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## Review

# Using advanced X-ray spectroscopy to reveal molecular level insights into water treatment

 Hande Demir<sup>1</sup>, Pinar Aydogan Gokturk<sup>1,2</sup> and Ethan J Crumlin<sup>2,3</sup>


Water treatment technologies separate relevant solutes from water resources for water reuse, valuable resource recovery, and increasing the equity and availability of clean water worldwide. Although a variety of treatment methods exist, their performance needs to be improved to enable selective separation with increased durability and fouling resistance. To achieve this, we need to gain a better understanding of how molecular-level physics and chemistry impact integrated systems. Regarding current research on water treatment techniques, there is a clear need to study such systems under realistic environmental conditions. In this review, we aim to show that X-ray spectroscopic techniques are uniquely positioned to provide such information by obtaining detailed molecular insight into phenomena relevant to water research. By doing so, we hope to accelerate the rational design of novel treatment materials and processes. Specifically, a deeper understanding of the complex and interconnected phenomena that impact multilevel water treatment processes will lead to the successful development of next-generation water purification technologies.

## Addresses

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## Introduction

Accessing adequate and clean water is among the greatest challenges of our century. Nearly 96.5% of Earth's water is contained in oceans, while only about

2.5% of the total water is fresh [1]. A majority of fresh water is used in agriculture and industrial processes, which leads to the pollution of already limited sources. In addition, factors such as population growth, increasing energy and land use, socioeconomic changes, and climate change further increase water demand and are placing additional strain on existing water infrastructure [2]. Addressing this challenge requires significant advances in water treatment technologies.

Depending on the intended application and its source, various methods can be employed to treat water. Commercialized membrane technologies for drinking water purification, wastewater treatment and reuse, and water desalination include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) [3,4]. MF, UF and NF membranes are porous materials that can separate pollutants based on conventional size-exclusion separation mechanisms. RO membranes employ a dense selective top layer to reject small, charged contaminants. Most of these membrane filtration techniques rely on pressure to drive the separation of the pollutants from water.

Other techniques include electrical processes, such as electrochemical oxidation, electrochemical reduction, electrocoagulation, capacitive deionization (CDI), and electrodialysis (ED) [5,6]. Of these techniques, electrochemical oxidation/reduction and electrocoagulation involve electrode reactions. Simply, electrochemical oxidation generates powerful oxidizing agents or free radicals, such as superoxide or hydroxyl radicals, to degrade organic pollutants in water [7]. Electrochemical reduction is used for the treatment of oxidized contaminants (e.g. oxyanions, halogenated compounds, nitrates) and heavy metal ions through the direct or indirect transfer of electrons to these contaminants [8–10]. In the electrocoagulation process, a metal anode is dissolved to produce ions upon oxidation, and they act as a coagulant to attract contaminants having an opposite charge [11,12]. On the other hand, CDI and ED use the electric potential gradient as the driving force for the ion removal. These are nonfaradaic (capacitive) processes that do not include any redox reactions. ED relies on ion exchange membranes (IEMs). These membranes allow only specific ions to pass, that is, cation-exchange membranes (CEMs) permit positively charged ions (counter-ion), while anion-exchange membranes (AEMs) permit negatively charged ion. In ED, water flows through compartments separated by alternating

CEMs and AEMs between the cathode and the anode [4,13,14]. When an electric field is applied, cations move toward the negative electrode (cathode) and pass through CEMs, while anions move toward the positive electrode (anode) and pass through AEMs. This movement alternates between compartments, creating streams of purified water (where ions are removed) and concentrated brine (where ions accumulate). Whereas in CDI, porous electrodes are employed to remove ions from water upon the application of an electric field. When voltage is applied across two porous electrodes, ions in the water migrate toward the oppositely charged electrode. Positively charged ions (cations) are attracted to the cathode, while negatively charged ions (anions) move to the anode. These ions are then electrostatically adsorbed onto the electrode surfaces, effectively deionizing the water [15–17]. Once the electrodes are saturated, the system is regenerated by reversing or turning off the voltage, releasing the adsorbed ions into a small brine stream. IEMs can be placed adjacent to the electrodes in the CDI cell, also known as membrane CDI, to increase the charging/discharging efficiency and enhance the selectivity for certain ions [18–20]. The formation of electrical double layers (EDLs) is the main critical process of CDI for the selective storage of ions.

Efforts to develop more efficient and high-performing desalination materials and techniques have been significant, yet a fundamental understanding of the molecular mechanisms driving key processes, such as transport, partitioning, selectivity, and fouling, remains limited. This gap in knowledge extends to the factors limiting the performance and lifetime of these systems. Traditional *ex situ* analyses, often conducted outside the operational environment and/or after the removal of analytes from a desalination system, fail to capture the true behavior under operating conditions. Thus, *in situ* and *operando* characterization tools are essential for accurately examining these processes as and where they occur.

X-ray core-level spectroscopies offer a powerful means of studying water treatment systems under *operando* conditions, providing both qualitative and quantitative insights into fundamental mechanisms. Among these, X-ray photoelectron spectroscopy (XPS) is a surface-sensitive technique that detects ejected core-level electrons. While conventionally performed under ultra-high vacuum (UHV) conditions, modifying the apparatus to decrease the distance electrons travel (electron optics) and introducing differential pumping stages enable XPS to operate at elevated pressures. This adaptation, known as ambient pressure X-ray photoelectron spectroscopy (APXPS) [21], facilitates the study of liquid interfaces and can achieve pressures up to 110 torr, or even 2.5 bar with specialized gas delivery setups [22], when combined with tender or hard X-rays for deeper electron penetration. X-ray absorption spectroscopy (XAS), including near-edge

X-ray absorption fine structure (NEXAFS) and extended X-ray absorption fine structure, involves the detection of characteristic electron excitations into unoccupied molecular orbitals by X-ray irradiation. XAS can also be equipped with either soft or hard X-rays. Generally, hard X-rays do not require UHV conditions, which makes *in situ* and *operando* experiments possible in numerous configurations and enables the use of solution flow and high pressures that are relevant to water treatment systems. The vacuum requirements of the soft X-ray energy regime make it challenging to implement this technique for the analysis of liquids or solid–liquid interfaces [23]. However, such soft X-ray analysis is still possible using custom cells with structurally sound windows that allow X-ray transmission. In principle, both the emitted electrons and photons can be detected in XAS as electron yield (EY) and fluorescence yield (FY), respectively [23]. X-rays can penetrate deep inside a sample, which makes FY detection bulk sensitive, while EY detection is surface sensitive. In addition, XAS is quite sensitive to the hydrogen bonds in water molecules, which makes this method suitable for the analysis of different forms of water, that is, bulk and interfacial water; the hydrogen-bonding network; and molecular reorientations [24].

X-ray spectroscopy beamlines are established at synchrotron facilities worldwide, enabling measurements under near-realistic conditions. Notable facilities include the Advanced Light Source (ALS) (USA), Advanced Photon Source (USA), MAX IV Laboratory (Sweden), Diamond Light Source (UK), BESSY II (Germany), DESY (Germany), Spring-8 (Japan), Shanghai Synchrotron Radiation Facility (China), Pohang (Korea), and SESAME (Jordan). For example, at ALS, Beamline 9.3.2 operates within the soft X-ray range (200–900 eV), while Beamline 9.3.1 works in the tender X-ray regime under pressures up to 30 mbar [25]. At Spring-8, Beamline BL36XU provides hard X-ray APXPS capabilities within the 4.5–35 keV range, suitable for high-pressure measurements with solution flow [26]. The HIPPIE beamline at MAX IV, with an energy range of 250–2200 eV, supports *in situ* and *operando* experiments under gaseous atmospheres up to 30 mbar [27]. BL 8A at Pohang Accelerator Laboratory is an undulator-based soft X-ray beamline, enabling APXPS, soft-XAS, and scanning photoemission microscopy experiments. APXPS instrument at the BL combines soft synchrotron X-ray with Cr source, allowing wide-range studies from UHV to elevated pressures both at the surface and buried interfaces [28]. SESAME's ID11L-HESEB beamline, the facility's first soft X-ray beamline founded by the Helmholtz Association of Research Centers in Germany, covers an energy range of 70–1800 eV [29].

Over the last few decades, advanced characterization using X-ray spectroscopy has provided significant insight into the atomic- and molecular-scale processes underlying electrochemical energy storage and energy conversion,

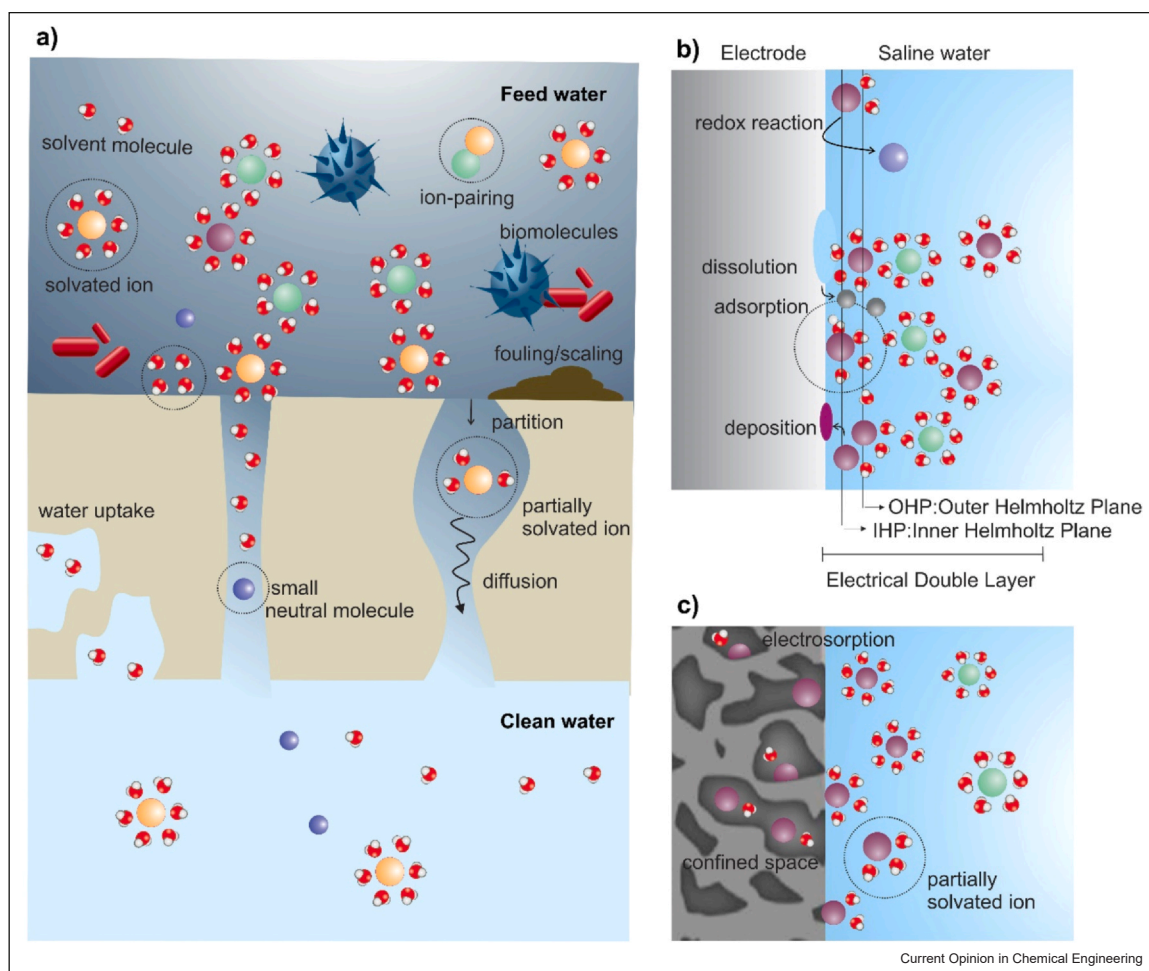
which has promoted the development of these processes. Unfortunately, utilization of such tools in water purification research and development is scarce, with only a few examples existing [30]. In this review, we highlight some of the unique ways in which advanced X-ray spectroscopy can provide a detailed understanding of fundamental processes that take place in desalination systems using several recent *in situ* studies on water treatment materials as well as *operando* measurements performed in relevant systems. Finally, we discuss the limitations of the current instrumentation and strategies for addressing current knowledge gaps in the field.

### Some of the fundamental water treatment processes requiring molecular-level understanding

Water treatment materials are often heterogeneous, and they interact with complex aqueous mixtures, which are

highly variable in terms of salinity, organic matter, pH, and micropollutants, over vast ranges of length and time scales. Thus, understanding these processes at the atomic and molecular scale is essential for the development of better performing technologies. For instance, the molecular-level interactions that occur between solutes, treatment materials, and water during treatment, such as water and solute (ad)sorption on the treatment material or (de)solvation of ions/solutes during the process, can induce significant cumulative effects that control the macroscopic properties of the treatment system, such as partitioning, fouling, water and solute transport, and electrochemical performance [31–34]. Several phenomena of interest in water treatment research are illustrated in Figure 1. At close proximity to the membrane-solution or electrode-solution interface, some ions and contaminants interact with the surface, resulting in adsorption, scaling, or fouling on the treatment material. Solvent molecules also

Figure 1



Schematics of (a) membrane-based, (b) faradaic, and (c) capacitive electrified water treatment processes showing some of the important phenomena taking place. Purple, orange, and green spheres are ions in the solution. Ions are solvated by water molecules, which is the solvent in this representation. Blue small spheres are representing small neutral molecules that are challenging to reject by synthetic membranes.

interact with the treatment materials, leading to hydration and water uptake. For electrified processes, ions and solvent molecules at the interface rearrange and change their orientation to screen the charge on the electrode. Electrochemical redox reactions, which involve a charge transfer between the electrode and electroactive species in the electrolyte, dissolution, and deposition processes, also take place at electrode–solution interfaces for faradaic treatments. For CDI, porous electrodes are used, and the EDL in confined electrode nanopores is a vital part of the process. In the following section, we introduce examples that use X-ray spectroscopic techniques to probe these fundamental phenomena to showcase how advanced spectroscopic characterization can further advance the water treatment science.

### Interaction of water near interfaces and in the bulk material

The interactions of water molecules with the treatment materials and solutes in complex aqueous mixtures play a critical role in a range of applications related to desalination, separations, and resource recovery. These interactions influence the dielectric and electrostatic properties of the system, directly impacting solute partitioning, selectivity, transport, and fouling behaviors [35,36]. In charged membranes, hydration governs proton dissociation and, consequently, conductivity [37]. Probing hydration states is therefore critical for uncovering the relationships between chemistry, structure, and conductivity. Current understanding of hydration relies on macroscopic and bulk measurement techniques that provide averaged properties, such as water sorption, hydrophilicity/hydrophobicity levels, and the average dielectric constant. While informative, these methods fail to capture the nuanced interactions shaped by local heterogeneities like surface chemistry, morphology, or solute/ion distribution. To bridge this gap, *in situ* X-ray spectroscopy offers a powerful tool to resolve hydration structure and dynamics at the molecular scale, enabling a deeper understanding of these complex interactions.

For example, APXPS can provide local chemical information and enables both qualitative and quantitative analysis near ambient conditions, providing insight into the impact of surface chemistry and ions/solutes on water sorption/desorption at water–solid interfaces. Since the invention of APXPS, the interaction between water and metals or metal oxides has been of interest due to their applications in catalysis [24]. APXPS has been previously used to evaluate the water adsorption of metal and metal oxide surfaces, including Cu, TiO<sub>2</sub>, SiO<sub>2</sub>/Si, and MgO, under various relative humidity (RH) conditions through the introduction of water vapor to the analysis chamber [38–40]. These studies showed the dissociation, adsorption, and hydration of well-defined surfaces on a molecular scale.

Recently, investigation of water interactions has been extended to other desalination materials, such as polymeric membranes and layered materials. Aydogan Gokturk *et al.* showed the effect of surface chemistry on the hydration of polymers by using tender-APXPS under conditions from UHV to 100% RH [41]. In the study, polystyrene, polyvinyl phenol, and polystyrene sulfonate (PSS) thin films were chosen as model platforms to represent hydrophobic, hydrophilic, and charged surfaces, respectively. Through the quantification of adsorbed water at different RH levels, it was shown that water sorption is controlled by the polar and charged groups in the polymer. In the same work, the influence of counter-ion-specific water sorption on PSS polyelectrolytes and its relevance to the fraction of dissociated ionic groups has also been investigated. Similarly, Liu *et al.* investigated the hydration process of a Nafion membrane using a laboratory-based APXPS system equipped with a Cr X-ray source from vacuum up to 90% RH at room temperature. The O 1s and S 1s spectra provided quantitative data for the water content and the transformation of the sulfonic acid group to its deprotonated sulfate form during the hydration process [42]. Another study utilized soft-APXPS and Monte Carlo simulations to examine the role that solutes and surface chemistry play in water adsorption properties in multilayer ternary transition-metal carbide (MXene) interfaces [43]. The authors showed that in the presence of electrostatically bound hydrophilic cations, the 2D MXenes exhibit greater water adsorption at the surface and slower water removal from the surface at elevated temperatures (> 200°C).

On the other hand, NEXAFS is sensitive to the local bonding environment and can be useful to probe the degree of hydration and the hydrogen-bonding configuration around water treatment materials. For instance, a previous study analyzed Nafion via sulfur K-edge NEXAFS under varying electrical potential and humidity conditions using an *in situ* flow cell [44]. Measurements from the cell indicated humidity-dependent reversible changes in the spectra interpreted as the transformation of the sulfonic acid groups of Nafion into the deprotonated sulfate groups under hydrated conditions. Upon drying, the sulfonate ion was bound to hydrogen again. In the same study, the decomposition of a small fraction of the sulfonic acid to atomic sulfur was also observed [44]. Similarly, Su *et al.* investigated various perfluorinated sulfonic acid membranes, including Nafion, to understand the effect of the side chains in hydration and ion conduction [45]. Using XAS guided by first-principles calculations, the authors revealed different sulfur-bonding environments in the different ionic groups (e.g. sulfonic acid or bis(sulfonyl)imide groups) to distinguish various degrees of hydration and hydration configurations. They showed that perfluoro ionene chain extended ionomers with a tunable number



of protogenic bis(sulfonyl)imide groups on the side chain promote hydrogen-bonding configurations of water that facilitate proton dissociation.

### Selectivity-enhancing and fouling-minimizing interactions between solutes and treatment materials

Understanding and modifying the interaction between solutes, water, and treatment material is vital to solve two main challenges in water treatment systems: selectivity and fouling. First, the need for higher selectivity and specificity for certain species is increasing as the research focus shifts to the removal of trace contaminants and resource recovery [46–48]. However, rejection of small, neutral solutes and effective discrimination between ions of the same valence remain significant challenges for synthetic membranes. Treatments with high solute selectivity could separate problematic contaminants from water and minimize the disposal of concentrated waste streams into the environment, which is one of the major problems with current RO-based filtration systems. In addition, selective decontamination could also reduce the need for the remineralization of treated water for drinking purposes, thereby reducing treatment costs and the use of chemicals [18,49,50]. Moreover, feed water can contain high concentrations of critical resources used in many products that are important to the economy and national security. For example, lithium demand is expected to increase significantly due to the rapid expansion of electric vehicles and other technologies that rely on lithium-ion batteries, which, if recovered, would mitigate potential resource shortages [51]. Second, the fouling on the surface or inside pores of membranes caused by specific organic solutes and inorganic scaling poses a major challenge for the long-term performance and operation of the treatment material, causing severe flux attenuation and a decline in performance of the treatment process. Eventually, it generally requires chemical cleaning or replacement, increasing the operating costs of a treatment plant. Fouling/Scaling is typically caused by strong interactions of solutes (i.e., organic molecules, inorganic salts and microorganisms) with the surface of treatment material. Increasing fouling resistance and inorganic scaling in treatment materials has been extensively studied [52–54], yet factors controlling the ability to tune binding/interaction of solutes with treatment materials (i.e. role of water and dehydration of ions, material chemistry) are still poorly understood.

To develop novel materials with high selectivity and fouling resistance, a better understanding of the mechanisms underlying such interactions at the molecular level is crucial. XAS and XPS can be applied to determine the speciation of elements within the fouling layer of membranes or electrodes and can provide information on the chemical

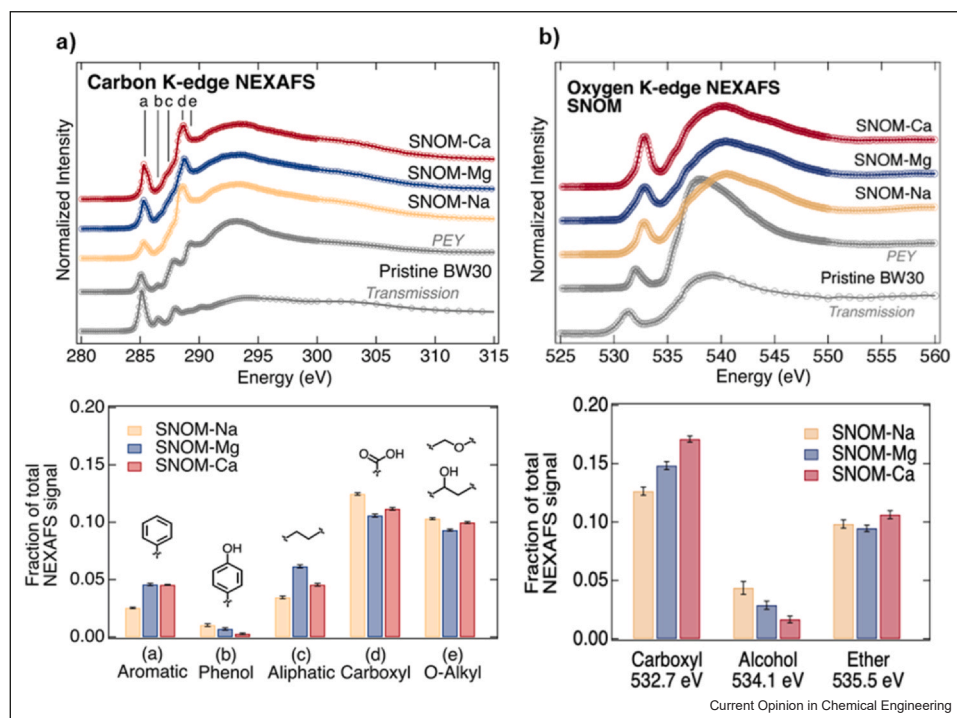
composition of membranes and electrodes under operating conditions. Recently, Landsman *et al.* surveyed the mechanism of fouling by using natural organic matter (NOM) in the presence of divalent and monovalent ions in the feedwater (i.e.  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ). The NEXAFS was used to determine the composition of fouled membrane samples; however, the analysis was conducted *ex situ* [33]. From the C K-edge and O K-edge NEXAFS spectra collected in partial electron yield (PEY; surface sensitive) mode, shown in Figure 2, the authors showed that divalent cations promote significant fouling by hydrophobic NOM containing aromatic and carboxyl groups, while NOM fouling in the presence of a monovalent cation such as sodium occurs by smaller, oxygen-rich organics that have little impact on flux. These findings showed the importance of specific interactions between the ions and NOM that cause fouling in combination with the electrostatic interactions.

### Electrical double layers – potential/concentration polarization near the interface

The EDL is crucial to all electrified processes, such as electrochemical oxidation/reduction, electrocoagulation, and CDI. When an electrolyte solution comes into contact with a polarized/charged surface, ions at the interface rearrange to screen this charge. As a result, a concentration and, therefore, a potential profile is formed at the solid–liquid interface, which governs charge transfer processes and influences the kinetics and thermodynamics of the electrochemical systems. Fundamental insight into the EDL is intrinsically difficult, as the EDL extends only a few nanometers from the solid surface; however, over the past few decades, considerable efforts have been made to adopt surface-sensitive techniques for the investigation of such interfaces [55]. Among those techniques, XPS is notable, mainly due to its sensitivity to local electrical potentials in addition to surface and chemical sensitivity [56–59].

Using the combined tender-APXPS and dip and pull method, Favaro *et al.* succeeded in directly probing the potential drop at the electrified solid–liquid interface by following the changes in binding energy shifts and spectral broadening of electrolyte-related core-level peaks as a function of applied electrical potential [60]. Their experiment used a three-electrode electrochemical cell containing an Au working electrode grounded to the analyzer, a polycrystalline Pt foil counter electrode, and an Ag/AgCl reference electrode. Aqueous potassium hydroxide was used as the electrolyte solution. As it is hard to detect ion-specific core levels in low electrolyte concentration, a high concentration of (1.0 M) neutral probing molecule, pyrazine, was also added to the electrolyte solution to make the spectral analysis easier. In this way, probing molecule provided a high-intensity peak within the electrolyte without interfering or disturbing the formation of EDL.

Figure 2



Organic composition of NOM-fouled layers compared to the pristine BW30 membrane. **(a)** Carbon K-edge and **(b)** oxygen K-edge NEXAFS spectra of pristine and fouled membranes. Spectra of the pristine BW30 membrane are collected using both transmission and PEY detection modes, while only PEY spectra are shown for NOM-fouled membranes. Fractions of individual components of NOM extracted from fitted spectra of NOM-fouled membranes are shown at the bottom.

Adapted from Ref. [33] with permission from Elsevier.

In order to follow only the EDL-related processes, the amplitude of the external potential was chosen such that the faradaic sources and possible redox reactions would not contribute.

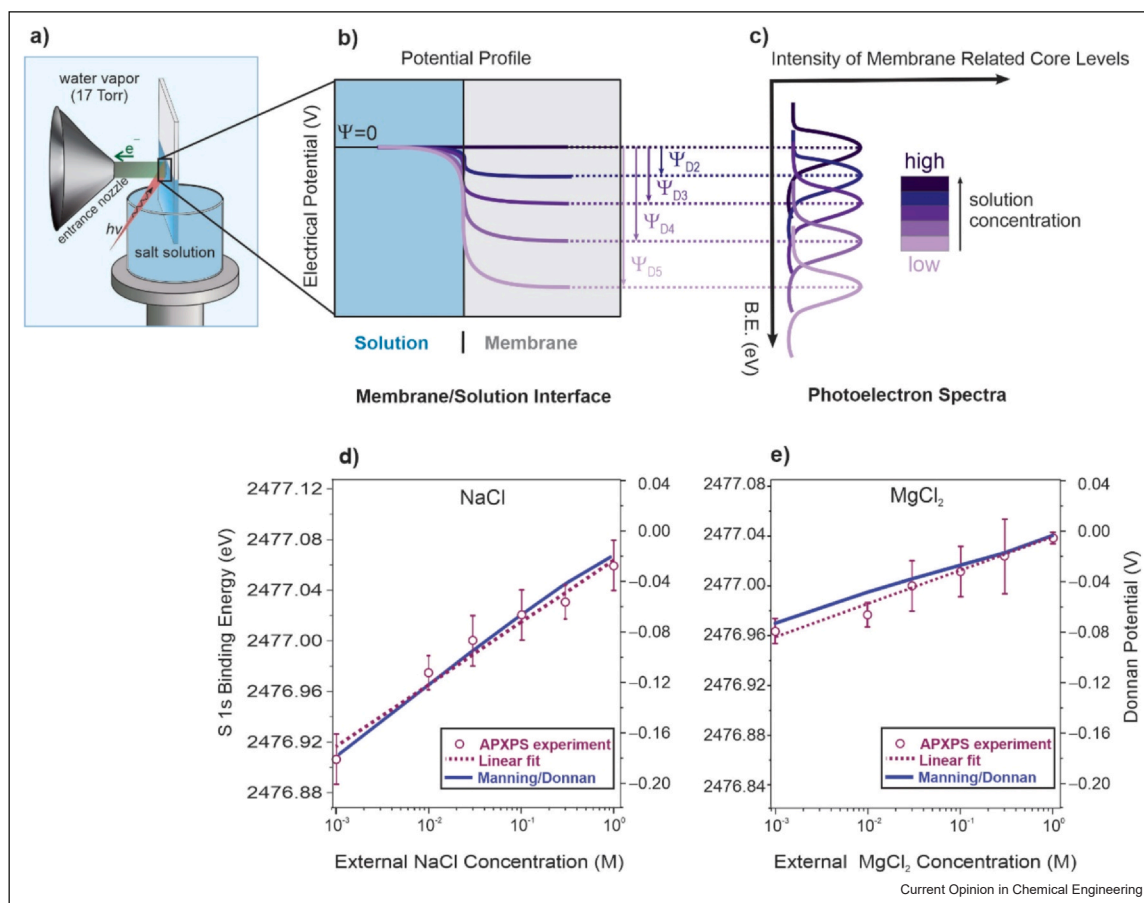
More recently, the so-called Donnan electrical potential, developed at the charged membrane–solution interface due to unequal distribution of ions between phases, was measured for the first time using APXPS [61]. This discovery was an important step toward understanding the molecular mechanisms of selectivity because the Donnan potential restricts co-ion sorption into the membrane and counter-ion desorption into the solution (i.e. Donnan exclusion). In the experiment, aqueous salt solutions with concentrations ranging from 0.001 to 1 M were equilibrated with a commercial cation-exchange membrane bearing negatively charged groups. Tender-APXPS measurements at the solution–IEM interface were performed using the dip and pull method. At equilibrium, the binding energies of the membrane-related core-level peaks showed a shift to lower binding energies due to the decreasing electric potential in the membrane phase. This shift in binding energy was shown to be directly related to the Donnan potential

formed at the interface (Figure 3). Despite the long history and widespread use of ion exchange membranes in water–energy nexus research and applications, the Donnan potential has been thought to be unmeasurable until recently. This study has been a notable contribution to the field and a good example of how advanced characterization can further water treatment science.

### Electrochemical oxidation and reduction processes

Electrochemical control during data acquisition, in addition to its chemical sensitivity, makes both XPS and XAS very useful for investigating various electrochemical phenomena under operating conditions. Over the past decade, electrochemical half reactions of water splitting (i.e. hydrogen evolution reaction and oxygen evolution reaction) and fuel cell reactions (i.e. oxygen reduction reaction and hydrogen oxidation reaction) have been extensively investigated with X-ray spectroscopy to advance the field of electrochemical energy storage and conversion [62–66]. Recently, these techniques have been applied for probing electrochemical water treatment processes under operating conditions.

Figure 3



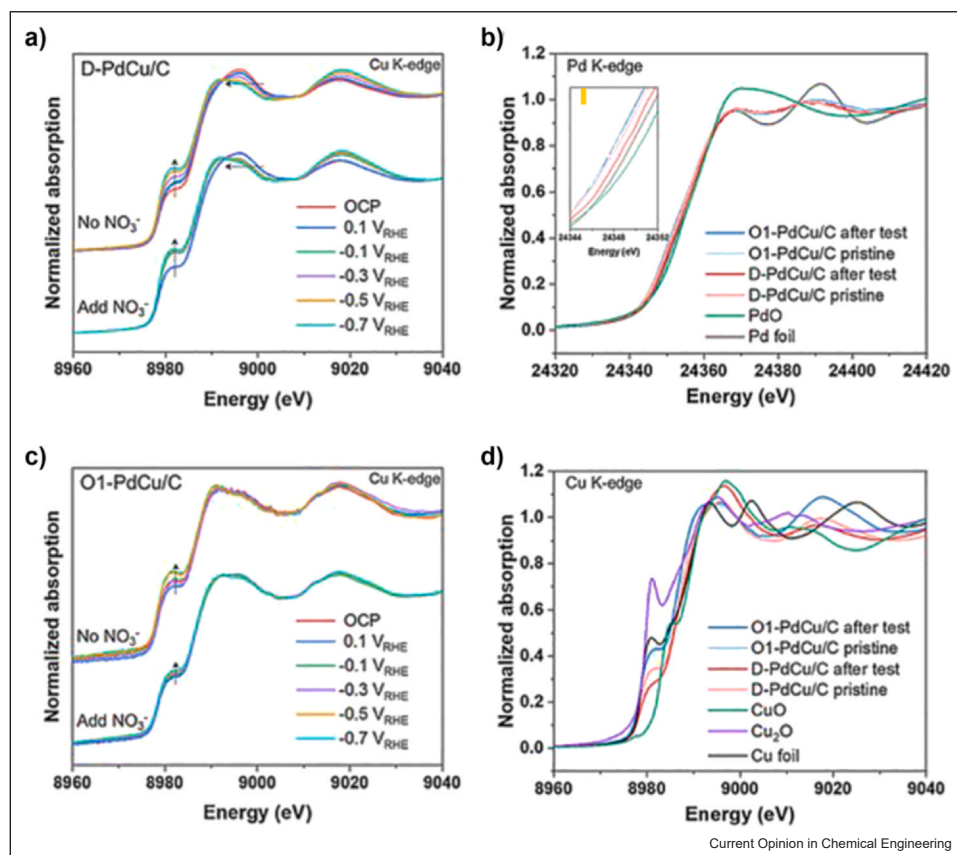
**Overview of direct Donnan potential measurement using tender APXPS. (a)** A schematic of the experimental setup during data acquisition from the membrane equilibrated in aqueous salt solution. **(b)** Illustration of the potential drop at the membrane–solution interface. **(c)** Corresponding binding energy (BE) shifts in the membrane-related core levels. **(d)** and **(e)** Experimentally measured Donnan potential values obtained from BE shifts in membrane-related S 1s core levels as a function of the external NaCl and MgCl<sub>2</sub> solution concentrations, respectively. Adapted with permission from Ref. [61]. Copyright 2022 Springer Nature.

One of the most common water pollutants, nitrate, can be a source of nitrogen for the electrochemical synthesis of ammonia. Selective capture and conversion of nitrate into value-added products is much more advantageous than the current Haber–Bosch technology and can create a sustainable nitrogen cycle [10,12,19,67,68]. However, the reduction of oxidized nitrogen species involves complex reaction mechanisms where the stability of critical reaction intermediates (e.g. nitric oxide) dictates selectivity toward ammonia as a final product. Thus, researchers have started to utilize APXPS to explore the adsorption affinity and ability of a surface to dissociate nitric oxide for a series of transition metals (Fe, Co, Ni, Cu) [69]. Similarly, electrochemical nitrate reduction (NO<sub>3</sub>RR) to dinitrogen has also been explored using XAS. Lim *et al.* conducted *in situ* and *ex situ* XAS

measurements to examine changes in the oxidation states and coordination environment near the Pd and Cu atoms and showed near-complete removal and selective conversion (91% N<sub>2</sub>) of nitrate in a highly ordered PdCu alloy-based catalyst (O1-PdCu/C) [70]. *In situ* measurements performed using customized cell showed the oxidation of Cu clusters in a disordered PdCu alloy-based catalyst (D-PdCu/C) compared to Cu sites in O1-PdCu/C *in situ* XAS measurements. Under negative potentials from 0.1 to –0.7 versus reversible hydrogen electrode (RHE), the XAS spectra showed a trend for CuOx reduction to metallic Cu regardless of catalyst type or the existence of NO<sub>3</sub><sup>–</sup> (Figure 4a,d). *Ex situ* measurements indicated no changes in the Pd K-edge for both the ordered and disordered catalysts before and after the long-term operations. However, the Cu K-edge



Figure 4



The *in situ* XAS measurement of Cu K-edge for (a) D-PdCu/C and (c) O1-PdCu/C during NO<sub>3</sub>RR in the absence and presence of nitrate ions. *Ex situ* XAS of (b) Pd K-edge and (d) Cu K-edge for D-PdCu/C and O1-PdCu/C catalysts before and after long-term electrolysis tests. Adapted from Ref. [70]. Copyright 2023 The Authors. Published by American Chemical Society. The publication is licensed under CC-BY 4.0.

spectrum for the disordered catalyst showed a significant change after long-term electrolysis due to the higher Cu oxidation states, while the O1-PdCu/C spectrum did not show any changes.

### Conclusions and future perspectives

Energy storage and conversion field have greatly benefited from the advanced characterization of electrodes, electrolytes, and cells using X-ray spectroscopic techniques in the last few decades. Interestingly, the utilization of such characterization tools in water treatment research has been sparse, despite the challenges and scientific problems of these two fields being similar. To help bridge these gaps and facilitate *in situ* and *operando* spectroscopic studies in water research, in this review article, we highlighted some recent publications that exemplify opportunities for using advanced characterization to obtain detailed information about the interface and bulk properties of water treatment materials and processes.

Although each example we presented here exhibits great significance for enabling *in situ/operando* characterization and revealing the fundamental aspects of water treatment systems, all these approaches are still new, and there will be many challenges and opportunities to address in the future. The fundamental challenge of these types of experiments is expanding the pressure limit to more realistic conditions, close to atmospheric pressure, and to use of solution flow and high pressures that are relevant to water treatment systems. In this regard, operating spectroscopic instruments with high photon energies is particularly promising. Another limitation, which has been discussed very little but is relatively important, is the beam-induced chemical changes during characterization of the treatment systems involving soft materials, such as polymeric membranes. To mitigate beam-induced damage, the X-ray photon flux can be lowered, or the beam exposure time can be minimized by constantly changing the analysis position. However, a thorough evaluation of chemical changes induced by the

beam should be conducted first to ensure the accurate interpretation of the data sets.

Ongoing advancements, including *in situ* and *operando* sample environments, digital twins, and computational approaches for data analysis and interpretation, should further facilitate the use of these techniques by water researchers in the coming years. Such *operando* cells, mimicking different fuel cell geometries, have been used in energy research to reveal the fundamental mechanisms underlying such technologies. Similar strategies can be employed to study ion/mass transport at the cell level to probe the nature and concentration of ions within CDI devices. These cells can also provide information regarding fouling, electrode degradation, and corrosion to obtain mechanistic insights into the working and failure mechanisms of these devices. In addition, novel pump–probe techniques can provide unique time-resolved information. Such studies with temporal resolution can help unravel the reaction intermediates and ion/mass transport kinetics and provide further insight into electrified processes under dynamic conditions.

Additionally, predictive knowledge of the EDL, particularly in confined environments such as porous electrodes, has vital importance in electrified treatment processes. XPS with electrical potential sensitivity can help to understand such phenomena at the electrode/electrolyte interface. We believe that the transition from fundamental research advancements to applied technologies will be accelerated when the community begins to make use of these tools to gain understanding of the physics and chemistry underlying fundamental aspects of treatment.

## Data Availability

No data were used for the research described in the article.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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- of special interest
- of outstanding interest

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