Electrochemical Techniques for Uranium Extraction from Water

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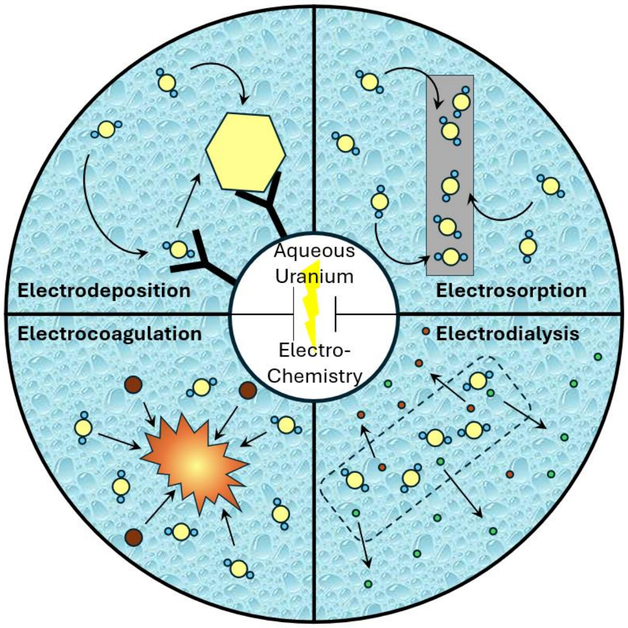
Abstract

Electrochemical removal of uranium from water is an emerging topic that addresses the treatment of drinking water, remediation of contaminated sites, and mining from seawater. Electrochemical strategies compare favorably to conventional processes, such as adsorption and coagulation/flocculation, with advantages in speed and efficiency, materials regeneration, uranium recovery, and recycling. This review assesses all published work on electrochemical techniques for uranium extraction from water, including capacitive deionization (electrosorption), electrodeposition, electrodialysis, and electrocoagulation. This work compares these approaches with conventional techniques and discusses their applicability in different use cases. Environmental and economic considerations are discussed, as well as the current outlook and opportunities for engagement in this emerging field.



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Introduction

Chronic exposure to uranium-contaminated water has clear health impacts as it is a radioactive and toxic heavy metal that increases the incidence of kidney disease, cancer, and other diseases [1]. As the primary energy resource for the nuclear power industry, uranium is a critical resource that is obtained mainly through mineral exploitation [2]. However, uranium processing poses significant health risks and ecological security risks [3,4]. Uranium can also be easily dissolved and transported in water via small environmental changes, rendering water sources a major pathway for uranium to enter the food chain (**Figure 1**A). The increasing concern over uranium-contaminated water has therefore spurred research into innovative and sustainable methods for remediation [5,6]. Importantly, this goal overlaps with resource extraction for the nuclear industry, rendering uranium extraction a highly valuable field.

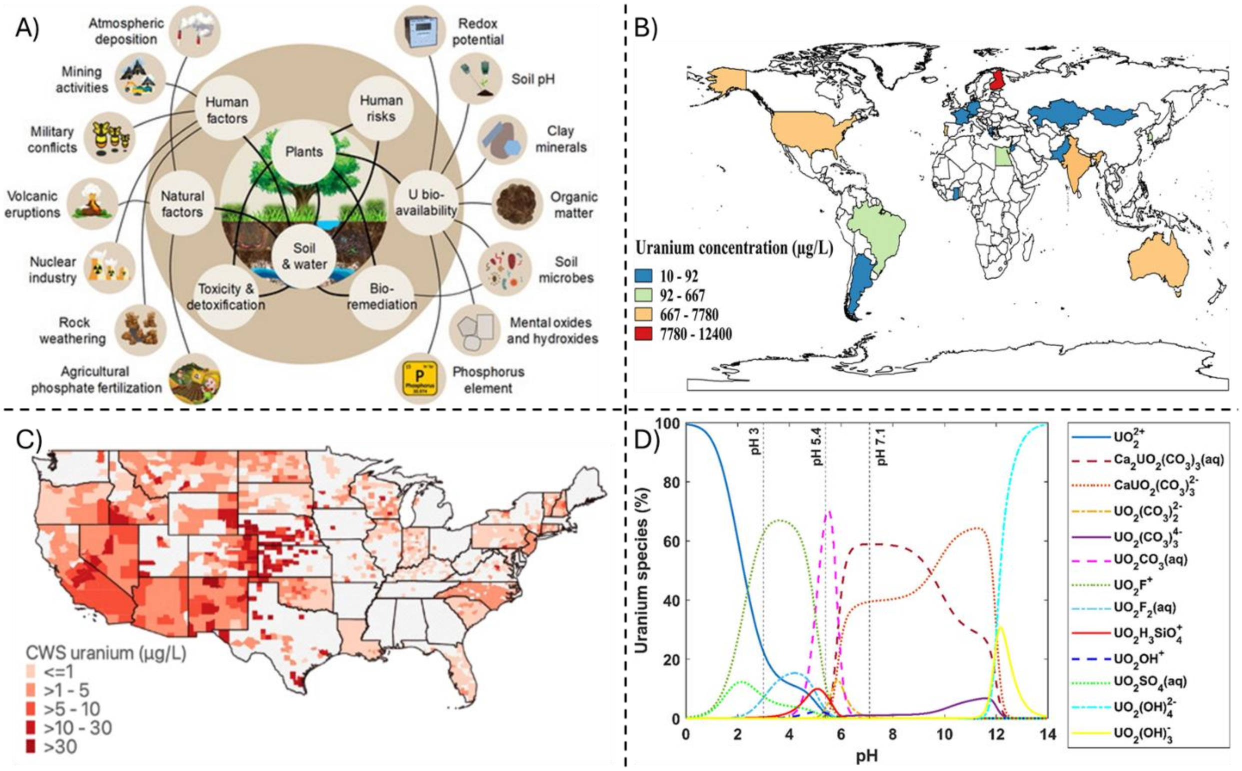


Figure 1: A) Biogeochemical cycle of uranium in water-soil-plant systems. Adapted with permission from Cui et al. [6] Copyright 2022 Taylor & Francis. B) Global estimation of uranium concentrations in groundwater bodies. Adapted with permission from Gandhi et al. [7] Copyright 2022 Elsevier. C) United States spatial distribution of county-level community water system (CWS) uranium concentrations. Adapted with permission under a Creative Commons CC-BY license from Martinez-Morata et al. [8] Copyright 2022 Springer Nature. D) Predicted uranyl speciation in water across different pHs. Adapted with permission from Bales et al. [9] Copyright 2023 American Chemical Society.

Often the public is most concerned with anthropogenic sources of uranium contamination including mining and milling [10], nuclear fuel production [11], fertilizers [12], industrial activities, radioactive waste disposal, and military operations. These are especially noticeable after industrial accidents where contamination may require the long-term evacuation of the local population and prolonged and costly remediation procedures [13,14]. However, uranium also forms a part of the underlying geology of many countries where it can be leached into groundwater resources and consumed by the local population (Figures 1B and C) [15]. Dissolved uranium most commonly naturally occurs in the hexavalent state as the uranyl ion (UO_2^{2+}) and/or its complexes (Figure 1D), which have high solubility and mobility in the environment. Given the very low safe exposure limits proposed by governments and organizations (~20–30 μg/L) [16–19], it is apparent that vigilance and treatment are required to mitigate the public health risk. This is especially important for users without access to centralized municipal water treatment, such as private well users.

Uranium removal strategies primarily involve adsorption [7], chemical precipitation [20], ion exchange [21,22], membrane filtration [22,23], photocatalysis [24–28], and electrochemical methods, with applications varying input and output concentrations, selectivity, removal kinetics, and recovery procedures. In addition to drinking water treatment systems, these techniques can also be used for mine tailing remediation systems that are designed to remove much larger concentrations of uranium, as well as uranium extraction from the oceans, wherein the incident concentration is ~3 μg/L [29], already well below the safe drinking water quality guidelines and in a much more challenging matrix. Primary concerns are centered around the removal capacity and kinetics, selectivity, energy efficiency, device regeneration and production of secondary wastes, ion speciation, and recovery and disposal of uranium.

Research into the electrochemical removal and recovery of uranium from water is an emerging field that has recently expanded in popularity. However, compared to conventional uranium removal technologies, the electrochemical techniques have not been systematically reviewed yet, although being briefly mentioned in some recent review articles regarding the general strategies of uranium remediation [7,30]. To address the gap herein, this work comprehensively reviews the advances in electrochemical methods for uranium removal, compares these methods to their conventional equivalents, and assesses the state of the art with respect to its strengths, weaknesses, economic and environmental impacts, and opportunities for improvement in the coming years. The electrochemical strategies that have been adopted for uranium remediation include capacitive deionization, electrodeposition, electrodialysis, and electrocoagulation.

Capacitive Deionization (Electrosorption)

Capacitive deionization (CDI, also known as electrosorption) is currently the most prolific subject of research in electrochemical uranium removal. It is an adsorption process promoted by the application of an electric field to porous electrodes immersed in an electrolyte solution containing dissolved uranium (Figure 1) [31]. CDI increases the adsorption rate even if uranium is present in a low concentration by providing an attractive force to the uranium ions (electromigration) rather than relying on passive diffusion to the electrode surface. The resulting accumulation of charge on the porous electrode surface is also related to the capacitance of the electrode system and results in the deionization of the bulk solution. As such, it provides immediate advantages over passive adsorption. The electrosorption process is generally reversible by switching the polarity of the electrodes, allowing for charging and discharging cycles and recycling of the electrodes (**Figure 2**A) [32,33]. Conversely, conventional adsorption generally requires chemicals to desorb uranium and regenerate the adsorbent.

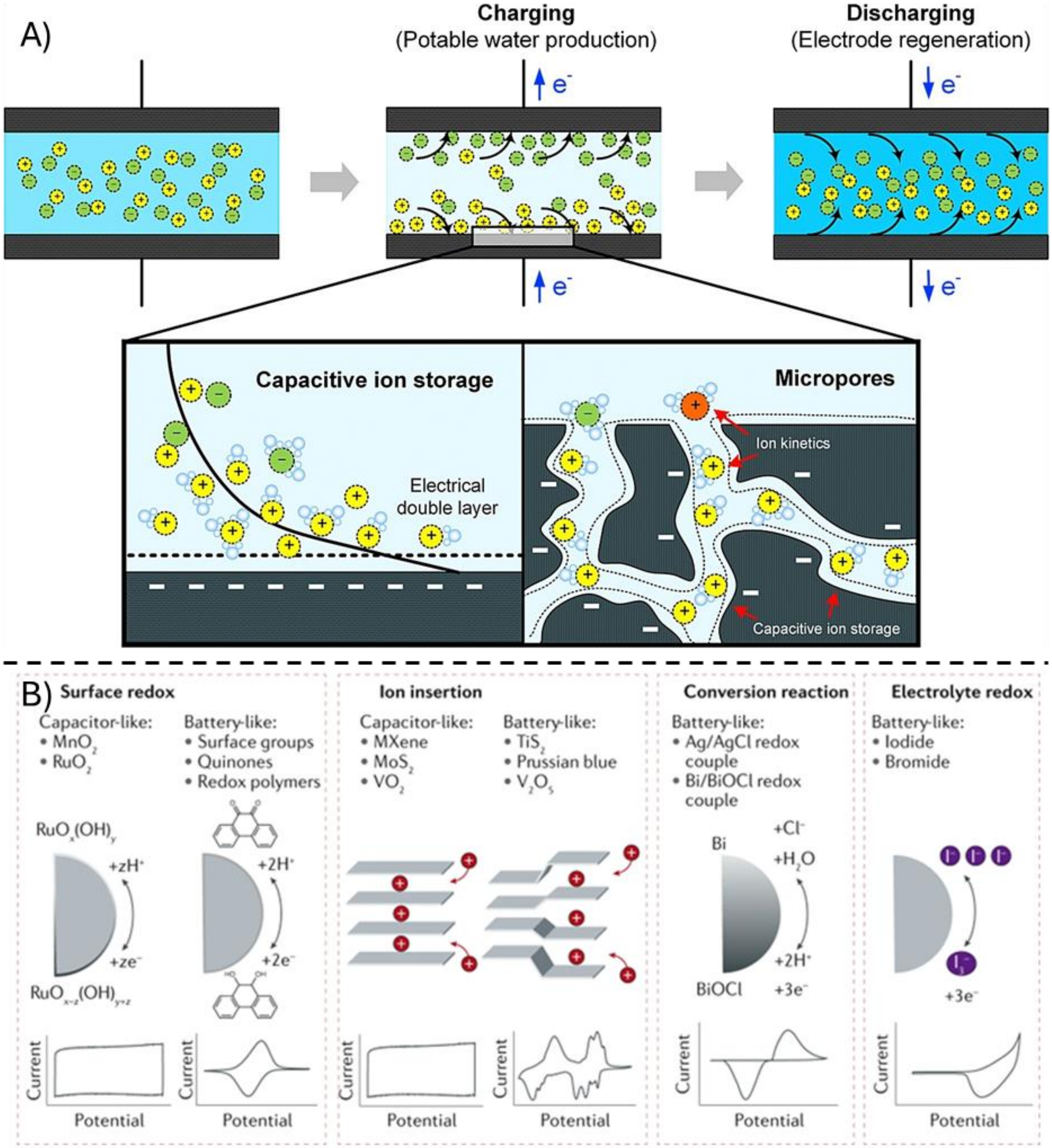


Figure 2: A) Schematic of the capacitive deionization (CDI/electrosorption) process and subsequent discharging and desorption steps to regenerate the electrode surfaces and recover the adsorbed ions. Adapted with permission from Zhang et al. [34] Copyright 2018 Elsevier. B) Examples of possible faradaic charge transfer (redox reactions) occurring during pseudocapacitance. Adapted with permission from Srimuk et al. [35] Copyright 2020 Springer Nature.

There are two primary electrosorption mechanisms that may apply depending on the electrode construction: supercapacitance and pseudocapacitance. Applying an electrical potential to a porous electrode can generate a supercapacitor, which involves the formation of an electrochemical double layer (EDL) of ions with opposite charges on the surfaces of the electrodes (Figure 2A). Supercapacitance is generally exploited for energy storage but can also be used to remove ions, including uranyl, from the solution (deionization) by trapping them within the EDL (Equation 1). Comparatively, pseudocapacitance involves reversible Faradaic electron transfer (reduction-oxidation (redox) reactions) between the electrode surface and the charged ions (Figure 2B) [34–37], which promotes ion electromigration and adsorption by removal of uranyl ions within the EDL. Composite electrodes may be constructed to exploit both supercapacitance and pseudocapacitance simultaneously [38–40]. However, for example, Zhou et al. demonstrated a six-fold increase in uranyl ion adsorption onto a floriform cathode composed of WO_3 on carbon (WO_3/C) composite materials that exhibited both supercapacitance and pseudocapacitance after applying a 1.2 V potential [38]. The efficiency of supercapacitance can be self-limiting as the formation of the EDL will retard the adsorption of further ions through electrostatic repulsion. This presents a challenge when the analyte ions are at a much lower concentration than those innocuous cations, such as sodium ions. Thus, supercapacitive systems generally rely on electrodes coated with some chelating or sequestering functionality that can selectively bind and thus immobilize uranyl ions on the electrode surfaces (Figure 2A). This will not prevent innocuous cations from joining the EDL but will prevent uranyl ions from leaving the electrode surface.

$$UO_{2(aq)}^{2+} \rightleftharpoons UO_{2(EDL)}^{2+} \rightleftharpoons UO_{2(ads)}^{2+} \qquad \text{(Eq. 1)}$$

Appropriate application of electrical potential to the porous electrodes can greatly increase the efficiency of uranyl ion capture from the electrolyte. For example, applying any potential to the electrodes will generate an EDL on their surfaces; however, increasing the potential too high may result in inefficiencies caused by water splitting or electrode degradation. Alternatively, modulating the electrode potential over time can result in increased efficiency. For example, applying a half-wave rectified alternating current (or double potential step technique) allows for the formation of an EDL and chemical adsorption of uranyl ions with subsequent self-repulsion of non-specific cations when the potential is removed (**Figure 3**) [29,41,42]. Liu et al., for example, were able to increase the adsorption capacity by nine times (to 1932 mg/g) and adsorption kinetics by four times relative to conventional adsorption using the half-wave rectified alternating current method [29]. Huang et al. showed that when the potential on:off time ratio was <3:2, it resulted in insufficient contact time with the adsorption moieties on the electrode surface, which compromised uranyl ion adsorption; however, at >3:2 inefficiencies were generated by excessive water splitting [41]. Overall, switching the potential off and on greatly improves the efficiency of supercapacitive electrodes for uranium removal. Conversely, pseudocapacitance is less susceptible to most dissolved cations, e.g., alkali and alkaline earth metals, because they are not redox-active and cannot participate in electron transfer processes with the electrode surfaces. However, complex electrolytes containing redox active metal species, e.g., iron or copper, can still pose selectivity challenges that can be somewhat addressed by careful control of the applied potential.

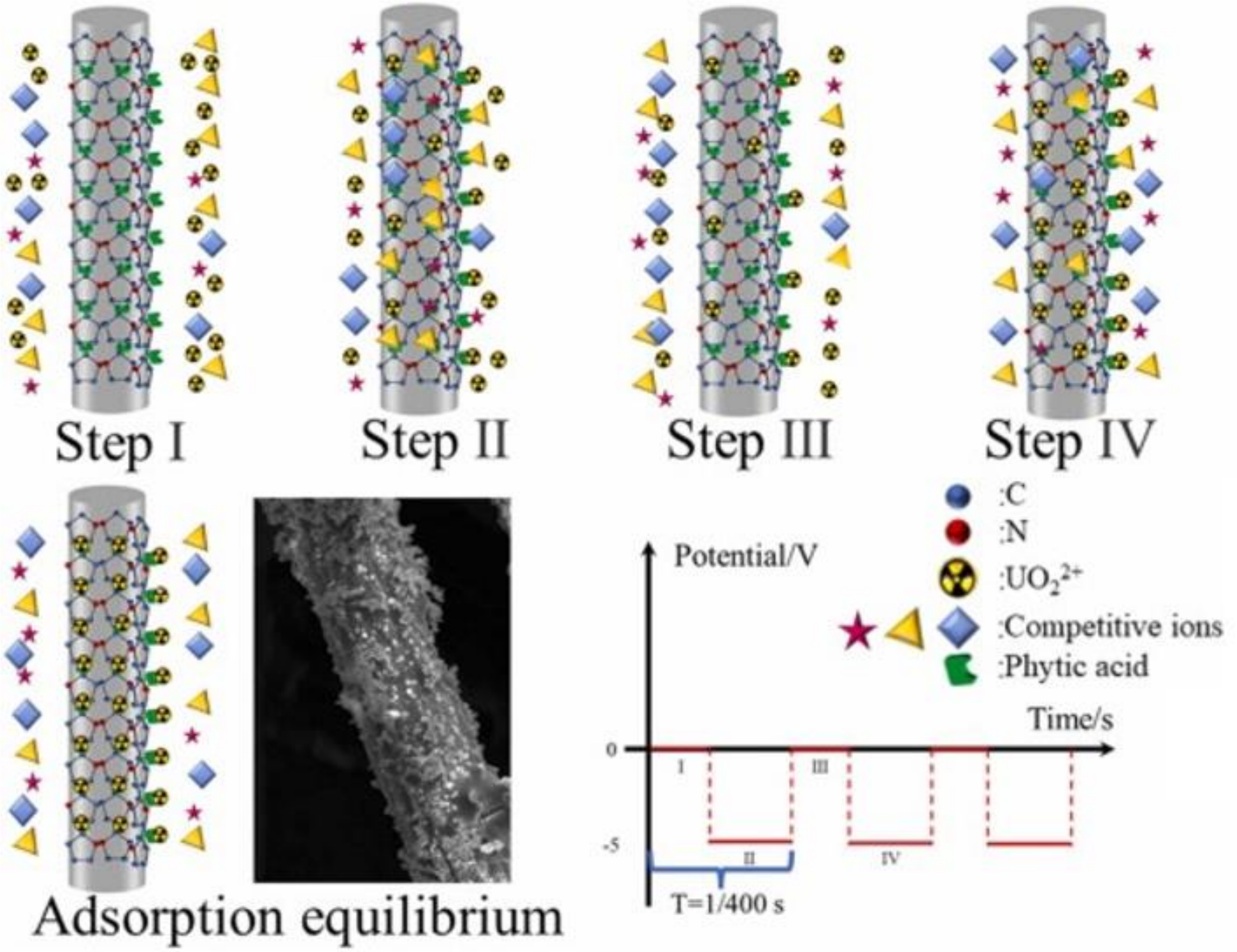


Figure 3: Application of a half-wave rectified alternating current (double potential step technique) for the capture of uranium. In Step I, no voltage is applied to the electrolyte and only passive adsorption occurs. In the step II, a voltage is applied for capacitive deionization (CDI). In step III, the applied voltage is removed. By using a uranyl-capturing ligand, uranyl ions will be retained while other ions will separate from the electrode surface via charge-repulsion. In step IV, the voltage is reapplied for both CDI and the reduction of captured uranyl ions into urania (electrodeposition). This cycle can be repeated until the uranium is fully removed from the water. Adapted with permission from Huang et al. [41] Copyright 2022 Elsevier.

In addition to the applied potential, there are several physical attributes of electrodes designed for CDI systems that will impact their efficacy. As surface area is a primary consideration for the maximum adsorption capacity, it is standard to use porous three-dimensional materials. However, the pore structure is also critical (Figure 2). Although microporous systems have high surface areas, it is easy for those pores to become clogged, e.g., by electrostatic repulsion, precipitation of insoluble salts, or the electrodeposition processes. Subsequently, much of the electrode's surface area can become inaccessible. As such, it is more advantageous to use a hierarchical pore structure with sufficient macro- and mesoporous structure to improve the diffusion of the electrolytes throughout the electrode [43–46]. Liu et al., for example, showed that nitrogen-doped hierarchical porous carbon had improved uranyl electrosorption capacity (67.25 mg/g) by 26–29% relative to similar electrodes without hierarchical structures [43].

Electrode conductivity is required for efficient capacitive deionization as it increases the rate and efficiency of charge accumulation, EDL formation, and pseudocapacitive charge transfer on the porous electrode surfaces. Conductivity is dependent on the electrode materials and structure, such as pore wall thickness. Some electrode materials, such as graphene and MXenes, have good intrinsic conductivity. However, some pseudocapacitor materials, such as niobium phosphate, have poor conductivity that can be improved by forming a composite electrode with graphene (composition with holey graphene decreased the bulk resistance and charge transfer resistance of niobium phosphate from 7.98 to 5.15 and 27.06 to 12.44 Ω, respectively) [47]. Alternatively, conductivity can be improved through the electrodeposition of a conductive polymer layer, such as polypyrrole or polyaniline [48–50]. In addition, Hu et al. interpenetrated the pores of carbonized MOFs with multi-walled carbon nanotubes to improve local conductivity [51].

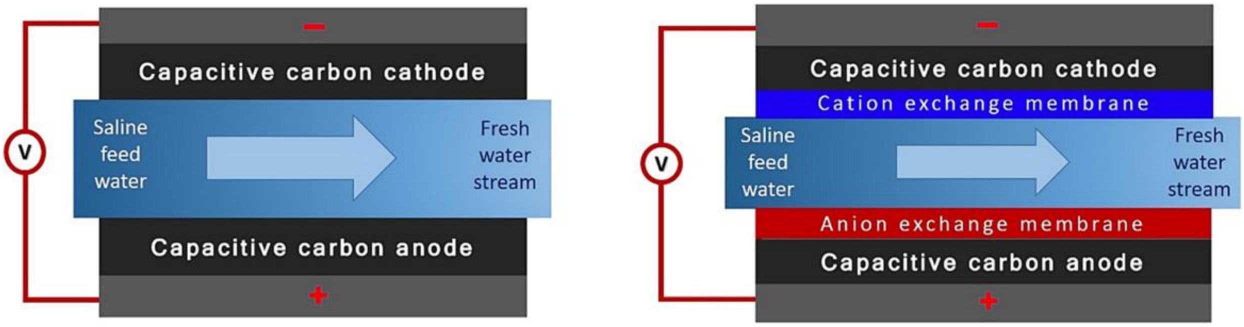
Owing to their increased disorder, hierarchical porous materials with high heterogeneity often have lower conductivity than uniform porous materials. As such, several strategies have been used to generate a suitable pore structure while maintaining the conductivity of the electrode. Laser-induced graphene (LIG), prepared via CO_2-laser conversion of polyimide, or graphene prepared via the hydrothermal reduction of graphene oxide can generate porous graphene electrodes in situ [37,52,53]. Cao et al. prepared LIG/Co_4S_3 electrodes that achieved an adsorption capacity as high as 2702.79 mg/g [37]. Floriform WO_3/C is a pseudocapacitive electrode material with a hierarchical open pore structure [38]. Two-dimensional MXene sheets are effective electrodes but tend to stack and lose accessible surface area. Intercalation of metal-organic frameworks (MOFs) or conductive carbonized MOFs can hold the layers apart, improving the accessible surface area and active adsorption sites [54,55]. Li et al. showed that intercalation of MOFs within the MXene sheet structure greatly increased the electrode capacitance, ultimately resulting in a uranyl uptake of 2224.54 mg/g [54]. Zhang similarly showed that the incorporation of carbonized Zr-MOF into an MXene composite electrode enhanced the electrosorption capacity up to 8:1 Zr-MOF:MXene ratio, resulting in a capacity of 582.46 mg/g at 1.2 V [55]. In some cases, two-dimensional nanosheets can be separated by the intercalation of both cations and anions, this also reduces the accumulation of charge repulsion during EDL formation [47]. It should be noted that intercalation of ions between two-dimensional nanosheets may promote electrode exfoliation and reduce electrode cycle lifetime, so care is required in electrode engineering and exhaustive recycling studies should be performed before their adoption and implementation.

Increasing adsorption sites (or binding sites), which are generally comprised of donor sites or defects on the electrode surface, can also improve the efficiency and selectivity of uranium removal. These sites can be provided intrinsically by choosing the right electrode materials or through surface modification [56–58]. For example, two-dimensional MoS_2 is a pseudocapacitive material with a naturally high affinity for UO_2^{2+} [48]. Similarly, boron phosphide nanosheets strongly coordinate with uranyl ions, facilitating their removal with a high capacity of 2584 mg/g [59]. Nitrogen-doped carbon materials have improved electron transfer because of the increased electronegativity of N, which also forms intrinsic binding sites [43,60]. Interestingly, Mn doping was found to further increase the polarity of the N-doped adsorption sites, increasing their capacity despite its significantly lower surface area relative to nitrogen-doped carbon (20.7 vs 346 $m^2\ g^{-1}$) [60]. Phosphorous doping also can be used alongside N-doping to improve uranyl ion adsorption, specific capacitance (95.4 $F\ g^{-1}$), and charge transfer, resulting in improved adsorption rate and binding capacity (300.6 mg/g) [48]. Extrinsic binding sites can be appended through the addition of phosphates [47], phytic acid (containing phosphate groups) [41,42,61], chitosan (polysaccharide containing hydroxyl, amino, and acetamido groups) [62–65], and xanthan gum (polysaccharide containing hydroxyl and carboxylic acid groups) [65]. For example, by incorporating phytic acid into a polypyrrole-carbon felt electrode, Huang et al. were able to increase the equilibrium adsorption of uranyl nitrate from 372.8 to 1562.0 mg/g under alternating voltage conditions (Figure

3) [41]. However, the most common uranyl-ion-selective functional groups used are amidoximes [29,54,66–71].

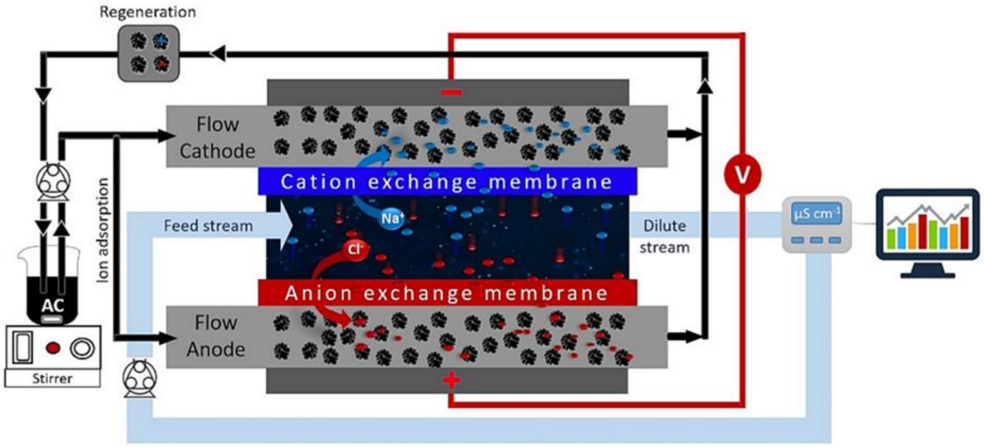
The hydrophilicity of the electrode surfaces is also of concern. Enhancing the wettability of the electrode improves its interactions with the electrolyte solution and the subsequent removal of uranium. The hydrophilicity of CDI electrodes can be improved by the use of polysaccharides, i.e., xanthan gum or chitosan [65], or poly(vinyl alcohol), which all possess hydroxyl groups that hydrogen bond to water [72]. For example, Liao et al. demonstrated a decrease in the water contact angle from 105.8º for hydrophobic poly(vinylidene difluoride)-doped hierarchically porous reduced graphene to 43.9º and 29.2º for hydrophilic chitosan- and xanthan gum-doped analogous materials, respectively [65].

Membrane capacitive deionization (MCDI) is an implementation of capacitive deionization that exploits ion-exchange membranes to only allow the passage of ions of corresponding charge to adsorb to the electrode surfaces (**Figure 4**A and B)). Importantly, ion-exchange membranes can be designed to favor the passage of divalent or multivalent ions, such as uranyl ions, over monovalent species. This allows for improved selectivity of the CDI process. This technique also provides advantages when dealing with groundwater with high hardness, where the complex speciation of uranium yields a significant amount of uncharged species, e.g., $Ca_2(UO_2)(CO_3)_3$ [73]. MCDI can efficiently remove charged uranium species through the spacer channel between the membranes, which then induces uncharged species to subsequently dissociate into charged species to maintain the dissociation/association equilibrium in the feed stream. These new ions can then be removed, initiating a feedback cycle to promote complete metal removal. MCDI provided good flow rates (0.15–0.23 m^3 h^{-1}) and energy use (0.28–0.51 kWh m^{-3}) compatible with household use [9]. This technique is typically very effective; however, membrane fouling is a potential limitation to the long-term use of MCDI as it cannot be easily reversed. Additionally, significant amounts of adsorbed uranium (13–53%) remained on the electrodes during discharge, which limited their recyclability [9]. In a seawater extraction application, unfolded bovine serum albumin was coated onto electrode surfaces to provide uranium binding sites and increase marine biofouling resistance [74].



A) Capacitive deionization

B) Membrane capacitive deionization



C) Flow-electrode capacitive deionization

Figure 4: Comparison of A) normal capacitive deionization (CDI) to B) membrane capacitive deionization (MCDI) and C) flow capacitive deionization (FCDI). Adapted with permission from Tauk et al. [31] Copyright 2024 Elsevier.

Flow capacitive deionization (FCDI) is a variation of MCDI wherein fixed electrodes are replaced by flow electrodes, e.g., carbon particles in suspension, to achieve a pseudo-infinite adsorption capacity and high efficacy as the electrode surfaces are always “fresh” (Figure 4C) [75–77]. FCDI is most effective when employing a countercurrent exchange mechanism between two fluids moving in opposite directions; therefore, the efficiency of uranium desorption into the receiving concentrate solution will also impact the overall efficiency of the removal process, because it determines the steady-state concentration of adsorbed uranium ions on the “fresh” carbon particle surfaces that enter the feed stream. The uranium removed from the feed stream can then be concentrated in a smaller volume of electrolyte solution. Similar to MCDI, dissociation of uncharged species within the applied field is required for successful uranium removal, and membrane fouling is potentially an issue [73].

Electrodeposition/Electrolysis

Electrodeposition (or electrolysis) is the electrochemical reduction of soluble uranium complexes to insoluble species by electrons on the electrode surface [78–81]. This method is commonly applied in tandem with CDI to increase the overall uranium removal efficacy (**Figure 5**A) [62]. Electrodeposition is similar to pseudocapacitance in that there is a reversible electron transfer process between metal ions and the electrode surface, but the specific purpose of electrodeposition is to reduce dissolved metal ions to insoluble compounds. Uranyl ions (UO_2^{2+}) are positively charged and highly soluble species that can be reduced to uncharged and insoluble urania (UO_2) (Equation 2) or other insoluble species [70,78,79,82–86]. When coupled to CDI systems, this reduction removes charged uranyl ions and the associated charge-repulsion effect on EDL formation. As such, it can further push equilibrium toward uranium removal and improve efficiency. For example, Lin et al. used CDI and electrodeposition to remove 99.2% of uranyl ions from simulated groundwater onto TiO_2 nanotube arrays. The uranium was then recovered (98.3%) by washing the surface in dilute nitric acid [15].

$$UO_{2(aq)}^{2+} \rightleftharpoons UO_{2(EDL)}^{2+} \rightleftharpoons UO_{2(ads)}^{2+} \overset{2e^-}{\longleftrightarrow} UO_{2(s)} \qquad \text{(Eq. 2)}$$

Like CDI, electrode materials, applied potential, and coexisting chemicals affect uranium removal efficacy. For example, Wang et al. found that doping of nitrogen and sulfur into the graphene oxide foam electrode was essential for generating nucleation sites for the removal of uranyl ions via electrolysis [87]. Meanwhile, the hydrogen evolution reaction reduced the overpotential while increasing the local pH, which both contributed to the reversible electrodeposition of uranium. This allowed for the recycling of the electrode and uranium, where the uranium could then be eluted and concentrated in solution. The local pH increase was necessary to produce hydroxide ions that polymerize uranyl cations and deposit a charge-neutral uranium polymer. Sulfur defects are also highly efficient active sites for uranium reduction at the edges of MoS_2 nanosheets [88]. In another example, the electrodeposition of uranyl ions from alkaline wastewater onto platinum or titanium electrodes can be promoted by introducing high concentrations of carbonate, which converts uranyl ions within precipitates in mine water into more soluble species, e.g., $[UO_2(CO_3)_3]^{4-}$ and $[UO_2(CO_3)_2]^{2-}$. Unlike other heavy metals, uranium is unique in its ability to form soluble carbonates. Furthermore, careful control of the applied potential prevents the co-deposition of other elements [89,90]. For example, carbonate-containing systems exhibited >98% mass separation compared to <60% when other ions were present, e.g., Fe, Mn, Ni, and Cr [89]. Electrodeposition can also be photochemically assisted [91]. Yan et al., for example, used an asymmetric electrode system where uranyl ions that were adsorbed onto a phosphate-functionalized graphene anode were reduced with photocatalytic assistance using a graphene/TiO_2 cathode. This method avoided the high potentials, unnecessary water splitting, and energy inefficiency of direct electrode reduction [92].

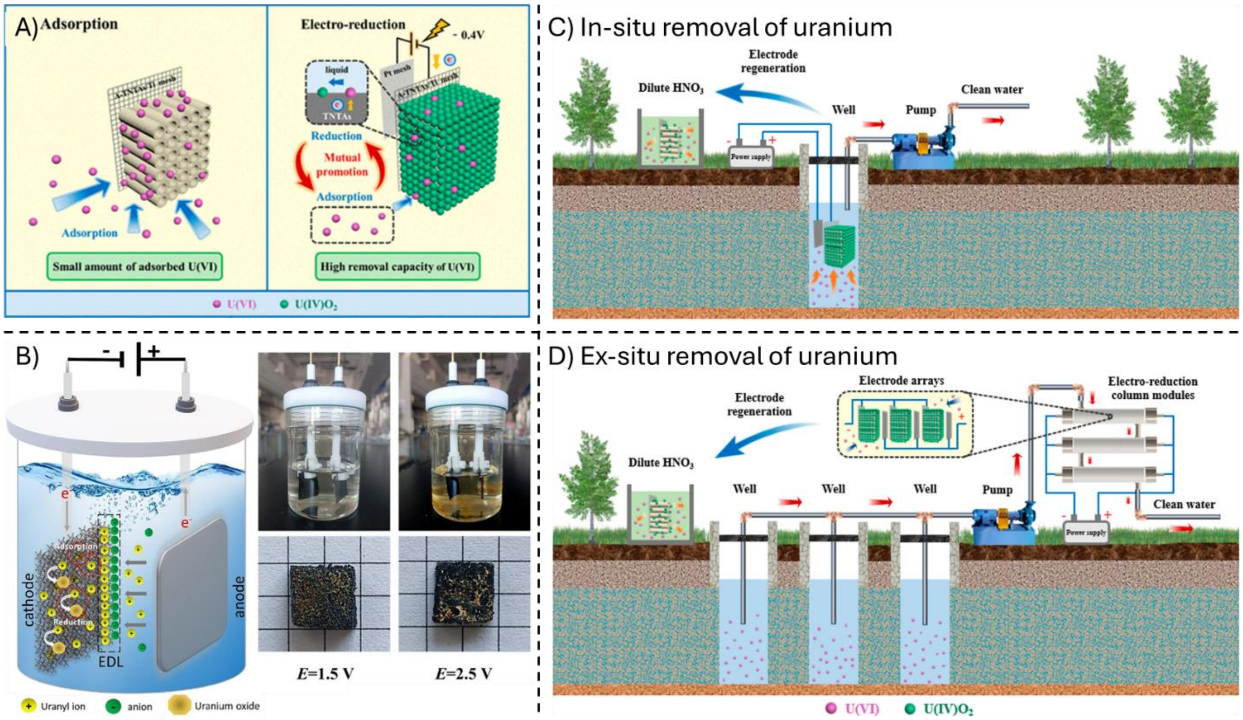


Figure 5: A) Comparison of the adsorption process to the electrodeposition process for uranium removal. B) Simplified electrochemical cell for the conversion of soluble uranyl ions (UO_2^{2+}) to solid urania (UO_2) in tandem with capacitive deionization (CDI), forming an electrochemical double layer. Adapted from Tang et al. [46] Copyright 2023 Elsevier. C) A proposed in-situ system for uranium removal. D) A proposed ex-situ system for uranium removal. A, C, and D were adapted with permission from Lin et al. [15] Copyright 2022 American Chemical Society.

Notably, the selectivity of the electrodeposition method is complicated in electrolytes with several reducible species. For example, Ye et al. demonstrated that in uranium-spiked water electrodeposition proceeds via a single-step one-electron reduction to pentavalent uranium. However, in uranium-mining wastewater, the interference of the sample matrices led to the formation of tetravalent and hexavalent uranium extraction products [93]. Coexisting species in the electrochemical cells can also lead to premature fouling of the porous electrode surfaces, which can result in obstruction of the pores, reduced electrode surface area, and thus compromised performance. Recovery of the insoluble species can be difficult when they are embedded within pores, resulting in low efficiency in subsequent applications. Reoxidation of electrodeposited urania to regenerate the electrode surfaces can also result in incomplete oxidation and particulate matter becoming dislodged in the electrode pore spaces, inhibiting uranium recovery and electrode cycle life.

Electrodialysis

Electrodialysis (ED) is a technique using a stack of alternating semipermeable ion-exchange membranes sandwiched between two electrode plates, forming multiple ED cells, to deionize water in flow (Figure 6) [94,95]. Each ED cell consists of a dilute channel and a concentrate channel formed by anion- or cation-exchange membranes (AEMs and CEMs, respectively) between the anode and cathode. AEMs permit the passage of anions but reject cation permeability, while CEMs permit the passage of cations but reject anion permeation. When feed water is passed between each ED cell pair, the ion concentration decreases in the dilute channels and increases in the concentrate channels. The electric potential applied across the electrode system ensures that the cations will drift toward the cathode and the anions toward the anode, and each can only pass through their respective ion-exchange membrane, being rejected by the other. As such, ions will become trapped in the concentrate channels and purified water will be ejected through the diluate channels. Varying the characteristics of the ion-exchange membranes can modify the selectivity of the process.

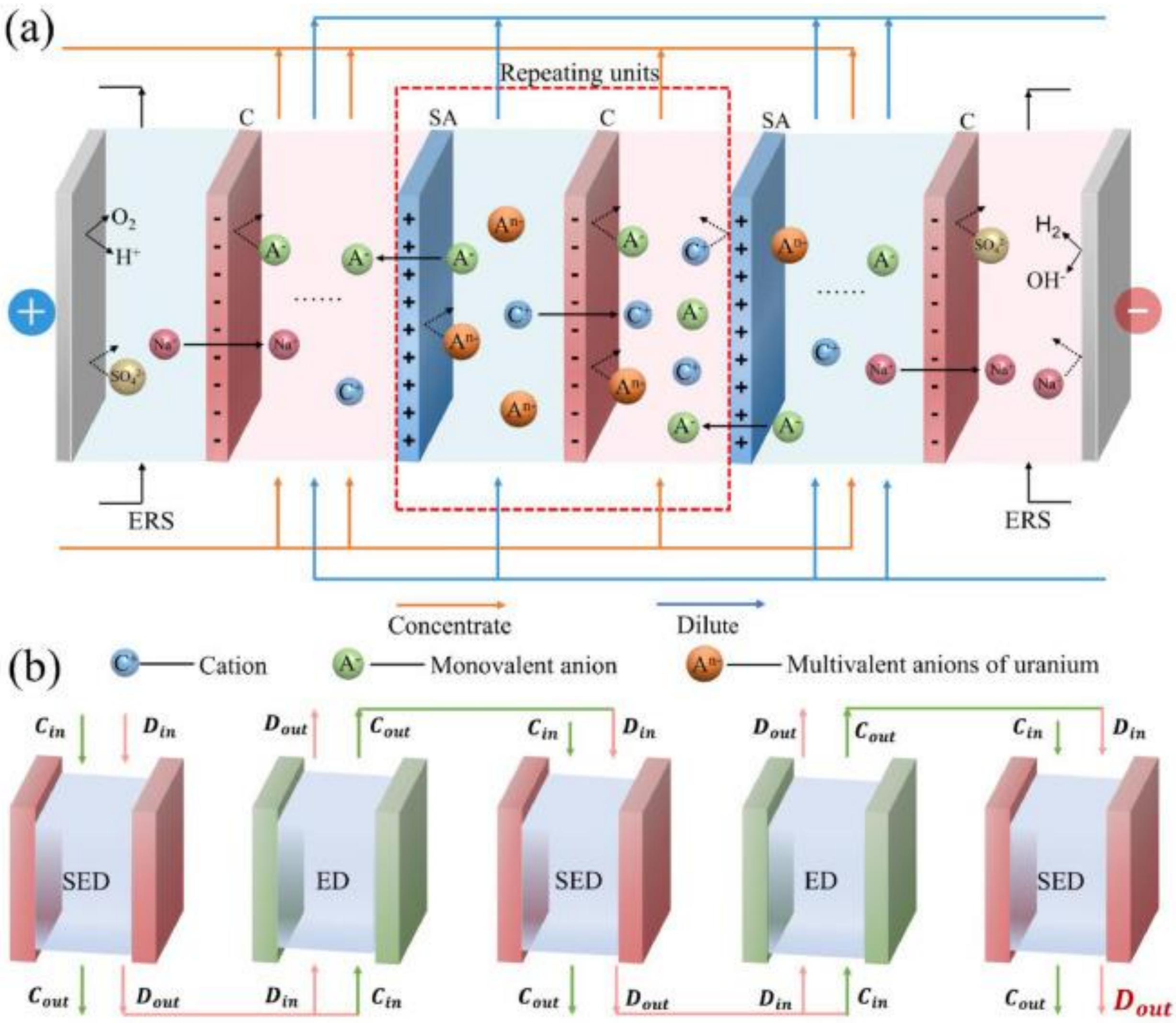


Figure 6: A) Illustration of the operating principles of uranium extraction using selective electrodialysis (SED). Ions migrate under an applied electric field but are restricted from passing through an ion exchange membrane of the same charge. As a result, ions are funneled from diluate channels into concentrate channels where the solutions can be collected separately. (Electrode rinsing solution (ERS); cation-exchange membrane (C); monovalent permeation selective anion-exchange membrane (SA)). B) A cascade electrodialysis process for simultaneous uranium extraction and enrichment from simulated seawater. Adapted with permission from Li et al. [94] Copyright 2023 Elsevier.

To demonstrate the use of ED for uranium removal, Li et al. used a cation exchange membrane with a high permeation selectivity for monovalent ions to extract uranium from seawater (Figure 6). As the predominate uranium species was $[UO_2(CO_3)_3]^{4-}$, its size and charge prevented it from transporting across the membranes, whereas the highly concentrated monovalent ions, e.g., Na^+, were selectively removed. As the monovalent ions migrated across the membranes, they also transported the water within their solvation shell, which further concentrated uranium in the output [94]. Hernández and Ruiz similarly used ED to remove chloride ions from a leaching solution that then improved uranium extraction through ion exchange [96]. As a primary benefit of electrodialysis is the isolation of specific ions from a complex electrolyte, its efficacy is highly dependent on the permeation selectivity of the membranes used in the stack. However, like all membrane-based technologies, membrane fouling and scaling within the devices are potential issues. These will depend on the input water quality and may require frequent maintenance. Efficiency is also highly dependent on the applied potential, current densities, and flow rates, which results in complex operating conditions that require frequent monitoring and adjustment as the input water changes, e.g., composition, flow rate, temperature, etc., and the membranes' age [95].

Electrocoagulation

Electrocoagulation involves the trapping of uranium into sludge and flocs. In conventional water treatment systems, coagulating agents are added to water samples containing organic compounds to initiate the coagulation/flocculation process. In electrocoagulation, the coagulants are generated in situ through a sacrificial anode rather than through chemical addition [97,98]. The metal ions generated from the oxidation of the anode and the hydroxide ions generated on the cathode during water splitting combine to form metal hydroxide flocs. These flocs then adsorb dissolved uranium and precipitate via sedimentation or transport toward the liquid surface via froth flotation when adhered to gas bubbles generated in the electrochemical cell (Figure 7) [99–102]. Electrocoagulation has advantages over conventional coagulation/flocculation in that it does not require chemical inputs, produces less voluminous sludge, can have higher energy efficiency, and can be used in continuous operation.

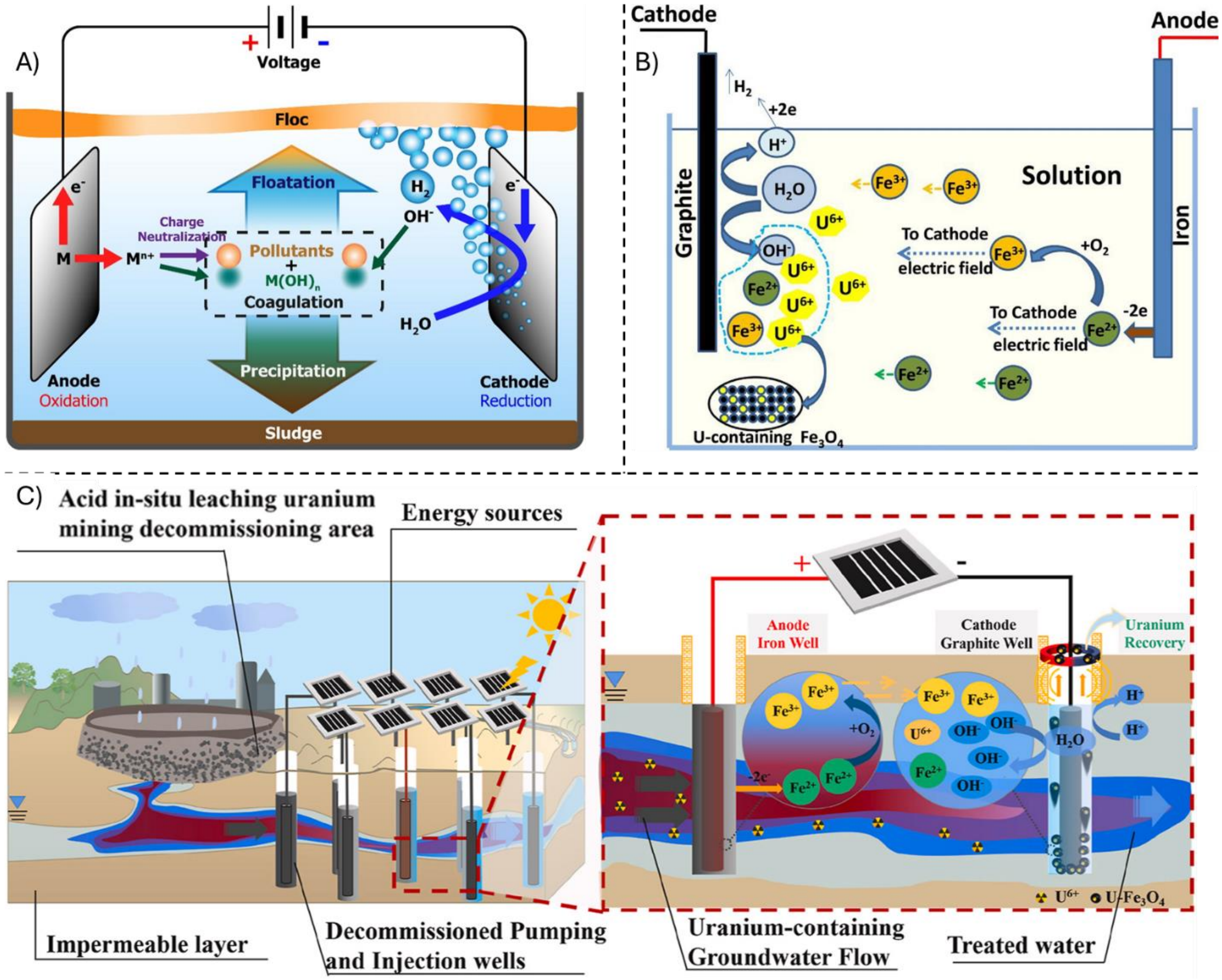


Figure 7: A) Schematic of a generic electrocoagulation system. Coagulating agents (metal cations) are generated electrochemically within the cell, eliminating external chemical inputs and reducing the volume of sedimented sludge. Adapted from An et al. [97] Copyright 2017 Elsevier. B) Electrocoagulation via the use of iron oxide electrodeposition to trap uranium. Adapted with permission from Lu et al. [99] Copyright 2018 Elsevier. C) Proposed on-site application of electrocoagulation for uranium remediation. Adapted with permission from Zhang et al. [98] Copyright 2022 Elsevier.

Although normally electrocoagulation systems do not require coagulants, organic chemical additives can still increase the coagulation efficiency by reducing the interfacial charge between the flocs, allowing for more rapid and thorough agglomeration and separation. The additives accomplish this by reducing charge density on the floc surfaces by distributing charge throughout their structure or by presenting a more hydrophobic moiety on the surface. Some of these organic ligand additives include iminodiacetic acid, polyaniline, EDTA, and alizarin S [103]. When using alizarin S, Li et al. were able to recover and recycle the uranium precipitated in the flocs with 89.71% efficiency [104]. Additionally, Lu et al., for example, encapsulated uranium ions into the matrix of magnetite particles generated electrochemically, which resisted leaching; however, the process was inefficient at low uranium concentrations [99]. Subsequent thermal treatment recrystallized the uranium and iron, enabling their recovery [105]. Nariyan et al. used a response surface methodology to optimize uranium removal from the Pyhäsalmi mine (Finland) through electrocoagulation using iron-stainless steel or aluminum-stainless steel anode/cathode combinations. They found that a current density of 70 mA cm^{-2} and reaction time of 120 min resulted in 99.7 and 97.7% removal of uranium when using iron-stainless steel and aluminum-stainless steel electrode systems, respectively [100]. Notably, the stability of iron-uranium minerals exceeded typically other compounds due to the similar atomic radii of iron and uranium. As such, iron-based electrodes are particularly useful for uranium removal. Interestingly, Li et al. reported that the co-presence of calcium could enhance the level and stability of uranium trapped in Fe_3O_4 while the presence of phosphates could inhibit Fe_3O_4 crystallization [106]. Further work is needed to understand how different ions can impact uranium extraction.

Environmental and Economic Considerations

When selecting a uranium removal strategy, the effectiveness must be weighed against the environmental and economic costs. Electrochemical strategies incur costs associated with electrical power generation and utilization beyond ancillary uses, such as pumping, that are not associated with conventional treatments like adsorption and coagulation/flocculation. However, electrochemistry generally does not require chemical inputs, which provides an important advantage in remote and rural locations where electricity can be generated on-site via solar or wind power whereas transporting treatment chemicals is expensive and logistically difficult, e.g., ice roads are only traversable in winter [98,107,108]. Regeneration of adsorbents and the disposal and/or collection of uranium (locally or off-site) is also an important consideration. These metrics are strongly associated with each specific application scenario. For example, a distributed household water treatment system would likely generate reject water with extracted uranium concentrations at levels below relevant wastewater discharge guidelines. Conversely, treatment systems in place to remediate mine tailings leachate may have uranium concentrations too high to be dischargeable, but may be economically viable for resource extraction [109]. As such, although electrochemical uranium removal systems are generally more efficient and convenient than conventional techniques, the exact choice of treatment strategy requires insight into the required performance metrics and the disposition of recovered uranium.

Importantly, uranium will generally contaminate any materials used in its removal, including adsorbents, resins, electrodes, and any rejected water or sludge [7]. Radioactive waste must be disposed of appropriately according to local regulations, e.g., as outlined by the US Environmental Protection Agency in the United States of America. As the cost and long-term environmental and health risks of radioactive waste disposal sites are high, it is sensible to use removal techniques that minimize the generation of secondary waste. In this way, electrochemical water treatment systems provide an advantage in the reduction of sludge generation relative to the traditional uranium remediation methods that are based on chemical inputs for adsorption, coagulation, and flocculation. Some electrochemical treatment strategies allow for reversible uranium binding, e.g., CDI, which enables the reuse of electrodes and the facile recovery of uranium in concentrates where it can be economically recovered and reused, avoiding long-term disposal in waste sites.

Conclusion and Outlook

In this review, advances in the rapidly expanding field of electrochemical treatment strategies for the removal of uranium from water were presented. Electrochemical treatment strategies provide important advantages relative to conventional adsorption- and coagulation and flocculation-based treatments, in terms of both speed and efficiency, reduced secondary waste generation, the potential for reuse of the electrochemical system, and recovery and recycling of sequestered uranium. Although the techniques presented are promising, there are many opportunities for improvement in research design and method development, including electrode engineering, applied potentials, compartmentalization, regeneration and recovery, etc.

Electrodes are made of diverse and typically heterogeneous materials, and therefore it is difficult to directly compare their efficacy and experimental conclusions between studies. To improve comparability between studies, the adsorption capacity should be reported based on the mass, surface area, and volume of the electrodes to compensate for differences in their bulk density and porosity. It is also important that studies of electrode-based systems have well-constructed control experiments to clearly measure the impact of the modifications, e.g., pore structure, binding sites, conductivity, applied potential programming, etc., that can be translated to subsequent research. This would allow for the development of mathematical models that incorporate all the identified parameters and that can be subsequently used to optimize the performance characteristics of novel electrochemical treatment systems and yield commercially viable solutions for drinking water treatment, remediation, and uranium mining applications.

A critical aspect that is often overlooked is the complete lifecycle assessment of electrochemical-based uranium removal systems. This evaluation is critically important to environmental regulators and can inform the responsible use of these devices by individuals or industries. The mass balance of uranium throughout the treatment process must therefore be tracked. Additionally, the energy and materials used, the generation of waste, the device lifespan and maintenance requirements, and user-friendliness must be addressed in the context of the target application, e.g., a water treatment plant engineer is more equipped to maintain and understand complex devices than a private well user who employs an electrochemical device for water treatment at home.

There are still many basic research questions in this field to be addressed. Most recent research is focused on CDI-based approaches. Improvements to CDI techniques in addressing issues with electrode fouling and accommodating complex electrolyte systems will contribute to the development of more practical devices for more challenging matrices, such as mine water. Engineering uranium binding sites may also improve selectivity and tune binding strength. In combination with applied potential programming, this can be used to optimize uranium extraction efficiency while balancing electrode regeneration and uranium recovery, where the binding should be efficient but reversible. Electrodeposition is often used to solidify and remove uranium after it is adsorbed to the electrode surface in a CDI system. Engineering electrodes with the required structure and materials that facilitate the removal of insoluble uranium species from electrode surfaces and pore spaces would make these processes more efficient. Membrane-based modifications to CDI, i.e., MCDI and FCDI, are exciting ideas with specific advantages. Highly selective ion-exchange membrane engineering would improve both of those techniques, whereas the investigation of fluid electrodes for FCDI towards the development of rapidly reversible uranium adsorption with high affinity could make this a rapid and efficient method for stripping uranium from water.

Electrodialysis, though less well studied, provides unique operating mechanisms that will find use in specific applications where CDI is unsuitable. Electrodialysis devices consist of sandwiches of several layers of anion and cation exchange membranes with varying permeation selectivity. As such, most of the challenges associated with electrodialysis are concerns regarding their maintenance; when the dialysis membranes are damaged or fouled, the device must be disassembled and repaired or replaced. More robust membranes would alleviate some of these concerns, but maintenance will eventually be required. A pressing concern is the complexity of optimizing the operating conditions to ensure the ions are fully sorted before exiting the device. Changes to the incoming water stream or damage to the membranes would also necessitate adjusting the operating parameters to ensure efficacy. To an extent, this can also be mitigated through automated analysis of the input and output water streams and feedback-informed adjustment of the operating parameters. An exciting opportunity in electrodialysis is the engineering of a series of permeation-selective membranes that can effectively sort uranyl ions into individual output streams. This would greatly improve the purity of uranium extracted from seawater.

Electrocoagulation is based on well-established coagulation and flocculation water treatment systems. Opportunities in this field are mostly centered on energy efficiency, electrode lifespan, and reduction of sludge volume. As this technology is compatible with water containing suspended solids and in general does not require chemical inputs, it is highly relevant to isolated communities.

Although electrochemical removal of uranium from water has gained popularity only very recently, particularly in the context of resource extraction from the ocean, the field of electrochemical water treatment systems is likely to keep expanding in the future as a potentially green solution to both anthropogenic and geogenic contamination of drinking water. There are consequently many opportunities to contribute to this globally relevant field.

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