



HAL
open science

Recent advances of reactive electroseparation systems for water treatment and selective resource recovery

Emmanuel Mousset, Mélanie Fournier, Xiao Su

► **To cite this version:**

Emmanuel Mousset, Mélanie Fournier, Xiao Su. Recent advances of reactive electroseparation systems for water treatment and selective resource recovery. *Current Opinion in Electrochemistry*, 2023, 42, pp.101384. <10.1016/j.coelec.2023.101384>. <hal-04685707>

HAL Id: hal-04685707

<https://hal.science/hal-04685707v1>

Submitted on 3 Sep 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Recent advances of reactive electroseparation systems for water treatment and selective resource recovery

Emmanuel Mousset^{1,*}, Mélanie Fournier², Xiao Su^{2,*}

¹ Nantes Université, ONIRIS, CNRS, GEPEA, UMR 6144, F-85000 La Roche-sur-Yon, France

² Department of Chemical and Biomolecular Engineering, University of Illinois Urbana-Champaign, Urbana, Illinois 61801, United States

ACCEPTED IN

Current Opinion in Electrochemistry Journal

Special Issue: Innovative Methods in Electrochemistry Section (2023)

Contacts of corresponding authors:

- Emmanuel Mousset: emmanuel.mousset@cnrs.fr
- Xiao Su: x2su@illinois.edu

Abstract

Electro-separations (e.g., electro-filtration, electrosorption, electro-deposition, electro-precipitation, electro-coagulation) have received growing interest towards the selective recovery of value-added compounds from wastewater. The coupling of electro-separations with electro-conversion (e.g. advanced electro-oxidation, organic electro-synthesis) has given rise to new materials and systems that uniquely combine reactivity and selectivity. These new reactive separation platforms offer several synergistic advantages beyond each individual component, such as (i) mass transport enhancement, (ii) increased removal rates and yields towards biorecalcitrant pollutants, and the (iii) improvement of recovery and regeneration of porous electrosorptive materials. Significant efforts have recently been devoted to the functionalization of tunable conductive materials for enhanced selectivity (e.g., by leveraging redox-electrochemistry), and in parallel, hybrid systems designs are emerging that enhance efficiency and modularity. Going forward, a major challenge remains to evaluate the efficiency of reactive electroseparation schemes in real effluent contexts, and to test the lifetime and viability of these electrochemical systems at larger scales.

Keywords:

Capacitive deionization; Electrosorption; Membrane-based electrodes; Peroxycogulation; Redox polymers; Process Intensification

1. Introduction

The world is facing critical water issues with the concomitant rise of water stress, partly due to climate change, and partly due to the increase of water demand from agriculture, industry and households [1]. As such, new strategies for water and wastewater management are urgently needed to implement water reuse, which is recognized as one of the most reliable solutions to the impending crisis. The recovery of value-added inorganic (e.g., metals, phosphorus) and organic (e.g., phenols, short chain carboxylic acids, biomolecules) compounds represents an emerging co-development strategy, that enables the circular economy loop through generating value-added streams from waste.

The implementation of new advanced physico-chemical treatments is required in wastewater plants to achieve the removal of biorecalcitrant pollutants, while extracting the valuable molecules [2]. As a design target, these systems should reduce the overall capital costs, while achieving a high removal rate and yield of recovery even in dilute water streams. Furthermore, the treatment system should also minimize the release of unwanted byproducts. Advanced electrochemical systems are gaining interest through their modularity and possible pathways for process intensification. Electrochemical systems can combine several unit operations in hybrid reactors, especially through the combination of electro-conversion (i.e. involvement of electrochemical reactions) [3–10] with electro-separation (i.e. absence of conversion) technologies, which we will refer to as reactive electro-separation [11]. For these integrated reactive separation systems, a critical component is the control of interfacial selectivity, through the development of new electrode materials to enhance the separation performance [12]. In conjunction, at a systems scale, there is increased attention needed for the selection and optimization of operating conditions, and electrochemical process design. Here, we will highlight recent developments in reactive electroseparations, and discuss future opportunities in this growing area of research.

2. Main reactive electro-separation systems

2.1. Reactive electro-filtration

Reactive methods for breaking electroneutrality in water to drive salt migration have grown in attention as energy-efficient methods for selective separations and desalination. Core to these technologies are filters and membranes that enable charge and species separation and reaction. The major electrochemical technology for desalination is electrodialysis, which relies on water splitting at each electrode and alternating anion- (AEM) and cation-exchange membranes (CEM) between two electrodes to drive ionic transport [13–15]. While this technology has historically been used for desalination, modifications to the membranes and integration of ion exchange resins have led to

emerging applications, including resource recovery [14]. Recently, Kim et al. combined electro dialysis with redox-flow concepts and nanofiltration membranes (NFs) to eliminate the need for AEMs, which carry a high cost and propensity for fouling [16]. A poly(ferrocenylproylmethacrylamide-co-[2-(methacryloyloxy)ethyl]trimethylammonium chloride) (P(FPMAM-co-METAC)) was used as a water-soluble redox-copolymer containing redox-active ferrocene groups, to prevent crossover over nanofiltration membranes, while reducing the energy consumption of a conventional single-unit cell electro dialysis system by 88% [16]. Conventional electro dialysis relies on the water-splitting reaction to drive ionic transport through AEM and CEM while redox-mediated electro dialysis uses reversible redox reactions to drive deionization (**Fig. 1**). Since the standard reduction potential of the ferricyanide and ferrocyanide redox pair is lower than the water-splitting reaction, their redox-flow system lowered energy consumption by 52% compared to traditional electro dialysis [17]. Membrane tuning by layer-by-layer polyelectrolyte was also found to be able to impart ion selectivity to redox-electro dialysis – with the benefits of improving membrane stability by suppression of radicals or pH change [17]. In particular, these redox-mediated electro dialysis concepts have been expanded to different aspects of food and biomanufacturing, including the ion-selective recovery of carboxylic acids, and the sustainable valorization of whey proteins [17–19].

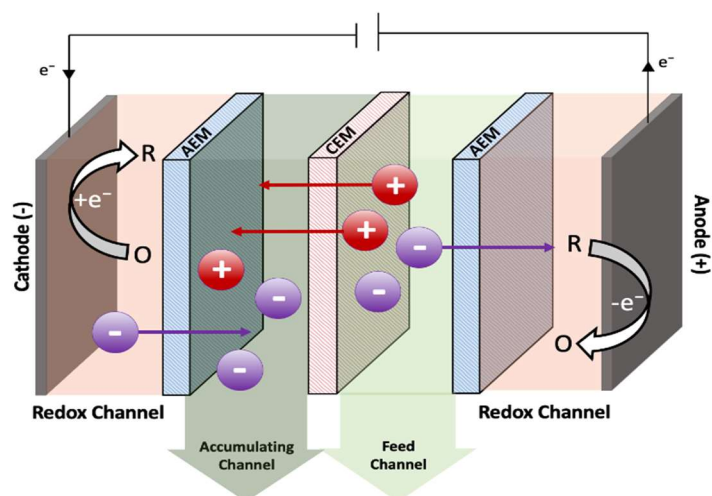


Figure 1. Schematic illustrating redox-mediated flow electro dialysis.

Reactive electrochemical membranes (REMs) can also be considered as a major technology class of reactive electrofiltration, in which the membrane is often the working electrode and promotes an electrocatalytic reaction (**Fig. 2**) [20,21]. For example, REMs can combine an electrochemical advanced oxidation process (EAOP) with physical separation and could mediate some drawbacks of even polymeric electro dialysis, including organic and mineral fouling and high production costs [22]. More recent work by Le et al. applied Magnéli phase Ti_4O_7 REM to the oxidation of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). After a single pass through the REM, they reported

concentrations of $< 86 \text{ ng L}^{-1}$ and 35 ng L^{-1} PFOA and PFOS, respectively, reduced from starting concentrations of 4 mg L^{-1} and 5 mg L^{-1} [23]. Work by Guo et al. in 2016 began tests on a novel chemically resistant Magnéli phase REM for water treatment that could eliminate fouling and scaling [22].

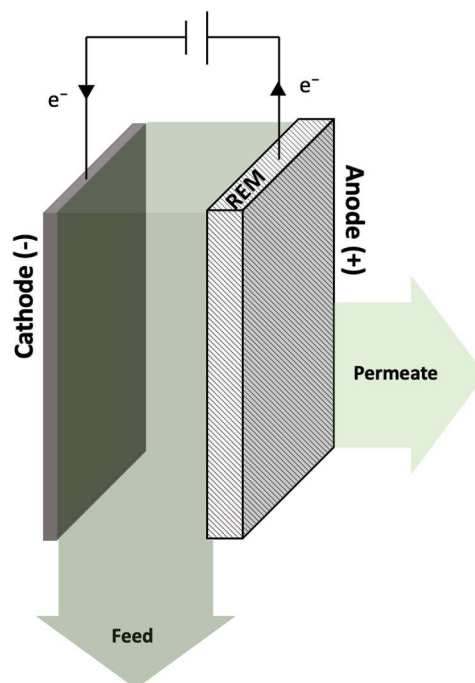


Figure 2. Schematic illustrating a reactive electrochemical membrane (REMs) system.

Overall, reactive electrofiltration methods that combine membranes with surface redox-reactions provide a modular platform beyond desalination. REMs provide a pathway for process intensification through combination of reaction and separations, while redox-flow electro dialysis concepts can provide a platform for both selective membrane separations as well as low energy, low-cost desalination. Going forward, we envision parallel efforts in process design and scaleup to de-risk many of these emerging technologies for practical applications, at the same time as growing studies in the materials design of redox-materials and membranes for more efficient separations and transformations.

Other electrokinetic-based water treatment methods have recently gained growing interest for desalination and selective ion removal include electrodeionization (EDI) and shock electro dialysis or shock ED. These technologies rely on electrokinetic processes, and the transport of charged contaminants in an electrolyte in response to an applied electric field and can remove organic and inorganic ions from water [24]. Among them, shock ED is an emerging electrochemical technique for water treatment in which deionization shock waves are generated in a charged porous material. A

relatively high over-limiting current is passed perpendicular to the direction of fluid flow between ion selective membrane [25]. This creates zones of ion depletion or enrichment within the fluid [26]. In 2015, Schlumpberger et al. published the first example of a continuous and scalable shock ED system [26], with over 99% of salt removal and a water recovery of 79% at high current. In 2019, Conforti and Bazant showed the first use of shock ED to continuously separate ions from multicomponent electrolytes [25]. They showed magnesium ion, Mg^{2+} , could be selectively removed from a mixture of sodium chloride, NaCl, and magnesium chloride, $MgCl_2$. For feed solutions with 9:1 Na:Mg, a peak magnesium removal of 99% is achieved at a total desalination of only 68% [25].

Finally, it must be noted that electrohydrodynamics (EHD) can be used for a range of applications of environmental remediation. EHD can play a key role in process intensification, which has led to a growing number of applications (e.g., water treatment, soil remediation, sensing, monitoring, synthesis, surface finishing of materials) [27–29]. Electrokinetic remediation in particular has seen extensive development over the years for a range of heavy metal decontamination, organic species removal, among others, with several reviews providing an extensive summary of the field [30,31].

2.2. Reactive electrosorption

Electrosorption, the mechanism in capacitive deionization (CDI), is a technique in which species in solution are attracted to a positively polarized electrode and subsequently released by applying a negative polarization [32–34]. While CDI has proven effective in certain contexts of desalination, recent studies have expanded beyond double layer effects to achieve selectivity through redox-reactions [35]. In order to transition from a purely capacitive method to more selective ion-binding, redox-active materials can be utilized [24,36,37]. Redox reactions can create a tunable surface charge on immobilized electrodes, attracting ions towards the respective electrodes – and the redox-site can be tuned for selectivity and also controlled voltage [38]. When the opposite bias is applied, the redox reaction is reversed, and the ions are expelled (**Fig. 3a**). Furthermore, this electrochemical ion binding process can be coupled with electrocatalytic moieties to promote reaction upon adsorption or desorption (**Fig. 3b-c**) [39,40].

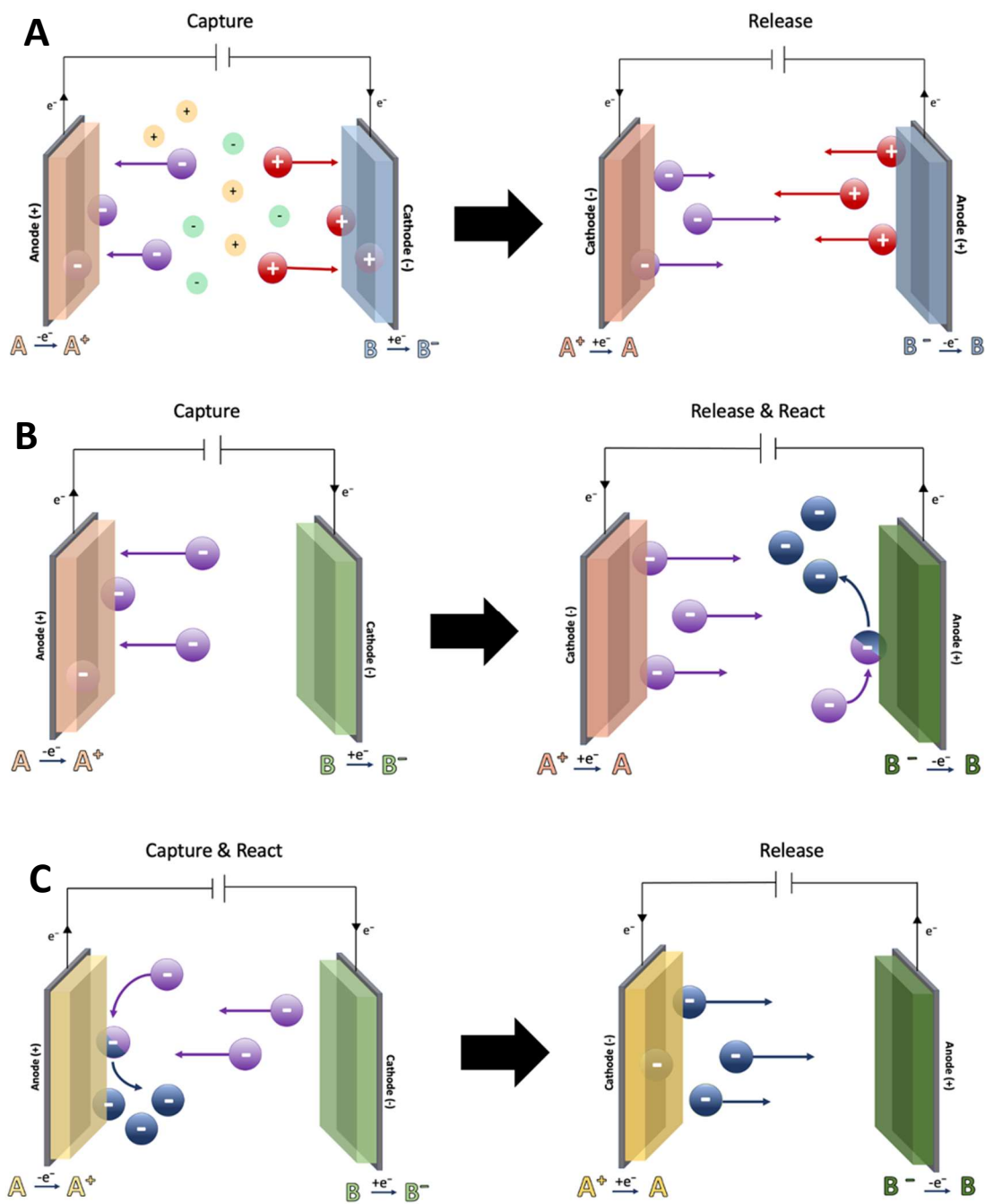


Figure 3. Schematic illustrations showing redox-mediated reactive separation mechanisms: A) Redox-reaction driven asymmetric electroadsorption (left) and release (right). B) Asymmetric electroadsorption by redox species (left) and reactive conversion upon desorption (right). C) Coupled reaction and reaction by redox-electrodes.

Redox-mediated electrosorption has been applied to a range of wastewater treatment and resource recovery contexts, with some of them highlighted as follow:

- **Arsenic**

In many cases, the removal of anionic As(V) over neutral As(III) species is favored by membrane separation and conventional adsorption techniques. As such, there is a growing focus on the development of electrochemical remediation techniques which transform As(III) into the less harmful As(V) [39,41]. Su et al. utilized redox-active polyvinylferrocene/carbon nanotubes (PVF/CNT) electrodes to selectively capture As(V) at concentrations as low as 100 ppb in the presence of competing excess ions [42]. Song et al. performed a similar study using PVF/CNT functionalized electrodes to adsorb arsenic at zero applied voltage leading to the selectivity of As over competing anions like Cl^- , SO_4^{2-} , and NO_3^- , which have low affinity at 0 V. A total As removal efficiency of 51% of the original 150 $\mu\text{g/L}$ present in the feed solution was performed with a low electrical energy consumption only on the order of 0.12 kWh/m^3 [41].

Next, through an asymmetric electrosorption and electrocatalytic system, Kim et al. achieved over 90% removal efficiencies in wastewater where the concentration of arsenic was as low as 10 ppb [39]. As(III) was selectively captured by a redox-active PVF electrode, and catalytically converted into As(V) during desorption by the TEMPO group of poly-TEMPO-methacrylate (PTMA), another redox-electrode [39]. This combined system showed an order of magnitude decrease in energy consumption compared to the sequential system (in which reaction and separation are decoupled), thus highlighting the importance of integration reaction and separations. Recent work by Shi et al. combined redox-active ferrocene with an iron(Fe) based metal-organic framework (MOF), Fe-MIL-88B-NH₂. From an initial arsenic concentration of 150 $\mu\text{g/L}$, they showed a reduction to < 10 $\mu\text{g/L}$ with the process requiring only 0.025 kWh/m^3 [43].

- **Nitrate**

The removal of hazardous NO_3^- , which accumulates in land and water [44–46], has been proposed by conventional desalination techniques like electrodialysis, reverse osmosis and ion exchange [32]. More recently, there has been an increase in the investigation of electro-adsorption based techniques which can be coupled with ion exchange membranes, to increase the selectivity of CDI-based technologies towards nitrate [32]. To expand upon conventional membrane capacitive deionization (MCDI), Kim et al. coated active carbon electrodes with AF20E, a nitrate-selective resin, in an ion exchange resin and tested their system using real municipal wastewater. The electrodes containing AF20E proved more selective for NO_3^- , over chloride (Cl^-) and sulfate (SO_4^{2-}), compared to an electrode coated with just an ion exchange polymer [35].

While the above techniques aim to remove the nitrate present in water, reactive electroseparation technologies can also offer a platform to convert nitrate into value-added ammonia [40]. Kim et al. recently combined polyaniline, a nitrate-selective redox-active polymer, with cobalt oxide, an electrocatalyst for nitrate-to-ammonium conversion. Using a wastewater source containing dilute nitrate of 0.27 mM, a wholly electrified system for capture, up-concentration, and conversion was demonstrated within a single electrochemical cell[40]. The impact of the electro-separation step on the efficiency of electro-conversion was highlighted, where concentration of the dilute nitrate into a more concentrated stream significantly enhanced current efficiency towards ammonia production.

- **Per- and polyfluoroalkyl substances (PFAS)**

Electrochemical methods have proven effective at removing highly persistent per- and polyfluoroalkyl substances (PFAS) [46,47] from water, with Kim et al. reporting an electrosorption system that effectively removed perfluorooctanoic acid (PFOA) with a high uptake capacity of $> 1000 \text{ mg g}^{-1}$ [48]. An asymmetric design of redox electrodes was accomplished by integrating P(TMAx-co-TMPMA1-x)-CNT with a boron-doped diamond (BDD) electrode to selectively adsorb/release and subsequently degrade PFOA. The developed redox-electrosorbent proved highly selective towards PFOA, with a separation factor of 500 PFOA versus Cl^- in the presence of 200-fold excess of chloride [48]. Beyond PFOA, other shorter chains have also been evaluated and treated using redox-electrosorption methods. Manufacturers have switched to short-chain PFAS compounds, like hexafluoropropylene oxide dimer (HFPO-DA, tradename GenX), which poses further challenges due to their higher mobility and recalcitrance to adsorptive treatments like granular activated carbon (GAC) and anion exchange [46,49]. The redox copolymer and BDD system described above was also evaluated for capturing and destroying GenX, with 100% defluorination being achieved after 24 hours of operations [50]. A recent study by Román Santiago et al. tuned redox-active copolymers with differing ratios of fluorinated and amine functional groups to study the effect of these interactions on short chain PFAS binding, including perfluorobutanoic acid (PFBA) and perfluorohexanoic acid (PFHxA) [51]. The key impact of fluorophilicity in promoting higher adsorption of the shorter PFBA was elucidated through both electrosorption tests and molecular dynamic simulations.

Overall, there has been a fast-growing interest in leveraging redox-electron transfer reactions for selective separations, as well as the integration of capture and conversion for different environmental remediation and resource recovery applications [52–55]. We envision that a growing combination of tools will be leveraged to increase predictive capabilities for tailoring electrodes for selective electrosorption, including (i) chemical design and synthesis, (ii) multiscale modeling from an atomistic

model all the way to macroscopic transport and process models, and (iii) operando methods for investigating interfacial binding.

2.3. Reactive electro-deposition

Electrodeposition is a widely and historically used technique to remove heavy metal ions from wastewater. In particular, three-dimensional porous electrodes have been extensively studied for the capture and removal of metals, especially from dilute solutions [56–58]. Electrodeposition relies on a redox process in which a metal ion in solution can be deposited onto the cathode upon reduction and subsequently oxidized upon acid leaching. Electrodeposition can be performed selectively by applying an optimal reduction potential to target deposition of specific ions [13,37,59,60].

More recently, electrodeposition has been applied for battery recycling, for the separation of cobalt and nickel from spent NMC cathodes [61,62]. A major challenge encountered is often the relatively close physicochemical properties of Co(II) and Ni(II), including close electrodeposition potentials under aqueous conditions. Armstrong et al. explored electrodeposition to separate Co and Ni, ultimately producing a 90% Co/10% Ni alloy, while concluding that additional steps, including predeposition and refining, were needed [61]. Yan et al. employed a unique technique combining electrodeposition with electrodialysis to treat spent electroless nickel plating bath, achieving 82% recovery of Ni(II) while simultaneously removing 52% of the HPO_3^{2-} present [63]. Kim et al. sought a more direct approach to control the selectivity of Co/Ni separation by tailoring an electrode with a polyelectrolyte, PDADMA [62]. The selectivity was tuned by polymer loading and electrolyte control. When concentrated chloride was used as a background electrolyte Co exists in the form of a stable anion CoCl_4^{2-} while nickel exists as the cationic complex $[\text{Ni}(\text{H}_2\text{O})_5\text{Cl}]^+$. This speciation led to a difference in onset potentials, creating a window in which nickel can be selectively electrodeposited [62].

Further redox reactions can be coupled to electrodeposition through electrodeposition-redox replacement methods (EDRR), a technique in which a target metallic element is deposited through the redox replacement reaction of a more reactive metal [64]. This method can be applied for noble-metal recovery, including platinum (Pt), silver (Ag), and gold (Au) [65]. Halli et al. applied EDRR to actual industrial hydrometallurgical process solutions, which contain primarily Ni and almost negligible concentrations of platinum (Pt) below one ppb. They achieved selective recovery of Pt by utilizing novel pyrolyzed carbon (PyC) electrodes, ultimately measuring an average of 90 weight percent Pt for the nanoparticles deposited on the electrode surface [64]. As seen, even though the field of electrodeposition has been well-established, the incorporation of new functional electrodes and modes of operation have expanded their applicability to a range of metal recovery and purification contexts. With the emerging supply-chain challenges and growing awareness towards recycling, we

envison the study of molecular selectivity in electrodeposition to play a key role for the efficient recycling of metals from complex, multicomponent feedstocks.

2.4. Reactive electro-precipitation

Electro-precipitation is based on the local alkalization at the vicinity of the cathode material, through the reduction of oxygen (O_2) and/or H_2O into hydroxyl ions (OH^-) (**Fig. 4**) [66,67]. This local OH^- accumulation is known to favor the cathodic precipitation of mainly calcium carbonate ($CaCO_3$) and magnesium hydroxide ($Mg(OH)_2$) in the presence of hard water [68–71]. This phenomenon can be implemented in water softening systems to remove the divalent cations. In practice, the reverse polarity technique is implemented in other electrolytic systems whose objective is to avoid scaling [72]. It consists of reversing the roles of cathode and anode at a given frequency, leading to the redissolution of precipitates in the bulk. This method could not be effective enough with effluents having high water hardness and/or with systems implementing cathode materials that do not stand for high anodic potentials. Therefore, efforts have been made to propose alternatives to minimize the scaling. The hybrid combination with advanced electro-oxidation has been investigated recently.

The generation of powerful oxidant such as hydroxyl radical ($\cdot OH$) at a high O_2 evolution overvoltage anode (e.g., BDD), has shown to decrease the cathodic scaling (~5-10%) issue at higher current density (16 mA cm^{-2}) in a thin film reactor ($500 \mu\text{m}$ interelectrode distance) [73]. This approach was concomitant with the local anodic acidification that converted (bi)-carbonates (HCO_3^-/CO_3^{2-}) into CO_2 , which reduced carbonates content in the bulk. In the meantime, the use of porous carbon-based cathode material (e.g., carbon paper) was shown to increase the electro-precipitation phenomena [74]. Thus, the microfluidic conditions along with the types of cathode and anode materials are critical parameters to consider for increasing efficiency of the process [75,76]. These factors could be tuned to favor phosphate recovery, which is listed as critical raw material [77], especially because the interest of phosphate electro-precipitation was previously shown in simpler system (i.e., without involvement of microfluidic) [78]. However, the efficiency of the process to achieve high purity of phosphate needs to be improved in real matrices. It has been noted that organic matter can adsorb on amorphous calcium phosphate during physical cathodic co-precipitation, which slows down the electro-precipitation mechanism and could reduce the purity of crystallized calcium phosphate recovered [79].

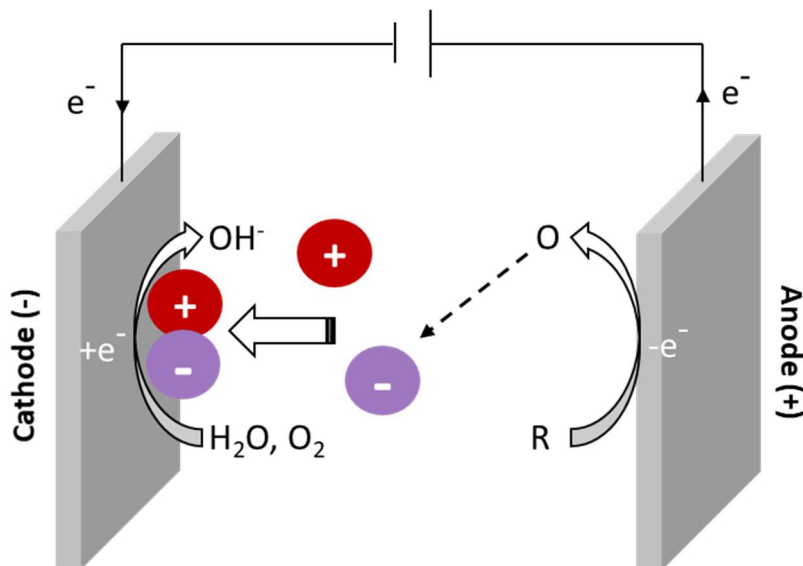


Figure 4. Schematic illustrations of cathodic electro-precipitation with possible interaction (dashed arrow) with oxidant generated at anode.

2.5. Reactive electro-coagulation

Electro-coagulation is known for a long time by promoting the *in situ* generation of coagulant from anodic dissolution of the materials (e.g. iron, aluminium) [80,81]. It provokes the subsequent coagulation with particulate matter, colloidal matter and part of dissolved pollution, that are removed by decantation of the solid phase (i.e., flocs). Additional mechanisms such as precipitation and adsorption on flocs can contribute to the removal of contaminant species. This technology is known to remove inorganic (e.g., phosphate, nitrate, heavy metals) and organic compounds (e.g., natural organic matter) [82]. Electro-coagulation has more recently shown to be particularly useful to remove micro-plastics from wastewater [83].

In combination with an electro-conversion system, namely the peroxi-coagulation [84], the dissolved organic pollution can be also removed with high yield (> 90%) [85]. When iron is polarized as anode, it can react after dissolution with the hydrogen peroxide (H_2O_2) electrogenerated at the carbon-based cathode and produce $\cdot\text{OH}$ through Fenton reaction [86,87]. This leads to the concomitant degradation and mineralization of dissolved organic pollution (e.g., 1,4-dioxane [88], 2,4-dichlorophenoxyacetic acid [89], 7-hydroxycoumarin [90]). This process combination could be particularly useful for micro- and nano-plastics removal, while eliminating the persistent dissolved pollutants and recovering value-added compounds (e.g., metals). However, since the value-added compounds are trapped into the hydroxide sludges, there is the need for an additional selective post-treatment to recover the products from the sludge.

3. Conclusions and perspectives

Reactive electro-separations technologies are gaining increased attention for their role in achieving environmental remediation, water treatment and purification, and a circular economy for valuable resources. These advanced systems could benefit from the electrochemical control through the polarization of emerging conductive materials to increase the selectivity of recovery, by tailoring electrode materials characteristics (porosity and pore size distribution, electroactive surface, conductivity, surface functions, elemental composition, among others) and optimizing operating conditions (including current density/electrode potential, inter-electrode distances and more generally the reactor design, ionic membranes, among others). The physico-chemical properties of the target compounds (such as molecular size, electrophoretic mobility, molecular structure, point of zero charge, acid dissociation constant) along with the matrix composition (type and concentration of salts, etc) are also crucial parameters impacting the efficiency. There are several areas for continued study to improve existing reactive electroseparation systems, as well as opportunities to develop new technologies, including:

- Investigate the matrix effects (ions, organic matter, etc) on the reactive separation systems, particularly with real wastewater, and develop solutions to overcome potentially impacting side-effects such as fouling, electrode degradation, or competing ions that may impact selectivity.
- Develop sustainable and energy-efficient methods to recover the value-added compounds deposited on the electrodes after electro-separation step. A major challenge is the development of low energy/low waste technique for recovering the valuable electrodeposited species.
- Evaluate the long-term stability of newly proposed electrode materials, and associated cost-effectiveness, including environmental cost. The development of accurate process models and technoeconomic assessments can be a critical step in de-risking many technologies for application in the wastewater contexts [91,92].
- Make the full system sustainable, by recovering all valuable compounds, as well as co-electrogenerating green energy source (e.g., H₂, bioenergy [93–95]).
- Develop innovative, scalable, and flexible design to ensure synergies in reactive electro-separations systems (e.g., moving electrochemical cells that could combine advantages of micro-reactors with macro-reactors [96,97]). Innovative design should permit antagonist requirements (e.g., low/high overvoltage, low/high electrode gap, low/high current) for hybrid electro-processes combination, such as the proper integration of electrosorption (which is

usually operated lower current density) with advanced electro-oxidation (operated at high current density). Moreover, new designs should seek to intensify mass transport and promote homogeneous current and potential distributions, while avoiding the external addition of salts to increase the ionic conductivity.

- On the long-term, translating existing technologies from proof-of-concept and bench-scale demonstrations to pilot scale, ideally through industrial/academic partnerships that can provide a pathway for product development and real-market end use.

Acknowledgments

EM gratefully acknowledges the support by the French National Research Agency through the REMixSyn project (n°ANR-21-CE04-0006-01). XS and MF acknowledges support by the National Science Foundation (NSF) under CBET Grant# 1942971.

References

Papers of particular interest, published within the period of review, have been highlighted as:

* of special interest

* * of outstanding interest

- [1] UNESCO, The United Nations world water development report 2019: leaving no one behind., UN Educational, Scientific and Cultural Organization. (2019).
- [2] L. Rizzo, W. Gernjak, P. Krzeminski, S. Malato, C.S. McArdell, J.A.S. Perez, H. Schaar, D. Fatta-Kassinos, Best available technologies and treatment trains to address current challenges in urban wastewater reuse for irrigation of crops in EU countries, *Science of the Total Environment*. 710 (2020) 136312. <https://doi.org/10.1016/j.scitotenv.2019.136312>.
- [3] E. Mousset, K. Doudrick, A review of electrochemical reduction processes to treat oxidized contaminants in water, *Curr Opin Electrochem*. 22 (2020) 221–227. <https://doi.org/10.1016/j.coelec.2020.07.008>.
- [4] J. Alagesan, M.S. Jaisankar, S. Muthuramalingam, E. Mousset, P.V. Chellam, Influence of number of azo bonds and mass transport limitations towards the elimination capacity of continuous electrochemical process for the removal of textile industrial dyes, *Chemosphere*. 262 (2021) 128381. <https://doi.org/10.1016/j.chemosphere.2020.128381>.
- [5] E. Mousset, N. Oturan, E.D. Van Hullebusch, G. Guibaud, G. Esposito, M.A. Oturan, A new micelle-based method to quantify the Tween 80® surfactant for soil remediation, *Agron Sustain Dev*. 33 (2013) 839–846. <https://doi.org/10.1007/s13593-013-0140-2>.
- [6] P.V. Nidheesh, C. Trelu, H.O. Vargas, E. Mousset, S.O. Ganiyu, M.A. Oturan, Electro-Fenton process in combination with other advanced oxidation processes: Challenges and opportunities, *Curr Opin Electrochem*. 37 (2023) 101171. <https://doi.org/10.1016/j.coelec.2022.101171>.
- [7] P.V. Nidheesh, S.O. Ganiyu, C.A. Martínez-Huitle, E. Mousset, H. Olvera-Vargas, C. Trelu, M. Zhou, M.A. Oturan, Recent advances in electro-Fenton process and its emerging applications, *Crit Rev Environ Sci Technol*. 0 (2022) 1–27. <https://doi.org/10.1080/10643389.2022.2093074>.
- [8] E. Mousset, L. Quackenbush, C. Schondek, A. Gerardin-Vergne, S. Pontvianne, S. Kmiotek, M.N. Pons, Effect of homogeneous Fenton combined with electron transfer on the fate of inorganic chlorinated species in synthetic and reclaimed municipal wastewater, *Electrochim Acta*. 334 (2020) 135608. <https://doi.org/10.1016/j.electacta.2019.135608>.

- [9] R. de Mello, A.J. Motheo, C. Sáez, M.A. Rodrigo, Combination of granular activated carbon adsorption and electrochemical oxidation processes in methanol medium for benzene removal, *Electrochim Acta*. 425 (2022). <https://doi.org/10.1016/j.electacta.2022.140681>.
- [10] F. Deng, H. Olvera-Vargas, M. Zhou, S. Qiu, I. Sirés, E. Brillas, Critical Review on the Mechanisms of Fe²⁺ Regeneration in the Electro-Fenton Process: Fundamentals and Boosting Strategies, *Chem Rev*. 123 (2023) 4635–4662. <https://doi.org/10.1021/acs.chemrev.2c00684>.
- [11] E. Mousset, T.A. Hatton, Advanced hybrid electro-separation/electro-conversion systems for wastewater treatment, reuse and recovery: compromise between symmetric and asymmetric constraints, *Curr Opin Electrochem*. 35 (2022) 101105. <https://doi.org/10.1016/j.coelec.2022.101105>.
- *Note: recent review paper that newly centralized the data about the antagonists' requirements (e.g., gas evolution overvoltage, type of electrode material, inter-electrode distance, current density) in hybrid electro-separation/electro-conversion systems.
- [12] K. Zuo, S. Garcia-segura, G.A. Cerrón-calle, F. Chen, X. Tian, X. Wang, X. Huang, H. Wang, P.J.J. Alvarez, J. Lou, M. Elimelech, Q. Li, Electrified water treatment : fundamentals and roles of electrode materials, *Nat Rev Mater*. (2023). <https://doi.org/10.1038/s41578-023-00564-y>.
- **Note: recent state-of-the-art review that focus on the crucial roles of electrode materials in electrochemical treatment of water and wastewater, particularly when implementing electro-separations systems. The emphase is given on interface studies as well as on the development of novel materials and their associated advantages/drawbacks. A strategy of material improvement is presented.
- [13] A.R. Santiago, J. Jeon, E. Kayiwa, R. Cusick, X. Su, Chapter twelve - Membrane-based electrochemical technologies: III. Selective ion removal and recovery, in: Z. Wang, K.-H. Choo, C.Y. Tang, T.D. Waite (Eds.), *Electrochemical Membrane Technology for Water and Wastewater Treatment*, Elsevier, 2022: pp. 403–444.
- [14] H. Strathmann, Electrodialysis, a mature technology with a multitude of new applications, *Desalination*. 264 (2010) 268–288. <https://doi.org/10.1016/j.desal.2010.04.069>.
- [15] H. Kim, S. Kim, N. Kim, X. Su, C. Kim, Multi-electrode scale-up strategy and parametric investigation of redox-flow desalination systems, *Desalination*. 549 (2023) 116350. <https://doi.org/10.1016/j.desal.2022.116350>.
- [16] N. Kim, J. Elbert, C. Kim, X. Su, Redox-Copolymers for Nanofiltration-Enabled Electrodialysis, *ACS Energy Lett*. (2023) 2097–2105. <https://doi.org/10.1021/acsenergylett.3c00482>.
- [17] N. Kim, J. Lee, X. Su, Precision Tuning of Highly Selective Polyelectrolyte Membranes for Redox-Mediated Electrochemical Separation of Organic Acids, *Adv Funct Mater*. (2023). <https://doi.org/10.1002/adfm.202211645>.
- [18] N. Kim, J. Jeon, J. Elbert, C. Kim, X. Su, Redox-mediated electrochemical desalination for waste valorization in dairy production, *Chemical Engineering Journal*. 428 (2022) 131082. <https://doi.org/10.1016/j.cej.2021.131082>.

- [19] N. Kim, J. Jeon, R. Chen, X. Su, Electrochemical separation of organic acids and proteins for food and biomanufacturing, *Chemical Engineering Research and Design*. 178 (2022) 267–288. <https://doi.org/10.1016/j.cherd.2021.12.009>.
- [20] M. Sun, X. Wang, L.R. Winter, Y. Zhao, W. Ma, T. Hedtke, J. Kim, M. Elimelech, Electrified membranes for water treatment applications, *ACS ES&T Engineering*. 1 (2021) 725–752. <https://doi.org/10.1021/acsestengg.1c00015>.
- [21] C. Trellu, B.P. Chaplin, C. Coetsier, R. Esmilaire, S. Cerneaux, C. Causserand, M. Cretin, Electro-oxidation of Organic Pollutants by Reactive Electrochemical Membranes, *Chemosphere*. 208 (2018). <https://doi.org/10.1016/J.CHEMOSPHERE.2018.05.026>.
- [22] L. Guo, Y. Jing, B.P. Chaplin, Development and characterization of ultrafiltration TiO₂ magnéli phase reactive electrochemical membranes, *Environ Sci Technol*. 50 (2016) 1428–1436. <https://doi.org/10.1021/acs.est.5b04366>.
- *Note: This work describes the development of a Mangéli phase REM for water treatment and tested its use as a cathode in the separation of oxyanions. They achieved a 67% removal of a 1 mM NO₃⁻ solution with an energy consumption of 0.22 kWh/m³. The work achieves both high membrane fluxes as well as current efficiencies for the removal of oxyanions for water treatment.
- [23] T.X.H. Le, H. Haflich, A.D. Shah, B.P. Chaplin, Energy-Efficient Electrochemical Oxidation of Perfluoroalkyl Substances Using a Ti₄O₇ Reactive Electrochemical Membrane Anode, *Environ Sci Technol Lett*. 6 (2019) 504–510. <https://doi.org/10.1021/acs.estlett.9b00397>.
- [24] M.A. Alkhadra, X. Su, M.E. Suss, H. Tian, E.N. Guyes, A.N. Shocron, K.M. Conforti, J.P. De Souza, N. Kim, M. Tedesco, K. Khoiruddin, I.G. Wenten, J.G. Santiago, T.A. Hatton, M.Z. Bazant, Electrochemical Methods for Water Purification, Ion Separations, and Energy Conversion, *Chem Rev*. 122 (2022) 13547–13635. <https://doi.org/10.1021/acs.chemrev.1c00396>.
- *Note: the work provides an extensive review of electroseparation technologies for wastewater treatment and water purification, covering both electrosorptive and electrokinetic methods. The review offers a detailed view into the mechanisms of emerging electroseparations, as well as their opportunities and challenges for implementation.
- [25] K.M. Conforti, M.Z. Bazant, Continuous ion-selective separations by shock electrodialysis, *AIChE Journal*. 66 (2020). <https://doi.org/10.1002/aic.16751>.
- [26] S. Schlumpberger, N.B. Lu, M.E. Suss, M.Z. Bazant, Scalable and Continuous Water Deionization by Shock Electrodialysis, *Environ Sci Technol Lett*. 2 (2015) 367–372. <https://doi.org/10.1021/acs.estlett.5b00303>.
- [27] Castellanos Antonio, Pérez Alberto T., Electrohydrodynamic systems, in: Tropea Cameron, Yarin Alexander L., Foss John F. (Eds.), *Springer Handbook of Experimental Fluid Mechanics*, Springer, 2007: pp. 1317–1331.
- [28] Castellanos Antonio, *Electrohydrodynamics*, Springer-Verlag, Wien, 1998.

- [29] D. Han, X. Wu, R. Li, X. Tang, S. Xiao, M. Scholz, Critical Review of Electro-kinetic Remediation of Contaminated Soils and Sediments: Mechanisms, Performances and Technologies, *Water Air Soil Pollut.* 232 (2021). <https://doi.org/10.1007/s11270-021-05182-4>.
- [30] A. Abou-Shady, W. Yu, Recent advances in electrokinetic methods for soil remediation. A critical review of selected data for the period 2021–2022, *Int J Electrochem Sci.* 18 (2023) 100234. <https://doi.org/10.1016/j.ijoes.2023.100234>.
- [31] Y.B. Acar, R.J. Gale, A.N. Alshwabkeh, R.E. Marks, W. Puppala, M. Bricka, R. Parker, *Electrokinetic remediation: Basics and technology status*, 1995.
- [32] S.W. Tsai, L. Hackl, A. Kumar, C.H. Hou, Exploring the electrosorption selectivity of nitrate over chloride in capacitive deionization (CDI) and membrane capacitive deionization (MCDI), *Desalination.* 497 (2021) 114764. <https://doi.org/10.1016/j.desal.2020.114764>.
- *Note: Tsai et al. investigated the selectivity of NO_3^- over Cl^- in both active carbon-based CDI and MCDI systems, describing a possible mechanism for the selective removal for anions with the same ionic charge. The work describes a greater affinity for NO_3^- in CDI compared to MCDI, with a higher selectivity corresponding to a long charging time and high initial concentration of NO_3^- .
- [33] A. Lissaneddine, M.-N. Pons, F. Aziz, N. Ouazzani, L. Mandi, E. Mousset, A critical review on the electrosorption of organic compounds in aqueous effluent – Influencing factors and engineering considerations, *Environ Res.* 204 (2022) 112128.
- [34] A. Lissaneddine, M.N. Pons, F. Aziz, N. Ouazzani, L. Mandi, E. Mousset, Electrosorption of phenolic compounds from olive mill wastewater: Mass transport consideration under a transient regime through an alginate-activated carbon fixed-bed electrode, *J Hazard Mater.* 430 (2022). <https://doi.org/10.1016/j.jhazmat.2022.128480>.
- [35] D.I. Kim, R.R. Gonzales, P. Dorji, G. Gwak, S. Phuntsho, S. Hong, H. Shon, Efficient recovery of nitrate from municipal wastewater via MCDI using anion-exchange polymer coated electrode embedded with nitrate selective resin, *Desalination.* 484 (2020) 114425. <https://doi.org/10.1016/j.desal.2020.114425>.
- [36] R. Chen, T. Sheehan, J.L. Ng, M. Brucks, X. Su, Capacitive deionization and electrosorption for heavy metal removal, *Environ Sci (Camb).* 6 (2020) 258–282. <https://doi.org/10.1039/c9ew00945k>.
- [37] X. Su, Electrochemical interfaces for chemical and biomolecular separations, *Curr Opin Colloid Interface Sci.* 46 (2020) 77–93. <https://doi.org/10.1016/j.cocis.2020.04.005>.
- [38] X. Su, T.A. Hatton, Redox-electrodes for selective electrochemical separations, *Adv Colloid Interface Sci.* 244 (2017) 6–20. <https://doi.org/10.1016/j.cis.2016.09.001>.
- [39] K. Kim, S. Cotty, J. Elbert, R. Chen, C.H. Hou, X. Su, Asymmetric Redox-Polymer Interfaces for Electrochemical Reactive Separations: Synergistic Capture and Conversion of Arsenic, *Advanced Materials.* 32 (2020) 1–20. <https://doi.org/10.1002/adma.201906877>.
- [40] K. Kim, A. Zagalskaya, J.L. Ng, J. Hong, V. Alexandrov, T.A. Pham, X. Su, Coupling nitrate capture with ammonia production through bifunctional redox-electrodes, *Nat Commun.* 14 (2023). <https://doi.org/10.1038/s41467-023-36318-1>.

****Note:** a first example of a fully electrochemical approach for coupling of nitrate capture with ammonia production. A bifunctional redox-electrode was developed that demonstrated the importance of concentrating the nitrate before electroconversion, and the significant increase in current efficiency and yields of ammonium. The bifunctional reactive electroseparation system was used to concentrate nitrate from agricultural water streams and convert to ammonium under realistically occurring conditions.

- [41] Z. Song, S. Garg, J. Ma, T.D. Waite, Selective Arsenic Removal from Groundwaters Using Redox-Active Polyvinylferrocene-Functionalized Electrodes: Role of Oxygen, *Environ Sci Technol.* 54 (2020) 12081–12091. <https://doi.org/10.1021/acs.est.0c03007>.
- [42] X. Su, A. Kushima, C. Halliday, J. Zhou, J. Li, T.A. Hatton, Electrochemically-mediated selective capture of heavy metal chromium and arsenic oxyanions from water, *Nat Commun.* 9 (2018). <https://doi.org/10.1038/s41467-018-07159-0>.
- [43] W. Shi, J. Ma, F. Gao, R. Dai, X. Su, Z. Wang, Metal-Organic Framework with a Redox-Active Bridge Enables Electrochemically Highly Selective Removal of Arsenic from Water, *Environ Sci Technol.* 57 (2023) 6342–6352. <https://doi.org/10.1021/acs.est.2c09683>.
- [44] J.A. Camargo, Á. Alonso, Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: A global assessment, *Environ Int.* 32 (2006) 831–849. <https://doi.org/10.1016/j.envint.2006.05.002>.
- [45] M.H. Ward, R.R. Jones, J.D. Brender, T.M. de Kok, P.J. Weyer, B.T. Nolan, C.M. Villanueva, S.G. van Breda, Drinking water nitrate and human health: An updated review, *Int J Environ Res Public Health.* 15 (2018) 1–31. <https://doi.org/10.3390/ijerph15071557>.
- [46] A. Román Santiago, P. Baldaguez Medina, X. Su, Electrochemical remediation of perfluoroalkyl substances from water, *Electrochim Acta.* 403 (2022). <https://doi.org/10.1016/j.electacta.2021.139635>.
- [47] D.Q. Zhang, W.L. Zhang, Y.N. Liang, Adsorption of perfluoroalkyl and polyfluoroalkyl substances (PFASs) from aqueous solution - A review, *Science of the Total Environment.* 694 (2019). <https://doi.org/10.1016/j.scitotenv.2019.133606>.
- [48] K. Kim, P. Baldaguez Medina, J. Elbert, E. Kayiwa, R.D. Cusick, Y. Men, X. Su, Molecular Tuning of Redox-Copolymers for Selective Electrochemical Remediation, *Adv Funct Mater.* 30 (2020). <https://doi.org/10.1002/adfm.202004635>.
- [49] C.T. Vu, T. Wu, Adsorption of short-chain perfluoroalkyl acids (PFAAs) from water/wastewater, *Environ Sci (Camb).* 6 (2020) 2958–2972. <https://doi.org/10.1039/d0ew00468e>.
- [50] P. Baldaguez Medina, S. Cotty, K. Kim, J. Elbert, X. Su, Emerging investigator series: Electrochemically-mediated remediation of GenX using redox-copolymers, *Environ Sci (Camb).* 7 (2021) 2231–2240. <https://doi.org/10.1039/d1ew00544h>.
- [51] A. Román Santiago, S. Yin, J. Elbert, J. Lee, D. Shukla, X. Su, Imparting Selective Fluorophilic Interactions in Redox Copolymers for the Electrochemically Mediated Capture of Short-Chain Perfluoroalkyl Substances, *J Am Chem Soc.* 145 (2023) 9508–9519. <https://doi.org/10.1021/jacs.2c10963>.

*Note: Román Santiago et al. combined materials synthesis, molecular dynamic simulations, and electrosorption tests to determine how different ratios of fluorinated and amine functional groups in redox-active copolymers effect short chain PFAS binding. The work sheds fundamental insight into the impact of fluorination for short-chain PFAS binding, especially C4 PFAS, and points to new design principles for the design of copolymers to capture and release PFAS purely by electrochemical control.

- [52] L. Wang, S. Nitopi, A.B. Wong, J.L. Snider, A.C. Nielander, C.G. Morales-Guio, M. Orazov, D.C. Higgins, C. Hahn, T.F. Jaramillo, Electrochemically converting carbon monoxide to liquid fuels by directing selectivity with electrode surface area, *Nat Catal.* 2 (2019) 702–708. <https://doi.org/10.1038/s41929-019-0301-z>.
- [53] K.M. Diederichsen, R. Sharifian, J.S. Kang, Y. Liu, S. Kim, B.M. Gallant, D. Vermaas, T.A. Hatton, Electrochemical methods for carbon dioxide separations, *Nature Reviews Methods Primers.* 2 (2022).
- [54] M.A. Alkhadra, M.Z. Bazant, Continuous and selective separation of heavy metals using shock electrodialysis, *Ind Eng Chem Res.* 61 (2022) 16240–16246. <https://doi.org/10.1021/acs.iecr.2c02627>.
- [55] L. Wang, K. Frisella, P. Srimuk, O. Janka, G. Kickelbick, V. Presser, Electrochemical lithium recovery with lithium iron phosphate: What causes performance degradation and how can we improve the stability?, *Sustain Energy Fuels.* 5 (2021) 3124–3133. <https://doi.org/10.1039/d1se00450f>.
- [56] R.M. Gould, R.C. Alkire, Effect of multiple reactions on metal deposition in flow-through porous electrodes, *J Electrochem Soc.* 126 (1979) 2125.
- [57] R. Alkire, B. Gracon, Flow-through porous electrodes, *J Electrochem Soc.* 122 (1975) 1594.
- [58] B.K. Ferreira, Three-dimensional electrodes for the removal of metals from dilute solutions: A review, *Mineral Processing and Extractive Metallurgy Review.* 29 (2008) 330–371. <https://doi.org/10.1080/08827500802045586>.
- [59] L. Doulakas, K. Novy, S. Stucki, C. Comninellis, Recovery of Cu, Pb, Cd and Zn from synthetic mixture by selective electrodeposition in chloride solution, *Electrochim Acta.* 46 (2000) 349–356. [https://doi.org/10.1016/S0013-4686\(00\)00591-0](https://doi.org/10.1016/S0013-4686(00)00591-0).

* Note: in this study, Doulakas et al. used electrodeposition techniques to separate Cu(II), Pb(II), and Zn(II) from synthetic solutions recreating secondary fly ash. By optimizing the pH and overpotential they achieved purities above 99 mol%, thus demonstrating the applicability of electrodeposition methods for selective materials recycling from complex multicomponent feedstocks.

- [60] S. Li, M. Dai, I. Ali, H. Bian, C. Peng, Recovery of nickel from actual electroplating wastewater by integrated electrodeposition with adsorption pretreatment technique, *Process Safety and Environmental Protection.* 172 (2023) 417–424. <https://doi.org/10.1016/j.psep.2023.02.051>.

- [61] R.D. Armstrong, M. Todd, J.W. Atkinson, K. Scott, Electroseparation of cobalt and nickel from a simulated wastewater, *J Appl Electrochem.* 27 (1997) 965–969. <https://doi.org/10.1023/A:1018461920929>.
- [62] K. Kim, D. Raymond, R. Candeago, X. Su, Selective cobalt and nickel electrodeposition for lithium-ion battery recycling through integrated electrolyte and interface control, *Nat Commun.* 12 (2021) 1–10. <https://doi.org/10.1038/s41467-021-26814-7>.
- [63] K. Yan, P. Huang, M. Xia, X. Xie, L. Sun, W. Lei, F. Wang, An efficient Two-Chamber Electrodeposition-Electrodialysis combination craft for nickel recovery and phosphorus removal from spent electroless nickel plating bath, *Sep Purif Technol.* 295 (2022) 121283. <https://doi.org/10.1016/j.seppur.2022.121283>.
- [64] P. Halli, J.J. Heikkinen, H. Elomaa, B.P. Wilson, V. Jokinen, K. Yliniemi, S. Franssila, M. Lundström, Platinum Recovery from Industrial Process Solutions by Electrodeposition-Redox Replacement, *ACS Sustain Chem Eng.* 6 (2018) 14631–14640. <https://doi.org/10.1021/acssuschemeng.8b03224>.
- *Note: in this study Halli et al. propose a electrodeposition–redox replacement (EDRR) method to recover platinum below one ppb from real industrial hydrometallurgical process solutions. This was achieved by utilizing a novel pyrolyzed carbon electrode for metal recovery due to its high surface area and larger potential window. The work showcases significant enrichment ratios and final purity of the recovered Pt.
- [65] X. Su, Electrochemical separations for metal recycling, *Electrochemical Society Interface.* 29 (2020) 55–61. <https://doi.org/10.1149/2.F08203IF>.
- [66] Y. Lei, I. Hidayat, M. Saakes, R. van der Weijden, C.J.N. Buisman, Fate of calcium, magnesium and inorganic carbon in electrochemical phosphorus recovery from domestic wastewater, *Chemical Engineering Journal.* 362 (2019) 453–459. <https://doi.org/10.1016/j.cej.2019.01.056>.
- [67] C. Deslouis, I. Frateur, G. Maurin, B. Tribollet, Interfacial pH measurement during the reduction of dissolved oxygen in a submerged impinging jet cell, *J Appl Electrochem.* 27 (1997) 482–492. <https://doi.org/10.1023/A:1018430224622>.
- [68] C. Barchiche, C. Deslouis, O. Gil, P. Refait, B. Tribollet, Characterisation of calcareous deposits by electrochemical methods: Role of sulphates, calcium concentration and temperature, *Electrochim Acta.* 49 (2004) 2833–2839. <https://doi.org/10.1016/j.electacta.2004.01.067>.
- [69] F.H. Adnan, E. Mousset, S. Pontvianne, M.N. Pons, Mineral cathodic electro-precipitation and its kinetic modelling in thin-film microfluidic reactor during advanced electro-oxidation process, *Electrochim Acta.* 387 (2021) 138487. <https://doi.org/10.1016/j.electacta.2021.138487>.
- [70] F.H. Adnan, S. Pontvianne, M.N. Pons, E. Mousset, Unprecedented roles of submillimetric interelectrode distances and electrogenerated gas bubbles on mineral cathodic electro-precipitation: Modeling and interface studies, *Chemical Engineering Journal.* 431 (2022) 133413. <https://doi.org/10.1016/j.cej.2021.133413>.
- [71] Z. Belarbi, B. Sotta, L. Makhloufi, B. Tribollet, J. Gamby, Modelling of delay effect of calcium carbonate deposition kinetics on rotating disk electrode in the presence of green inhibitor, *Electrochim Acta.* 189 (2016) 118–127. <https://doi.org/10.1016/j.electacta.2015.12.089>.

- [72] F.H. Adnan, M.-N. Pons, E. Mousset, Thin film microfluidic reactors in electrochemical advanced oxidation processes for wastewater treatment: A review on influencing parameters, scaling issues and engineering considerations, *Electrochemical Science Advances*. Accepted (2022) e2100210.
- [73] F.H. Adnan, S. Pontvianne, M.-N. Pons, E. Mousset, Role of anodically electrogenerated hydroxyl radicals in minimizing mineral cathodic electroprecipitation in the presence of hard water, *Electrochem Commun.* 150 (2023) 107493. <https://doi.org/10.1016/j.elecom.2023.107493>.
- *Note: first paper that highlight the anti-scaling role of anode in combination with electro-precipitation at cathode, when using a high O₂ overvoltage anode and micrometric inter-electrodes distance. The hydroxyl radical generated at the anode, along with proton accumulation, could limit the cathodic precipitation of carbonates.
- [74] F.H. Adnan, S. Pontvianne, M.-N. Pons, E. Mousset, Roles of H₂ evolution overpotential, materials porosity and cathode potential on mineral electro-precipitation in microfluidic reactor – New criterion to predict and assess interdependency, *Electrochim Acta.* 428 (2022) 140926. <https://doi.org/10.1016/j.electacta.2022.140926>.
- [75] F.H. Adnan, M.N. Pons, E. Mousset, Mass transport evolution in microfluidic thin film electrochemical reactors: New correlations from millimetric to submillimetric interelectrode distances, *Electrochem Commun.* 130 (2021). <https://doi.org/10.1016/j.elecom.2021.107097>.
- [76] E. Mousset, Interest of micro-reactors for the implementation of advanced electrocatalytic oxidation with boron-doped diamond anode for wastewater treatment, *Curr Opin Electrochem.* 32 (2022). <https://doi.org/10.1016/j.coelec.2021.100897>.
- [77] European Commission, EU list of critical raw materials, 2020. <https://doi.org/10.1016/b978-0-12-823886-8.00023-3>.
- [78] Y. Lei, E. Geraets, M. Saakes, R.D. van der Weijden, C.J.N. Buisman, Electrochemical removal of phosphate in the presence of calcium at low current density: Precipitation or adsorption ?, *Water Res.* 169 (2020) 115207. <https://doi.org/10.1016/j.watres.2019.115207>.
- [79] Y. Lei, B. Song, M. Saakes, R.D. van der Weijden, C.J.N. Buisman, Interaction of calcium, phosphorus and natural organic matter in electrochemical recovery of phosphate, *Water Res.* 142 (2018) 10–17. <https://doi.org/10.1016/j.watres.2018.05.035>.
- [80] P. V. Nidheesh, A.A. Oladipo, N.G. Yasri, A.R. Laiju, V.R.S. Cheela, A. Thiam, Y.G. Asfaha, S. Kanmani, E. (Ted) P.L. Roberts, Emerging applications, reactor design and recent advances of electrocoagulation process, *Process Safety and Environmental Protection.* 166 (2022) 600–616. <https://doi.org/10.1016/j.psep.2022.08.051>.
- [81] P. V. Nidheesh, E. Mousset, A. Thiam, Recent advancements in peroxicoagulation process: An updated review, *Chemosphere.* 339 (2023). <https://doi.org/10.1016/j.chemosphere.2023.139627>.
- [82] A. Shahedi, A.K. Darban, F. Taghipour, A review on industrial wastewater treatment via electrocoagulation processes, *Curr Opin Electrochem.* 22 (2020) 154–169. <https://doi.org/10.1016/j.coelec.2020.05.009>.

- [83] F. Liu, C. Zhang, H. Li, N.A.O. Offiong, Y. Bi, R. Zhou, H. Ren, A systematic review of electrocoagulation technology applied for microplastics removal in aquatic environment, *Chemical Engineering Journal*. 456 (2023). <https://doi.org/10.1016/j.cej.2022.141078>.
- [84] E. Brillas, R. Saucedo, J. Casado, Peroxi-coagulation of aniline in acidic medium using an oxygen diffusion cathode, *J Electrochem Soc.* 144 (1997) 2374–2379. <https://doi.org/10.1149/1.1837821>.
- [85] S. Garcia-Segura, M.M.S.G. Eiband, J.V. de Melo, C.A. Martínez-Huitle, Electrocoagulation and advanced electrocoagulation processes: A general review about the fundamentals, emerging applications and its association with other technologies, *Journal of Electroanalytical Chemistry*. 801 (2017) 267–299. <https://doi.org/10.1016/j.jelechem.2017.07.047>.
- [86] P. V. Nidheesh, Removal of organic pollutants by peroxicoagulation, *Environ Chem Lett.* 16 (2018) 1283–1292. <https://doi.org/10.1007/s10311-018-0752-5>.
- [87] G. Ren, M. Zhou, P. Su, L. Liang, W. Yang, E. Mousset, Highly energy-efficient removal of acrylonitrile by peroxi-coagulation with modified graphite felt cathode: Influence factors, possible mechanism, *Chemical Engineering Journal*. 343 (2018) 467–476. <https://doi.org/10.1016/j.cej.2018.02.115>.
- [88] Y. Lu, H. Shi, J. Yao, G. Liu, H. Luo, R. Zhang, 1,4-dioxane degradation using a pulsed switching peroxi-coagulation process, *Water Reuse*. 11 (2021) 268–278. <https://doi.org/10.2166/wrd.2021.092>.
- [89] Y. Li, L. Liu, Q. Zhang, Y. Tang, M. Zhou, Highly cost-effective removal of 2,4-dichlorophenoxyacetic acid by peroxi-coagulation using natural air diffusion electrode, *Electrochim Acta*. 377 (2021) 138079. <https://doi.org/10.1016/j.electacta.2021.138079>.
- [90] J. Trevino-Resendez, N. Grajales, A. Medel, I. Sires, Y. Meas, Generation of hydroxyl radicals in the peroxi-coagulation process with an air-diffusion cathode : Fluorescence analysis and kinetic modeling, *Process Safety and Environmental Protection*. 172 (2023) 16–26. <https://doi.org/10.1016/j.psep.2023.01.080>.
- [91] S. Hand, J.S. Guest, R.D. Cusick, Technoeconomic Analysis of Brackish Water Capacitive Deionization: Navigating Tradeoffs between Performance, Lifetime, and Material Costs, *Environ Sci Technol*. 53 (2019) 13353–13363. <https://doi.org/10.1021/acs.est.9b04347>.
- [92] S. Hand, R.D. Cusick, Emerging investigator series: Capacitive deionization for selective removal of nitrate and perchlorate: Impacts of ion selectivity and operating constraints on treatment costs, *Environ Sci (Camb)*. 6 (2020) 925–934. <https://doi.org/10.1039/c9ew01105f>.

*Note: this study investigates the impact of ion selectivity on the technoeconomic feasibility of CDI technologies through a parameterized process model. The results quantify the costs associated with CDI for removal of NO_3^- and ClO_4^- ions in water. The work provides a comparative tradeoff analysis of selective NO_3^- removal with CDI, showing that it can be performed economically, but materials and/or processes with higher ion selectivity are required for removal of ClO_4^- ions to be cost-competitive.

- [93] S. Xue, S. Watzele, V. Čolić, K. Brandl, B. Garlyyev, A.S. Bandarenka, Reconsidering water electrolysis: Producing hydrogen at cathodes together with selective oxidation of n-butylamine at anodes, *ChemSusChem*. 10 (2017) 4812–4816. <https://doi.org/10.1002/cssc.201701802>.
- [94] S.O. Ganiyu, C.A. Martínez-Huitl, The use of renewable energies driving electrochemical technologies for environmental applications, *Curr Opin Electrochem*. 22 (2020) 211–220. <https://doi.org/10.1016/j.coelec.2020.07.007>.
- [95] P. V Nidheesh, S.O. Ganiyu, C. Kuppam, E. Mousset, N. Samsudeen, H. Olvera-vargas, G. Kumar, Bioelectrochemical cells as a green energy source for electrochemical treatment of water and wastewater, *Journal of Water Process Engineering*. 50 (2022) 103232. <https://doi.org/10.1016/j.jwpe.2022.103232>.
- [96] E. Mousset, Unprecedented reactive electro-mixing reactor: Towards synergy between micro- and macro-reactors?, *Electrochem Commun*. 118 (2020) 106787. <https://doi.org/10.1016/j.elecom.2020.106787>.
- [97] S. Ben Kacem, D. Clematis, S.C. Elaoud, A. Barbucci, M. Panizza, A flexible electrochemical cell setup for pollutant oxidation in a wide electrical conductivity range and its integration with ultrasound, *Journal of Water Process Engineering*. 46 (2022) 102564. <https://doi.org/10.1016/j.jwpe.2022.102564>.