are normally produced by mining calcium carbonate from large quarries and calcining at 900°C.[150]

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.[151] Tunable electrocatalysis for refining may require producing, stabilizing, and separating intermediates and controlling their delivery to distinct active sites.[152,153] For example, nitrite (formed by NO_3RR at Ti)[64] could be isolated and directed in cascading reduction reactions toward inorganic products like ammonium, nitrous oxide, or nitric oxide at MoS_2.[154,155]

Electrocatalytic co-reduction 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.[154,156,157] Co-reduction makes use of reaction intermediates, either surface bound or in the diffusion layer, to form heteroatom bonds.[94] Thus, engineering electrocatalytic microenvironments (catalyst active sites, interfacial pH, aqueous species transport, intermediate stabilization, pulsed electrolysis[158]) 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 reaction, 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. Thus, enzymes can be leveraged to enable selective and complex chemical synthesis or to serve as blueprints for the rational design of molecular catalysts.[159] 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 (all of which could be co-developed with catalysts) could serve as viable options for translating homogeneous catalysis into practice.[160,161] Analogous approaches for heteroatom bond formation in stoichiometric electrochemical conversions are also underexplored. For example, reductive amination to produce amines from ammonia and alcohols or aldehydes is prominent in biomass upgrading, but not for wastewater despite numerous ammonia-rich wastewater feedstocks.[162,163] Synthesizing higher molecular weight molecules in the wastewater environment can also minimize needs for dedicated separation steps of reaction intermediates[94] and enable facile separation processes like size exclusion. The concept of biomimicry also applies to selective electrochemical separations.[164] Nature's highly selective separations are achieved by complexation of solutes with enzymes and membrane transporter proteins.[165,166] These proteins may be purified, extracted, and incorporated into membrane materials or redox-tunable adsorption sites, or otherwise copied through synthetic chemistry.

The non-exhaustive examples provided are feasible tools that may expand the wastewater refining product portfolio with systematic, use-informed rationale. The reactant and wastewaters 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 ammonia or sulfide. 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.

Concluding Remarks

The future of chemical refining needs to achieve multifaceted 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 20th century linear, centralized chemical refining paradigms. It must adapt to growing and changing communities with complex chemical resource needs and variable 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. 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 bourgeoning wastewater-based electrochemical processes are simultaneously fundamental and applied. Electrochemical refining research therefore needs to be as circular as the chemical manufacturing we aim to achieve. Fundamental research cannot be siloed as a linear predecessor to applied research; the 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 relevance: Electrochemical research motivated by global wastewater challenges should be grounded in quantifiable wastewater-pollutant-product value propositions.
- Engineer reactive separations processes at multiple length scales: The influence of the microenvironment should be correlated to the performance of the reactor, while controlled perturbations at the reactor scale can be used to investigate the microenvironment.
- Diversify use cases: Electrochemical phenomena in complex electrolytes should be investigated and explained with sufficient mechanistic insight to tune to multiple value propositions and to integrate with multiple unit processes.
- Catalogue progress: Quantitative performance of reactor components, reactors, and systems should be compared to conventional benchmarks in both water treatment and chemical manufacturing.

Electrochemical refining research will rely on broadening participation of traditionally non-wastewater-focused fields to realize a diversified product portfolio. Wastewater refining also provides an opportunity for multiple disciplines to leverage their approaches. Novel reactions and separations will require down-selecting permutations of catalysts, materials, and reactors in use-informed operational frameworks. The recent push to use biological systems like enzymes as blueprints for electrocatalysis is but one example of how seemingly disparate research disciplines converge in the wastewater space.[159] 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, non-ideal, aqueous pollution as chemical feedstocks to support a modern circular, sustainable, equitable human society.

Supporting Information

Supporting tables for wastewater compositions and flow rates, chemical product monetary values, and representative instances of wastewater-relevant electrochemistry. This material is available free of charge via the internet at http://pubs.acs.org.

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