Macromolecular Chemistry and Physics
www.mcp-journal.de

Check for updates

Design Considerations for Next-Generation Polymer Sorbents: From Polymer Chemistry to Device Configurations

Jonathan Aubuchon Ouimet, Jialing Xu, Carsten Flores - Hansen, William A. Phillip, and Bryan W. Boudouris**

Adsorption-based separations have the potential to enhance the sustainability of established industrial processes and facilitate the adoption of new practices. They also provide ways to meet emerging needs in the isolation of resources from non-traditional supplies and the remediation of hazardous environmental contaminants. In this regard, there are significant opportunities to advance both fundamental polymer science and engineering applications through next-generation adsorbent systems. Here, after briefly reviewing the history, potential application space, and underlying physics of polymer sorbents, design considerations that connect macromolecular design with systems-level functionality, are discussed. First, polymer processing conditions are discussed in terms of the final nano- and microscale structures produced. Subsequently, the macromolecular chemistry of the materials is analyzed with respect to the ability of the separations systems to have analyte-specific binding. Finally, a similar analysis is performed regarding the desorption mechanism used to release the target solutes. In this way, the manuscript attempts to connect macromolecular architecture with polymer physics and materials processing to provide guidance on how these important interrelationships impact the ultimate performance of sorbent systems.

1. Introduction

The development of next-generation adsorbents can help to realize a more sustainable future by addressing challenges associated with existing separation processes and by enabling new applications.[1] For example, in the petrochemical industry, the energy efficiency associated with transitioning from thermal separations (e.g., distillation) to processes that rely on mass separating agents (e.g., membranes and adsorbents) is well-documented.[2,3] In the pharmaceutical industry, the cost associated with downstream purification is a significant hurdle to the more widespread use of biotherapeutics.[4–6] However, the lack of low-cost, high-performance adsorbents, which can be manufactured using scalable means, remains a challenge for advancing these established processes. Alternatively, the development of novel adsorbents capable of isolating dilute solutes from complex mixtures will enable a number of emerging applications.[7] For example, these separating agents could be deployed to extract resources from non-traditional sources (e.g., uranium from seawater),[8–17] to recycle critical materials (e.g., rare earth elements) from spent electronics,[18,19] and to forestall pending environmental disasters (e.g., through direct air capture of carbon dioxide[20–22] or the removal of per- and polyfluoroalkyl substances (PFAS)[23,24] from water resources). In comparison to permeation-based membrane separations, which struggle to separate dilute solutes due to low driving forces, adsorption-based separations are well-situated to execute these challenging separations.

Traditionally referred to as chromatography, adsorption-based processes, rely on the partitioning of analytes between a mobile phase (i.e., the solvent and dissolved solutes) and a stationary phase (i.e., the solid material) to create a separation. Energetically favorable interactions drive the adsorption of analytes onto the solid phase, which in turn, alters the rates at which they pass through the chromatography column. Broadly, chromatography can be classified along two lines that are differentiated by the strength of the interactions between the analyte in the liquid and solid phases.[25] Elution chromatography, which includes techniques such as size exclusion chromatography (SEC) and high-performance liquid chromatography (HPLC), is typically

J. A. Ouimet, J. Xu, W. A. Phillip
Department of Chemical and Biomolecular Engineering
University of Notre Dame
Notre Dame, Indiana 46566, USA
E-mail: wphillip@nd.edu
C. Flores - Hansen, B. W. Boudouris
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907, USA
E-mail: boudouris@purdue.edu
B. W. Boudouris
Charles D. Davidson School of Chemical Engineering
Purdue University
West Lafayette, Indiana 47907, USA

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/macp.202200032

© 2022 The Authors. Macromolecular Chemistry and Physics published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

DOI: 10.1002/macp.202200032

used for analytical and lab-scale preparative applications. The interactions between the solute and the stationary phase are relatively weak and reversible, or even based exclusively on geometric, entropic considerations, as is the case with SEC. Consequently, the strength of the interactions modulates the speed at which species move through the column. As the strength of the interaction increases, the velocity of the solute through the contactor decreases. Ideally, these conditions allow a mixture of solutes to elute from the device in a series of well-resolved bands, each containing a component solute. Frontal chromatography or bind-and-elute separations, which will be the focus of this review, is used in industrial scale processes such as ion exchange and affinity chromatography. This method relies on strong complexing interactions between the mobile and stationary phases. The target solute is bound to the solid phase such that it does not move while all other solutes from the feed solution pass through the column. After the solid phase is saturated, the bound solute can be eluted using a wash process.

There is ample room for fundamental advances in polymer science and engineering to catalyze the development of low-cost, high-performance adsorbents for use in established and emerging processes that address global societal needs. Motivated by this opportunity, this review focuses on how the design of polymers at the molecular through device scales can be used to develop next-generation sorbents for bind-and-elute separations. First, a brief discussion of the relationship between the microstructure of adsorbents and the mass transfer phenomena that limit adsorptive processes provides a basis for understanding how recent advances in polymer processing can be used to optimize sorbent microstructure at the 100 nm to 100 μm scales. Subsequently, the influence of macromolecular chemistry on sorbent performance is considered. Regarding analyte binding, the ability to tailor the identity and positioning of functional ligands within and across repeat units such that the resulting polymer sorbents exhibit high affinity capture of dilute solutes is analyzed. Critically, a similar analysis is performed regarding the desorption mechanisms that can be utilized to release target solutes and regenerate the sorbent in an effective and sustainable manner. The review concludes by discussing the significant opportunities for using multiscale modeling to create data-driven frameworks that can guide material design and process optimization.

2. Molecular through Device Scale Design Considerations

Figure 1 presents the cyclic process for the operation of a model bind-and-elute separation. A pressure difference drives the flow of feed solution, containing the target and competing analytes, through a contactor. As the solution flows through the contactor, a target solute diffuses toward and binds with unoccupied active sites (Figure 1ai) creating a saturation front that propagates down the contactor. The saturation front continues moving until it reaches the end of the column (Figure 1aii). At this point, all sorbent sites are saturated relative to the feed such that the analyte cannot be retained and passes through the device. The exhausted sorbent must then be disposed of or regenerated and reused. To desorb the analyte, the system is flushed to remove the feed solution and an external stimulus is used to disrupt the energetically favorable sorbent-analyte interactions. The desorbed analyte is washed away in a small volume of eluent solution (Figure 1b) that can be collected if the product is of high value or can be disposed of appropriately if the analyte presents an environmental hazard. Therefore, the sorbent is regenerated, and the adsorption-desorption cycle can begin again.

Adsorbents are evaluated based on equilibrium properties (e.g., saturation capacity, binding affinity, and selectivity towards target analytes), their regeneration mechanism, as well as their dynamic properties. Breakthrough curves can shed light on the dynamic parameters that influence the quality of the separation. Within these experiments, which mimic the operation of a bind-and-elute separation, feed solution is introduced to the sorbent bed at a constant flow rate and the analyte concentration in the effluent is measured as a function of the cumulative volume permeated. An ideal breakthrough curve will resemble a step function (Figure 1aiii, solid red line). This result implies none of the target analyte passes through the column until all of the sorbent is in equilibrium with the feed solution. When the analyte is detected in the permeate, its concentration is equal to the feed concentration (Figure 1aiii). In practice, breakthrough curves are more diffuse (Figure 1aiii, dashed blue line). At low treated volumes, the analyte is removed and its concentration in the effluent stream is nearly zero. As the experiment progresses, the concentration of analyte in the effluent increases gradually until it is equal to the feed concentration. During this gradual transition, a fraction of the solute remains in the effluent. Therefore, broad breakthrough curves correspond to a decrease in the performance because they imply product of value is lost or contaminant escapes into the environment. In practice, the sorbent is regenerated when the analyte breaks through, which is often defined as the point at which the concentration of solute in the effluent is ≈10% of the feed concentration. The sharpness of a breakthrough curve depends on several factors including the binding kinetics, the distribution of residence times,dispersion, and the relative importance of convective and diffusive transport.[8,26,27] When binding kinetics are rapid, sharper breakthrough curves can be realized by tailoring the microstructure of sorbents using novel polymer processing methodologies.

2.1. Polymer Processing Tailors Sorbent Morphology

The structure of a sorbent on the micrometer through nanometer scales impacts the characteristic time scales associated with convective and diffusive transport mechanisms. Moreover, the morphology at these length scales is critical to determining the specific saturation capacity (i.e., moles of analyte bound per sorbent mass). One sorbent configuration, packed beds, are composed of mesoporous particles (e.g., beads of silica, granulated activated carbon, or crosslinked polymer resins) that are loaded inside of cylindrical columns (**Figure 2**). State-of-the-art columns use spherical particles that are fabricated through controlled nucleation and growth methods in conjunction with size-selective filters that ensure a uniform particle size (see **Figure 3**, Beads [Low Magnification]).[28] The narrow particle size distribution reduces dispersion. At the nanoscale, the high porosities (Figure 3, Beads [High Magnification]) maximize surface area to generate large specific capacities which, in conjunction with the depth of packed beds, enables high overall capacities. Within

© 2022 The Authors. Macromolecular Chemistry and Physics published by Wiley-VCH GmbH

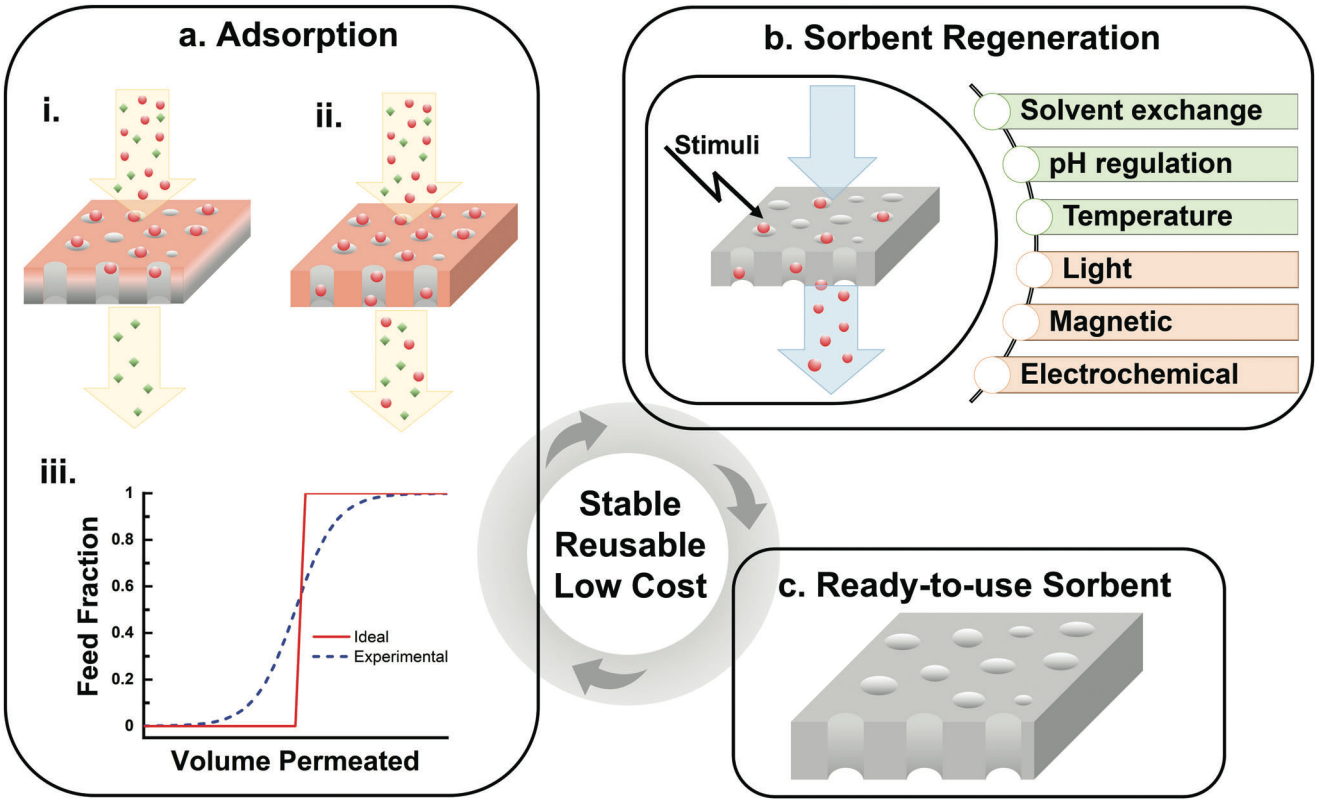


Figure 1. A schematic representation of the steps involved in adsorption-based separations. **a)** A feed solution containing multiple analytes is passed through the sorbent. (i) Ideally, the sorbent is selective towards one analyte and competing analytes pass through the membrane unhindered. (ii) A saturation front of bound solute moves through the sorbent until the available active sites are occupied. (iii) For an ideal sorbent, the feed fraction of analyte (i.e., the solute concentration in the effluent relative to the feed) will resemble a step function. However, due to phenomena including mass transfer and kinetic limitations as well as dispersion, this is unrealistic and experimental breakthrough curves are sigmoidal in nature. Innovative polymer processing methods provide opportunities for controlling sorbent structure to minimize these limiting phenomena. **b)** The sorbent is regenerated by subjecting it to an external stimulus that releases the adsorbate molecules from the selective sites so that the target solute can be eluted. Environmental stimuli (green) are introduced by changing the temperature or composition of the solution around the sorbent. Other stimuli (orange) effect the sorbent nanostructure directly to disrupt the energetically favorable sorbent-analyte interactions and promote the desorption of the analyte. **c)** Ideally, all sorbent sites within the sorbent are regenerated and the cycle can begin again.

the sorbent bed, convective flow occurs around the mesoporous particles. Once the analyte reaches the boundary layer, diffusive forces drive the solute into the pores towards the active sites of the sorbent. These diffusive, mass transfer limitations are one factor that lead to broader breakthrough curves. Assuming a well-packed column in which the dimensions optimize the density of beads and prohibit the flow from channeling,[29] the specific capacity can be increased and diffusion limitations reduced, by decreasing the particle size (i.e., increasing the surface area per volume). However, a tradeoff exists, as smaller particle sizes require higher operating pressures. For instance, HPLC operations, which use beads 5 μm in diameter to achieve high resolution separations operate at pressures of ≈400 bar.[30,31] In contrast, process scale operations use beads that are 300 μm in diameter and operate at pressures of ~5 bar.[32]

Membrane sorbents represent a separate configuration (Figure 2) where the convective flow of solution occurs directly through the adsorptive polymer material. Analytes only need to diffuse to the pore walls, a distance that can be orders of magnitudes lower than packed beds, to reach the active binding sites. These short diffusion lengths along with the high porosity of the membranes present opportunities for operating at higher flow rates and reduced pressures. Adsorptive membranes have been produced in many ways (e.g., binding moieties can be incorporated onto the surface of commercially available membranes using modification schemes such as layer-by-layer deposition[33–36] as well as grafting-to[37,38] and grafting from[39,40] polymerizations), and though these approaches take advantage of enhanced mass transfer, the materials tend to have relatively low specific binding capacities. Emerging fabrication methods, which utilize self-assembled materials in conjunction with phase separation or electrospray techniques, present simple and scalable approaches to generate materials with ideal mass transfer characteristics and high specific capacities.

Phase separation techniques [e.g., nonsolvent induced phase separation (NIPS) and vapor induced phase separation (VIPS)] rely on the liquid-liquid equilibrium of ternary polymer-solvent-non-solvent mixtures to generate porous polymers. To start, the polymer is dissolved in solvent to produce a homogenous solution that is then spread into a film using a casting blade. After,

© 2022 The Authors. Macromolecular Chemistry and Physics published by Wiley-VCH GmbH

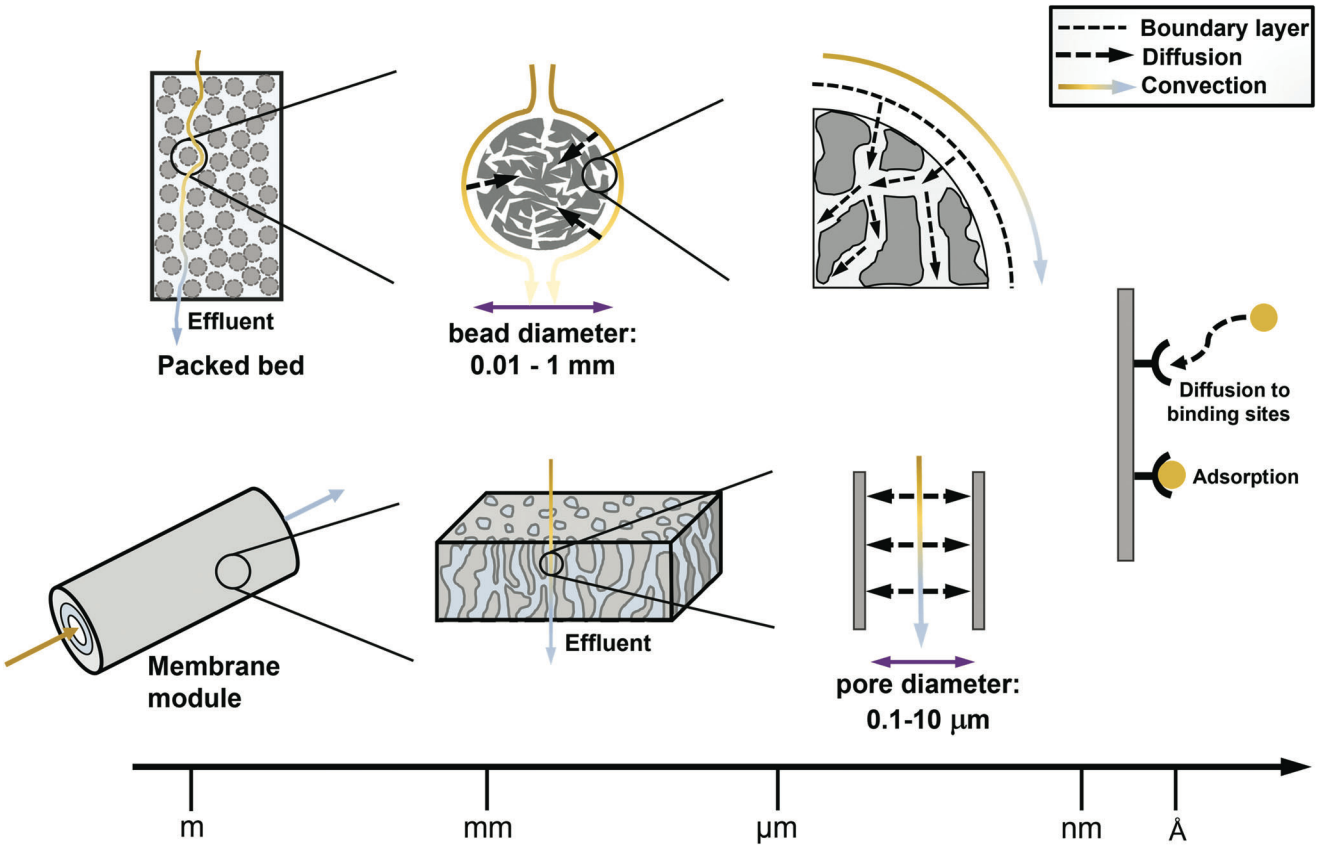


Figure 2. Two unique sorbent configurations (i.e., packed beds and membranes) are compared across lengths scales. As feed solution moves through the contactors, the analyte adsorbs to the sorbent surface such that its concentration in the effluent is depleted. Within packed beds, high pressures are used to drive the feed solution through ensembles of beads ranging between 0.01 and 1 mm in diameter. Convective flow occurs around the beads. Analytes cross a boundary layer where their transport is impacted by both convective and diffusive mechanisms. A concentration gradient drives the analyte into the pores of the beads where adsorption occurs at the active sites situated at the solid/liquid interface. In contrast, for membrane sorbents, convective flow occurs through pores 0.1 – 10 μm in diameter while a concentration gradient promotes radial diffusion toward the pore walls. Similar to packed beds, adsorption occurs when the analyte diffuses to an active site. Polymer processing plays a pivotal role in affecting sorbent properties including the surface area, flow path, characteristic diffusion lengths, and overall capacity. Likewise, polymer chemistry can be used to modify pore functionality to tailor sorbent properties, such as binding affinity and regeneration mechanism.

the film is introduced to a nonsolvent environment where the exchange of solvent and non-solvent alters the composition of the film initiating liquid–liquid de-mixing and creating porous structures.[43] Manipulating the polymer chemistry and the rate of solvent/non-solvent exchange allows membranes with uniformly sized pores and spongy morphologies (Figure 3, Phase Separation [Low Magnification]) to be generated.[44,45] Moreover, with appropriate tailoring of the chemical constituents, the phase inversion process allows for the desired functional groups to line the pore walls; in turn, this functionality can enable facile modifications of the material chemistry after fabrication (Figure 3, Phase Separation [High Magnification]).[46]

Electrospray methods fabricate porous polymer mats by depositing solution through a charged spinneret onto a stage of opposite electrical polarity.[47,48] The resulting nanofibers stack upon one another and display two types of porous architectures. The space between individual fibers form macropores that promote convective flow (Figure 3, Electro-spray [Low Magnification]).[42] The interior of the nanofibers contain micropores that enhance their surface area. (Figure 3, Electrospray [High Magnification]).[42] However, due to their thin nature, membrane sorbents possess smaller overall capacities relative to packed beds. Although this limitation can be overcome on a system scale (e.g., by stacking multiple membranes in series), this approach requires operating at higher applied pressures.

Additive manufacturing, a process that refers to the creation of three dimensional (3D) objects through the controlled deposition or fusion of material, presents one means to create structured sorbents that enable high throughput flows with increased bed depth while maintaining the rapid mass transfer characteristic of nanoporous membranes.[49–52] The ability to spatially control micrometer scale morphologies opens the possibility to engineer flow patterns within the sorbent.[53] For instance, modeling flow profiles within a woodpile structure (Figure 3, Additive Manufacturing, [Low Magnification]) provides structure-function insight on how 3D structures can modulate the contributions of diffusive and convective mass transport mechanisms.[41] Additionally, additive manufacturing techniques enable the creation

© 2022 The Authors. Macromolecular Chemistry and Physics published by Wiley-VCH GmbH

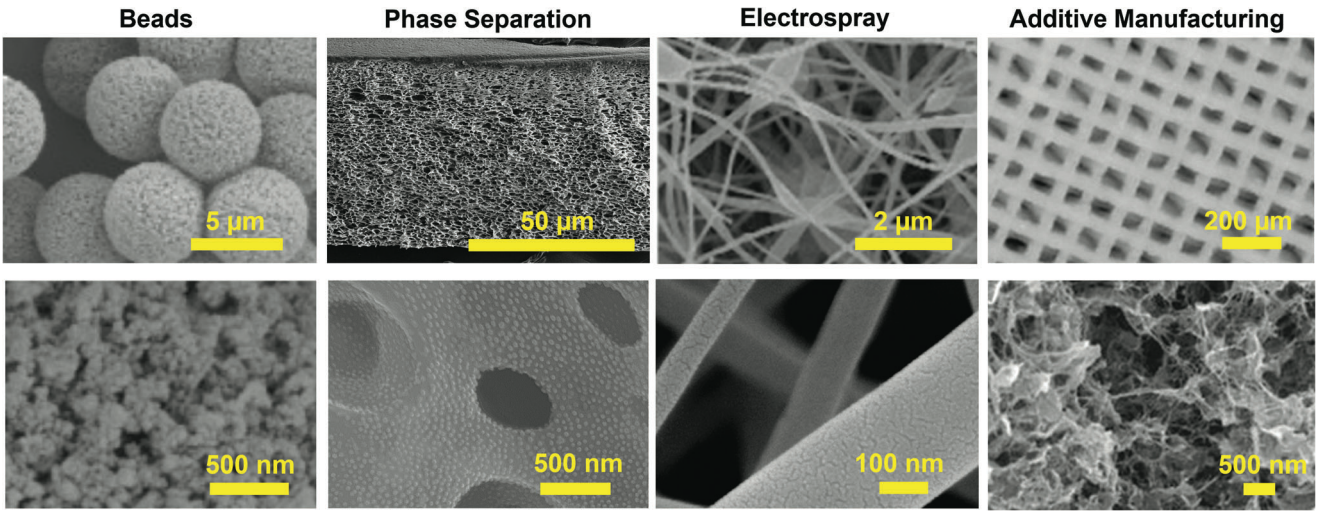


Figure 3. Micrometer- and nanometer-scale morphologies of adsorbents processed through various methods. Mesoporous **beads** are used in packed beds. The surface of uniformly sized beads, used for high-performance liquid chromatography, is functionalized through heterogenous chemistries to tailor sorbent-analyte interactions. Polymer materials enable the morphology of sorbents to be tuned through different processing techniques. **Phase separation** techniques can be used to fabricate thin films with spongy morphologies that correlate with high surface areas and promote high specific saturation capacities. At the nanoscale, select functional groups can be engineered to line the membrane surface. **Electro-spray** techniques are used to produce nanofiber mats with micron-sized pores. The nanostructure of the fiber remains highly porous. **Additive manufacturing** techniques tailor micrometer morphologies to create 3D structures with controlled flow paths that may promote secondary convective currents. The polymers maintain the high surface areas associated with their nanostructure. Adapted with permission.[28,41,42,44–46] Copyright 2016, Elsevier; Copyright 2018, Wiley-VCH GmbH; Copyright 2017, Elsevier; Copyright 2021, American Chemical Society; Copyright 2013, Elsevier; Copyright 2014, Wiley Periodicals, LLC.

of structures that promote secondary convective currents, which increase mass transport coefficients from the bulk to the active sites thus sharpening breakthrough curves.[54] These beneficial changes in the microstructure need to be realized while ensuring that the deposited polymer materials maintain the nanoscale properties (e.g., porosities and surface areas) that are attractive for producing high specific capacities.

Identifying ways to create hierarchical structures that balance the influence of convective versus diffusive transport mechanisms and maintain high specific saturation capacities for analytes is critical for advancing next generation sorbents. Controlling macromolecular design during synthesis and polymer physics during manufacturing provides key handles by which to enable structural control of adsorbents at the nanometer through micrometer scales, thereby altering the current technological landscape. Polymer scientists and engineers will also need to consider the molecular scale characteristics of the polymer materials as they are crucial in determining the affinity, selectivity, and reusability of the sorbent.

2.2. Polymer Chemistry Governs Adsorption Mechanism

Analytes are removed from solution when sorbent-analyte interactions are thermodynamically favorable. In general, adsorption is associated with a reduction in the entropy of the analyte. Consequently, creating conditions that favor adsorption requires manipulating the polymer chemistry to introduce binding sites that promote favorable enthalpic interactions and/or that increase the entropy of another species in the system upon analyte binding. Importantly, while polymers can be designed with a variety of functional groups to achieve this aim, subtle changes in chemistry can affect the sorbent morphology. This interdependency between chemistry and structure may require that new processing routes are identified to produce the desired sorbent morphology each time a new binding chemistry is developed. Conversely, post-fabrication functionalization techniques that use a versatile library of reactions to modify the polymer chemistry after the sorbent structure has been fixed can enable orthogonal control over the molecular design of the active sites and microstructure of the sorbent. As such, the targeted sorbent morphology is conserved and, with the appropriate ligand design and coupling reactions, the affinity to and mode by which analytes bind to sorbent materials may be tailored. In this way, sorbents can move away from the less selective adsorption mechanisms that are dependent on feed parameters (e.g., electrostatic interactions) and towards more specific interactions (e.g., host-guest complexes and chelation mechanisms) that are enabled by intentional ligand design.

3. Designing Selective, Multifunctional Sorbents

At the process scale, the performance of a sorbent is evaluated by its ability to recover analytes selectively. This process scale performance is directly related to the molecular scale interactions between active sites and analytes. To treat dilute feed streams, sorbents should possess high binding affinities, K, a material property that reflects the free energy change upon binding. In the linear portion of the equilibrium isotherm, K can be estimated as the ratio between the concentration of solute adsorbed to the sorbent surface and the concentration of solute in solution.[55] Feed streams are rarely pure and selective

© 2022 The Authors. Macromolecular Chemistry and Physics published by Wiley-VCH GmbH

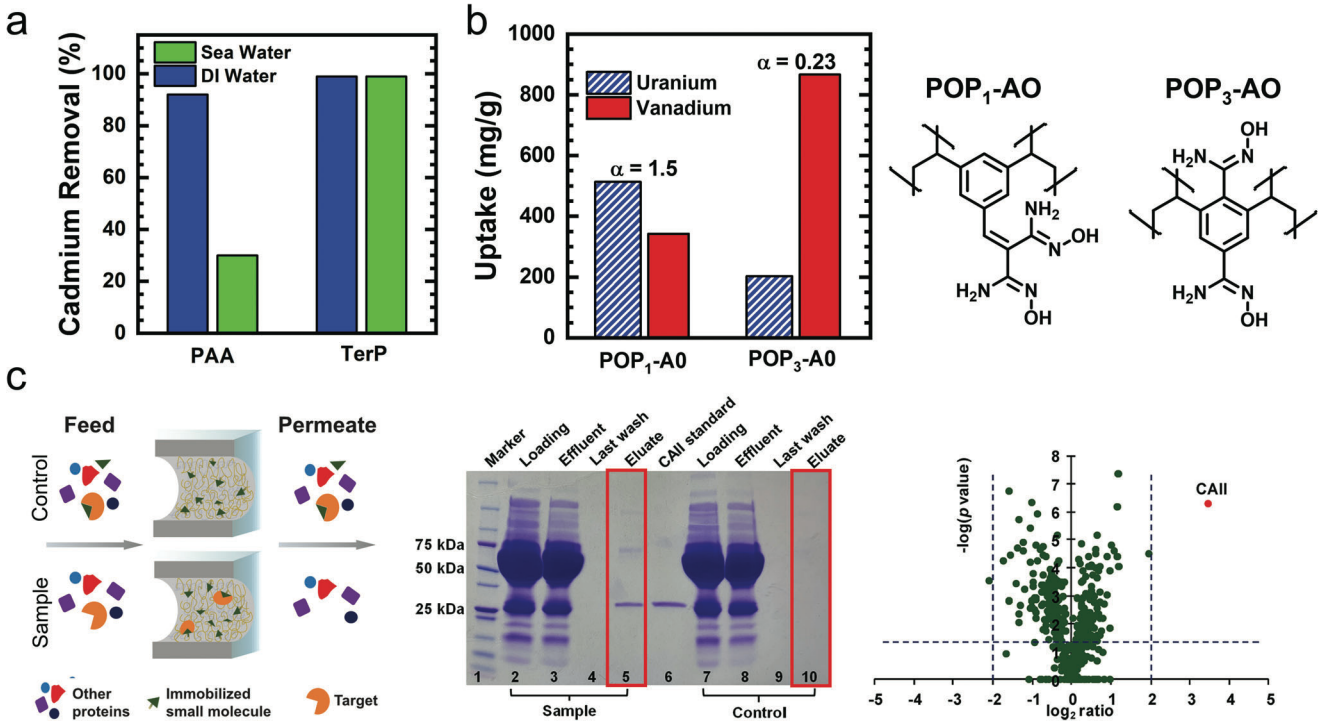


Figure 4. Targeted binding modes enhance selectivity. a) Poly(acrylic acid) removes 92% and 30% of the cadmium in DI and synthetic seawater, respectively. Terpyridine-functionalized polymers remove >99% of cadmium found within DI and synthetic seawater. The removal efficiency is directly related to the mechanism that the polyacrylic acid (PAA) and terpyridine (TerP) moieties use to adsorb cadmium. Reproduced with permission.[130] Copyright 2018, American Chemical Society. b) Bar graphs compare the uranium and vanadium uptake of two polymers from equimolar feed solutions. The selectivity towards uranium is tuned by controlling the orientation of two amidoxime moieties with respect to one another as highlighted by the repeat unit structures. Reproduced with permission.[9] Copyright 2021, American Chemical Society. c) The immobilization of a small molecule to a membrane allows for the selective adsorption of the target protein. A control experiment uses a cell lysate spiked with the target protein and small molecules. The small molecule saturates the protein binding sites, prohibiting protein adsorption onto the membrane surface. Sample experiments use a cell lysate spiked with the target protein. The protein binds to the immobilized small molecules and is removed from the permeate stream. The target protein is desorbed from the membrane by introducing a solution with a high concentration of small molecules. While the target protein is not detected within the control experiment (column 10), it is detected in the 25 kDa SDS PAGE analysis band (column 5) of the sample experiment. Volcano plots quantify the difference between the concentration of proteins in the standard and the sample (horizontal axis) and the confidence associated with the measurement (vertical axis). Reproduced with permission.[66] Copyright 2020, American Chemical Society.

materials are necessary to differentiate and sequester analytes from multicomponent streams. The separation factor, defined by Equation 1, quantifies selectivity.

$$\alpha_{AB} = \frac{q_{A,R}/q_{B,R}}{c_{A,F}/c_{B,F}} \Rightarrow K_A/K_B \quad (1)$$

Here, $q_{A,R}$ and $q_{B,R}$ are the concentrations of solute A and B adsorbed on the sorbent surface and $c_{A,F}$ and $c_{B,F}$ are the concentrations of the solutes within the liquid solution. If a competitive Langmuir adsorption model is assumed in the limit of 0% recovery, the separation factor reduces to the ratio of equilibrium constants, K_A and K_B, thereby highlighting the direct connection between separation process performance and the chemistry of polymer sorbents.

Competing analytes may decrease the selectivity in two ways. First, the competing analyte may have a higher equilibrium constant causing it to bind preferentially, thereby displacing the target analyte. Second, competing and interfering solutes may screen interactions and inhibit the mechanism used to adsorb the target analyte. Ligands designed to target analytes based on chemical identity (e.g., orbital and electron structure) rather than electrostatic (e.g., ion exchange) interactions can address these challenges associated with selective separations.[56,57] As an example, **Figure 4**a presents the capture efficiency of membrane sorbents designed for the removal of 6 ppm cadmium from deionized water (DI water) and synthetic seawater. One sorbent is functionalized with poly(acrylic acid) (PAA) brushes and the other is modified with terpyridine molecules. While both polymer chemistries achieve high Cd^{2+} removal from DI water, PAA is only able to remove 30% of the cadmium from the seawater solution. In comparison, the terpyridine-functionalized counterpart removes >99% of the Cd^{2+} from both solutions. The deficiency of PAA in seawater stems from a reliance on electrostatic interactions to adsorb analytes. As the ionic strength of the solution increases, electrolytes screen the charges on the PAA brushes.[58,59] Alternatively, the terpyridine-functionalized polymer uses a highly specific dπ–pπ* binding mechanism,[60] which relies on the exchange of an electron from the d-orbital of the heavy metal and the p*-orbital of the ligand. Ideally, ligands should be designed to maintain high selectivity in in complicated milieu.

© 2022 The Authors. Macromolecular Chemistry and Physics published by Wiley-VCH GmbH

3.1. Biological Entities Inspire Selective Ligands

Nature has evolved over millennia to develop selective binding motifs that are an ideal inspiration for the development of next-generation sorbents. For instance, hemoglobin is a tetrameric protein in which oxygen binding at one site affects the affinity of oxygen at the remaining binding pockets.[61] Due to these interactions, the isotherm is sigmoidal, which enables efficient oxygen uptake at high partial pressures (i.e., within the lungs) and rapid release at low partial pressures (i.e., in tissue)].[62] Similar to hemoglobin, an ideal sorbent would possess high affinity and selectivity for the target analyte as well as controlled uptake and release profiles.

One approach for exploiting the high performance of biological entities is to incorporate them directly into sorbent technologies. For instance, Protein A can be directly incorporated onto sorbents to selectively capture and purify monoclonal antibodies (mAb).[63] By interacting with the inactive region of the antibody, protein A ensures high fidelity monoclonal antibodies are isolated.[64] Unfortunately, Protein A chromatography resins are associated with high costs and limited lifetimes.[63] Conversely, proteins can be separated from a complicated milieu by modifying them to contain polyhistidine tags (His tags).[65] Notably, the functionalization of the N-terminus avoids disrupting the structure and function of the protein and enables the protein to be separated through metal ion affinity chromatography. A recent example demonstrating the selectivity associated with these types of interactions used membrane-bound substrates to rapidly identify the target proteins of small molecule drugs.[66] As demonstrated by the sodium dodecylsulfate polyacrylamide gel electrophoresis (SDS-PAGE) analyses in Figure 4c, binding to the immobilized small molecule drug isolates the target protein from hundreds of competing proteins found in human serum and cell lysates.[67,68] SDS-PAGE separates proteins based on their molecular weight and were used to qualitatively identify the bound protein. While no proteins are observed within the last wash solution (Figure 4c, column 4), an eluate, concentrated in the small molecule drug, desorbs the target protein and creates a strong band at 25 kDa (Figure 4c, column 5). Subsequently, protein concentrations can be quantitively identified through mass spectroscopy. Ultimately, proteins that possess highly specific binding pockets can motivate the design of novel ligands.[69,70]

Due to their high versatility and specificity, there exists increasing opportunities in the design of peptide and nucleic acid sequences to tailor material properties for specific tasks. Intentionally selecting amino acid sequences can be used to tailor the binding pocket shape, the location of charged residues, and the secondary interactions.[71–76] For instance, glutathione, a naturally-occurring tripeptide, selectively complexes heavy metals including gold, cadmium, and lead.[77] The glutathione moiety adsorbs zinc and cadmium through the coordination of adjacent sulfhydryl and amino groups.[74] Longer chained peptides may impart additional modes of freedom that enable amino acids to form unique binding sequences[78–80] that work cooperatively in biopharmaceutical purifications,[81,82] and metal chelation.[75,76] Aptamers, single stranded nucleic acids composed of 20–60 nucleotides, can also sequester small molecules. The increased complexity of these materials enable high affinities as evidenced by dissociation constants that extend into the nanomolar range.[83–85] Notably, the efficiency of adsorption is influenced by the confirmation of the immobilized aptamer. Therefore, after adsorbing target analytes, the aptamer binding sequence is regenerated through reversible (i.e., chemical or thermal) denaturing.[83] Engineering materials with ultra-high affinity and selectivity is aided significantly by fixing select functionalities into predetermined, optimized geometries.[86,87] This is exemplified within the highly organized tertiary structure of proteins that use alpha helices and β-sheets to shape the geometry of the active site.[88] Many of these geometries can be borrowed from nature and modified through point substitutions to tailor protein selectivity and affinity.[88,89]

While designer peptide and amino acid sequences have a substantial number of benefits, their applicability may be limited by their stability in harsh environments, scalability, and cost. We hypothesize that there exists a trade-off between the peptide chain complexity and the increase in selectivity/affinity. Generally, the ease of synthesis appears to be inversely proportional to the affinity. For instance, while short chained peptide sequences can be synthesized using solid-state reactions, proteins must be created using the molecular machinery of bacteria. Nevertheless, these entities provide platforms to execute fundamental studies and offer inspiration for the design of polymer materials.

3.2. Polymeric Designs to Enhance Selectivity

Peptides and proteins inspire one class of multifunctional sorbents, sorbents that use the precise placement of functional groups relative to one another to tailor analyte selectivity and affinity (**Figure 5**a). Using multiple functionalities to coordinate analytes (1) enforces a preferred geometry,[90] (2) exerts charge stabilization, and (3) enforces secondary bonding mechanisms, mechanisms that may enhance sorbent selectivity.[91]

To directly engineer coordinating bonds into polymers, it is paramount that moieties be positioned with nanoscale precision. Ideally, polymers could be controlled with a level of precision akin to that seen in metal organic frameworks (MOFs) and covalent organic frameworks (COFS). Although their inherent crystallinity enables sub-nanometer control over the orientation and distance between functionalities decorating the pore walls,[92–99] these materials currently fall short of the tailored flow paths and ideal mass transport conditions desired in sorbents.

The ability to tailor the molecular-scale orientation of functional groups enables ligand-solute interactions to be arranged in a manner that enhances sorbent properties. The positioning of amidoxime moieties is one example where this approach is used to increase selectivity when extracting uranium from seawater.[9–11,100] Figure 4b illustrates that the relative distances between two amidoxime moieties can be tailored by modifying the polymer structure. Consequently, the orientation between the two moieties is fixed and structure-function insights can be correlated to macroscopic sorbent properties. Interestingly, when the polymers were subjected to equimolar vanadium and uranium ions, they showed drastic differences in performance. Reducing the distance between the two moieties increased the separation factor for uranium by more than a factor of 6. Similarly, the affinity of amidoxime moieties for uranium can be enhanced with additional coordinating bonds from carboxylic acid[12] and

© 2022 The Authors. Macromolecular Chemistry and Physics published by Wiley-VCH GmbH

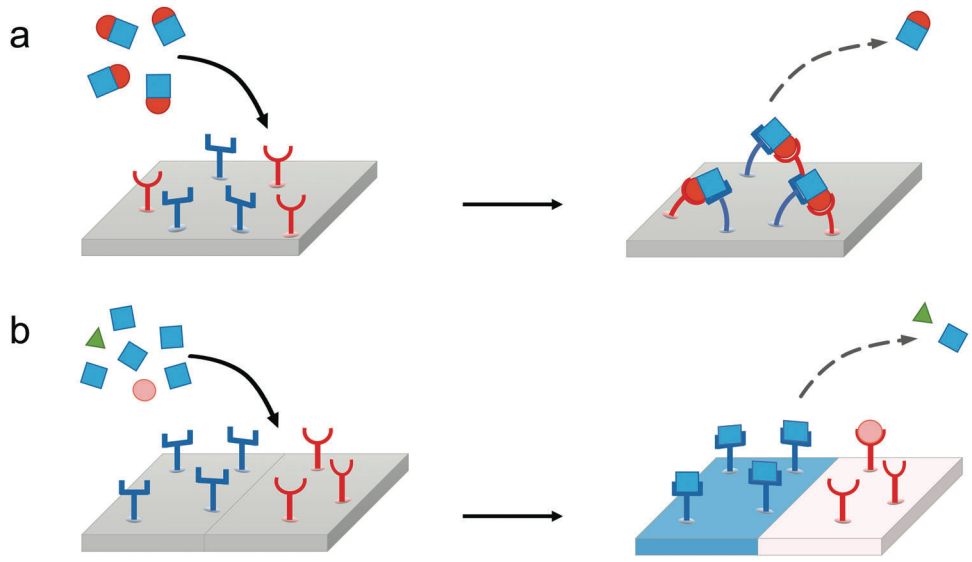


Figure 5. Multifunctional membranes incorporate distinct chemical functionalities that work together to target solute(s) in complex feed streams selectively. **a)** Multifunctional membranes consist of polymers molecularly tuned to incorporate chemistries adjacent to one another. The proximity of the ligands enables the moieties to form multiple coordination bonds with an analyte. This high degree of coordination with the target analyte can simultaneously increase the affinity and selectivity the sorbent possesses toward the molecule. **b)** Surface domains are selectively functionalized with multiple ligands each targeting unique analytes. When a feed solution is introduced to the polymer membrane, analytes adsorb to the surface until the available sites are saturated. Functionalities that undergo a physical change when complexing with analytes allows for information to be stored within the sorbent-analyte chemical bonds. Analytes that are not adsorbed to the polymer surface remain in the effluent.

amine moieties[101–103] adjacent to the amidoxime. Likewise, coordinating bonds have been formed to adsorb Hg(II) (e.g., coordinating sulfur and triazole moieties),[104–107] and form chelating bonds with Pb(II) (chelating bonds between lead and amine, hydroxyl or sulfur groups).[108–110] These case studies exemplify how the weaker adsorptive interactions (e.g., ion exchange) can be overcome through the synergistic interplay between multiple moieties, an effect that relies on analytes possessing multiple complexation modes (e.g., heavy metals form up to six coordination bonds and organic molecules may interact through hydrogen bonding and molecular orbital interactions).[111–116] In turn, nanoscale manipulations that position moieties adjacent to one another can tailor the kinetics[10] and strength[117] of solute-ligand interactions.

Many emerging polymer materials enable precise control over the material nanostructure (e.g., self-assembled block polymers, lyotropic liquid crystals, molecularly imprinted polymers[118,119]). Polymeric systems offer opportunities to tailor the density of sorbent sites, a priori, and synthesize precise macromolecular structures. For instance, polymer chemistries can be tailored to alter the macromolecular architecture (e.g., core morphology, brush length) of self-assembled polymers[120,121] and control the density of functional groups on polymer chains.[122] Additionally, synthetic techniques can manipulate molecular-scale properties that affect polymer dispersity and, consequently, macroscopic properties (e.g., spatial uniformity, electrical conductivity, flammability).[123] In turn, promising opportunities exist in synthesizing polymers with narrow molecular weight distributions and controlling the orientation of multiple functional groups on polymeric platforms as a means to enhance solute affinity and obtain solute-tailored selectivity.

3.3. Computational Simulations Help Target Polymer Chemistries

The synergistic interplay between computational simulations, which provide detailed molecular scale insights into sorbent-analyte complexes,[90,118,124] and experimental methods can help catalyze the design of selective, high affinity ligands. Computational simulations can readily elucidate the impact of macromolecular structure and arrangement on the interaction strength between ligands and solutes. For instance, electronic interactions rely on induced dipole moments, the delocalization of electrons, and the donation of lone pairs. Consequently, modeling may provide opportunities to enhance these interactions by increasing the electron-conjugated system or adding electron donating/withdrawing moieties as decorating appendages to the ligand.[125–127] Additionally, computational simulations can be used to vary the linker between multiple functional groups (i.e., rapidly enumerate through possible orientations) and evaluate how this difference effects the strength of sorbent-solute interactions. This requires a complete understanding on ligand-solute complexing modes. In one example, simulations have provided information to show that crown ether complexes are selective towards monovalent salts (e.g., sodium and potassium) due to the size-match effect and the decrease in free energy associated with the formation of host guest complexes.[128] Moreover, simulations provide information on solute-ligand free energy landscapes and bridge the gap between experimental phenomena and thermodynamics.[129] In turn, validating and applying fundamental models can provide forward looking insight into the design of novel ligands that target and enhance selective sorbent analyte interactions. As such, we anticipate that coupling high-throughput experiments with state-of-the-art computation in a manner that

© 2022 The Authors. Macromolecular Chemistry and Physics published by Wiley-VCH GmbH

allows for rapid feedback will help speed the discovery of new polymer sorbents in the near future.

3.4. Multicomponent Identification

Manipulating the molecular arrangement of functional groups provides a method for manipulating sorbent affinity and selectivity in a rational manner. In contrast, manipulating chemistry on the micrometer through millimeter length scales to pattern sorbents with varied ligands provides opportunities to simultaneously treat and identify multi-analyte feed streams. By selecting chromophores that change upon binding with analytes (e.g., through fluorescence,[75,92,130,131] UV-Vis absorption,[127,132,133] and potentiometric[134] sensing), information (e.g., the identity and concentration of analytes) is reflected in the formation of the ligand-solute complex. For instance, polymer membrane sorbents that complex copper ions turn blue. The absorption of the visible light in this region of the spectrum can be correlated to the concentration of copper. When membranes are functionalized with multiple ligands and sectioned into distinct domains, sensors can be created. Figure 5b illustrates each domain holds a unique sorbent molecule. When the polymer membrane is subject to a multicomponent feed stream, sorbents capture analytes until the sites are fully saturated. These multifunctional, patterned membranes enable the design of sensors that use spatiotemporal cues to continuously monitor the retentate stream. As additional domains are incorporated into the sensor array, more information is encoded, and the sensors generate unique fingerprints that are specific to particular analytes.[135] While controlling the nanoscale chemistry of polymer membranes can be accomplished through polymer design and synthesis, the control over micrometer scale patterns may rely on post synthetic modification schemes. Although multifunctional patterned membranes present promising strategies for next-generation polymer sorbents, opportunities for growth exist. For instance, analyzing the data will require methods capable of deconvoluting the spectra of sorbents that complex multiple analytes.

4. Sorbent Regeneration

Bound analytes need to be released from the sorbent surface so they can be recovered. For single use sorbents (e.g., those designed to purify therapeutic proteins), release is required prior to product formulation.[136] For processes that target the recovery of lower value analytes, releasing the bound material allows the sorbent to be regenerated and reused, improving process economics. Regardless of the mechanism used to adsorb a solute, energy must be exerted to disrupt the sorbent-analyte complex and stimulate the release of the analyte. The stimuli listed in Figure 1 are divided based on their mode of action. Certain stimuli (highlighted in green) are introduced by changing the temperature or composition of the environment surrounding the sorbent. Other stimuli (indicated in orange) act directly on the polymer material itself, displacing electrons or charges to promote the desorption of the analyte. Designing reusable sorbents requires engineering polymer materials that maintain stable capacity values through repeated cycling. Accomplishing this aim demands sorbents designed to resist chemical degradation and withstand deactivation due to irreversible analyte binding. With the ability to create and tailor the interaction strength of selective, multifunctional ligands, polymeric materials present one way to design sorbents that can be regenerated sustainably.

4.1. Environmental Stimuli

Solvent regeneration mechanisms: Manipulating the external environment can strip the analyte from the surface of the sorbent. A familiar example of this mechanism is found in ion exchange resins (e.g., water softeners), which are regenerated using a high concentration KCl or NaCl solution to remove bound divalent ions.[137] For metal ions that are strongly bound, compounds such as ethylene diamine and ethylenediaminetetraacetic acid (EDTA) can be added to the wash solution.[130,138–140] These compounds have greater affinities and/or are introduced at high concentrations to promote release of the analyte from the sorbent.[141–143] Changing the solvent identity can also be used to disrupt the interactions between the polymer sorbent and the analyte. For instance, organic analytes that are removed from aqueous solutions through hydrogen bonding interactions can be released, and the sorbent regenerated, by changing the solvent to an alcohol.[144–147] The regeneration efficiency can be further optimized through the use of mixed solvents and additives. In particular, the elution rate of nonpolar, charged pharmaceutical drugs, such as doxorubicin, can be controlled using water alcohol mixtures that contain dissolved salts.[148] While the water to alcohol ratio governs intermolecular interactions (i.e., solubility), excess potassium chloride displaces doxorubicin molecules that are bound by ion exchange mechanisms. Interestingly, subtle changes to these formulations (e.g., eluting with ions that possess comparably sized hydration shells) have been shown to influence the efficacy of the wash solution.[149,150] When organic solvents are used as eluents, polymer stability must be considered to ensure that the sorbent nanostructure and functionality do not degrade during operation.[151] While these regeneration methods can be efficient, they are associated with secondary environmental pollution.

The use of pH-responsive polymers has been well studied in many contexts.[152–155] For example, the protonation and deprotonation of ionizable functional groups can modulate polymer conformations such that pH-responsive materials can be used for drug delivery or gating applications.[156–159] These applications rely on locally induced charges to change macroscopic polymer properties highlighting the connection between repeat unit chemistry and the pH-response of polymer systems. The conformation of PAA chains depends on more than just repeat unit chemistry with demonstrated dependencies on molar mass, ionic strength, and brush density.[153–155] For instance, under a minimum molar mass (i.e., 16.5 kDa), PAA chains cannot undergo the reversible coil to globule transition associated with high to low pH swings. In fact, below this molecular weight, the chains remain solvated, and the conformation is independent of environmental pH. In turn, restricting access to particular conformations may modulate the ability of PAA brushes to adsorb ions from solution.[130,160–164] That is, the carboxylic acid moiety undergoes an ion exchange in which the hydrogen atom is replaced, with a dissolved heavy metal ion.[58] The stoichiometry of the PAA-ion complex has been a subject of debate, yet the macromolecule is known to form both 1:1 and 2:1 complexes with heavy

© 2022 The Authors. Macromolecular Chemistry and Physics published by Wiley-VCH GmbH

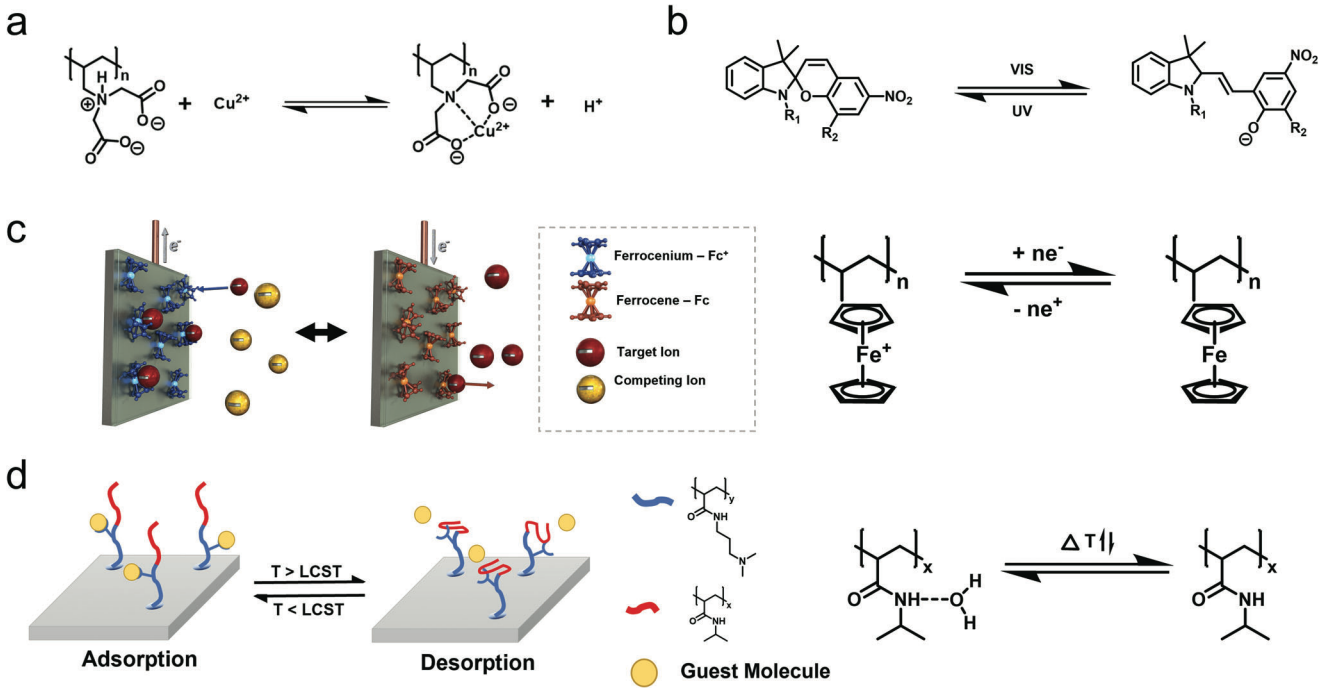


Figure 6. Adsorption and desorption mechanisms of multiple stimuli dependent chemistries. **a)** Iminodiacetic acid groups use a proton exchange mechanism to complex copper ions. The coordination of copper occurs when the solution pH is between the pK_a of the carboxylic acids (i.e., pK_{a1} = 1.8, pK_{a2} = 2.5) and the pK_a of the tertiary amine (i.e., pK_a = 9.1). Copper ions can be desorbed from the membrane by manipulating the pH. **b)** A neutral spiropyran isomer does not exhibit charge and is unable to complexions. Irradiating the isomer with UV light leads to the cleavage of a carbon-oxygen bond and the formation of a zwitterionic phenol derivative. In this state, the isomer complexes with transition metals by donating electrons to open "d" orbital subshells. The isomer can be incorporated into polymer materials through covalent bonding at the R_1 position. The R_2 position permits functionalization with electron donating functionalities that promote supplementary stabilizing analyte-sorbent bonds. Irradiating the molecule with visible light regenerates the uncharged spiropyran isomer. **c)** Poly(vinyl ferrocene) polymers can be reversibly oxidized and reduced. The uncharged ferrocene (Fc) polymer is unable to adsorb ions. Using an applied potential to oxidize the polymer into its ferrocenium (Fc^+) form leads to the selective adsorption of ions. The ions can be expelled into the solution through the application of a reducing potential. **d)** Incorporating thermo-responsive (TR) polymers adjacent to selective ligands/polymer moieties permits for cyclic, temperature sensitive adsorption/desorption cycles. TR polymers (e.g., poly(N-isopropylacrylamide)) undergo a reversible coil-to-globule transition as the solution temperature oscillates above and below the lower critical solution temperature (LCST). Above the LCST, the TR polymer favors the linear chain conformation, and the active sites of the selective polymer are exposed. When the solution temperature drops below the LCST, the TR polymer favors a compact globule state and deactivates the adsorbing polymer sites. In this state, solutes are desorbed and released into the solution.

metals. Exerting molecular-scale control over polymer synthesis can manipulate PAA properties such that the formation of specific complexes is favored, and it can modify the pKa of the repeat unit relative to the monomer to promote or hinder metal ion desorption. Polyethyleneimine (PEI) moieties follow a similar pH-dependent adsorption/desorption behavior yet, the change in the electron donating atom (i.e., from oxygen to nitrogen) leads to interactions that can also adsorb dyes.[130,163–170] Within iminodiacetic acid moieties, the complexation of copper involves a similar proton exchange mechanism yet requires the coordination of two carboxylic acid groups and an amine group (**Figure 6**a).[34] The use of complementary pH-sensitive moieties present additional opportunities to stabilize and target specific analytes, enhancing sorbent properties.

Thermally responsive polymers rely on temperature changes to switch between chain conformations that promote the adsorption and desorption of solutes.[171–173] The incorporation of thermoresponsive poly(*N*-isopropylacrylamide) (pNIPAAm) repeat units to selective poly{*N*-[3-(dimethylamino) propyl]methacrylamide} (PMA) blocks provides one means to regulate the adsorption of dyes (Figure 6d). When the temperature is below the lower critical solution temperature (LCST), the pNIPAAm blocks favor a stretched chain conformation, exposing the active sites of the PMA polymer and enabling the adsorption the analyte. At higher temperatures, the pNIPAAm polymer chains favor a globule confirmation. As the chains shrink in spatial extent, they block the active sites and desorb the analyte.[174] The temperature dependent coil-to-globule transition also influences the relative hydrophobicity of the pNIPAAm chains and can be used to retain proteins. Specifically, at temperatures above the LCST, proteins are absorbed due to enhanced ionic and hydrophobic interactions. Under the LCST, NIPAAm chains are hydrophilic and proteins are desorbed.[175,176]

4.2. Direct Stimuli

While environmentally responsive polymers present a means to eliminate the use of harsh solvents, the large amount of chemical and thermal energy associated with the oscillation of solution pH

© 2022 The Authors. Macromolecular Chemistry and Physics published by Wiley-VCH GmbH

and temperature, respectively, is not ideal. This insight suggests that inducing a change within polymer backbone themselves can lead to more efficient sorbent materials. The assertion is supported by recent analysis on the separation efficiency of dilute gaseous mixtures in pressure swing adsorption (PSA) and temperature swing adsorption (TSA).[177] Independent of the change in enthalpy upon binding, the thermodynamic efficiency of PSA processes decreases monotonically with feed solution composition. Conversely, the thermodynamic efficiency of TSA processes exhibited maxima in efficiency as a function of feed solution composition. As the enthalpy of binding increased, the location of the maxima moved to lower concentration, thereby suggesting that energy efficient separations occur when the work to desorb analytes is applied to the sorbent rather than the solution.

Electromagnetic radiation is easily manipulated, providing opportunities for the creation of light-responsive sorbents. For instance, molecular structures can be interconverted between multiple isomers by changing the wavelength of light.[178,179] Azobenzene moieties are one class of molecules that undergo a reversible *cis* to *trans* isomerization. The distribution of electrons changes based on the isomer conformation and induces a dipole moment. Additionally, spectral and kinetic properties can be tuned by the addition of substituents onto the benzene rings or through the electron donating and withdrawing groups incorporated into a polymer scaffold.[180] Ultimately, subtle *cis*-to-*trans* molecular changes have been used to modulate azobenzene-host complexes[181] and toggle the response of amine,[182] ethylene dioxy,[183] and crown ether moieties.[184]

A separate class of light-responsive molecules (e.g., spiropyran, coumarin, and diarylethene) form and break covalent bonds under different wavelengths. For instance, coumarin moieties can form a bridge, physically constraining molecules under one wavelength and subsequently releasing them under the appropriate stimulus. Spiropyrans have been the focus of a significant amount of research due to the reversible cleavage of a carbon-oxygen bond. The neutral spiropyran isomer is favored under white light and a charged merocyanine isomer is created under UV light irradiation (Figure 6b). Tailoring the polymer chemistry when attaching these moieties to membranes can impact the applicability and regeneration ability of the sorbent. For instance, efficiently switching between the two isomers requires the moiety to be a certain distance from the polymer backbone.[125] When the molecule is too close to the polymer surface, a variety of mechanisms (e.g., merocyanine stacking) can decrease the sorbent capacity after cycling. Similar space considerations need to be considered when spiropyran moieties are incorporated within confined pores.[185] Generally, when incorporating light sensitive molecules into macromolecules, polymers must be engineered to ensure that they do not adsorb the same wavelength of light that enables the moiety to isomerize.

Electroactive sorbents rely on potential swings to adsorb and desorb solutes. Applied voltages can promote the migration of ions towards the electrode, increasing adsorption kinetics,[186] and change the oxidation state of sorbent moieties, lending to interactions between functional groups and analytes. As such, metal ion sorption/desorption does not require harsh solvents and potential dependent mechanisms provide promising possibilities for polymer regeneration. Electroactive sorbents can be created by using dopants[187–190] or conductive polymers.[191–194] Notably, the oxidation state of ferrocenium and ferrocene can be switched by alternating the electric field of redox-active metallopolymers. While ferrocenium provides binding sites for anions, ferrocene releases them (Figure 6c).[194] Interestingly, the selectivity towards anions can be tailored by changing the locations of the ferrocene group (i.e., on side chain or main chain). This case study exemplifies the polymeric considerations that can be used to tailor sorbent properties. In addition to directly changing polymer sites for adsorptive processes, potential driven applications can affect adjacent moieties and bound analytes. For instance, the aforementioned redox-active ferrocene moieties can tailor the electron distribution within adjacent carboxylic acid groups and trigger the uptake and release of rare earth elements.[195] Likewise, sorbent dopants can generate electrons upon application of a potential. In the presence of the appropriate electrolyte, organic molecules could be oxidized by the generated radicals.[196]

Further regeneration mechanisms include the use of inorganic additives and bioenzymes. For example, magnets can be used to recollect sorbents blended with magnetic additives[197,198] or immobilized catalysts or bio-enzymes can be used to adsorb and subsequently oxidize pollutants.[199–201] Ultimately, sorbent regeneration techniques must be considered to design energy-smart, reusable and eco-friendly separation processes.

5. Summary and Future Outlook

Polymer materials are poised to make a significant impact in the realm of separations, and we anticipate high-impact efforts to be made in the field of adsorption, specifically. This is because the knowledge and capabilities of the polymer science community and separations engineering fields have developed to a point where they are primed to converge such that revolutionary advances can be had in a short period of time. In this way, we see an ideal opportunity for polymer scientists and engineers, separations technologists, and systems engineers to form diverse, interdisciplinary teams in a manner that enables rapid progress.

In particular, we envision that polymer sorbents will play increasingly important roles for the recovery of dilute products of value from non-traditional sources as adsorptive separations are uniquely suited for these applications (i.e., they may be able to break the paradigm established within the Sherwood plot).[22,202] Moreover, adsorption will continue to play a critical role in the purification of high-end and specialty products that are needed in the biological and pharmaceutical industries. Key advances here will focus on targeting emerging biologicals such as virus-based products[5,6] and transitioning toward the continuous manufacturing of established products such as protein-based therapies.[203,204]As designer macromolecules will be required, the cost of the active materials, scalability of the polymer systems, and lifetime of the separation units will be of key importance. Therefore, care must be taken to design synthetic protocols that allow for the creation of high-performance and sustainable solutions. Moreover, next-generation materials that can be used to produce systems with form factors consistent with current sorbent operations can be implemented in a drop-in replacement fashion and may have a better opportunity for translation. Similarly, the lifetime of separation systems can be extended by placing materials regeneration at the forefront of macromolecular design. This will positively impact both the initial

© 2022 The Authors. Macromolecular Chemistry and Physics published by Wiley-VCH GmbH

separations cost, minimize material turnover and production downtime, and can enhance energy efficiency. Importantly,as they have done in so many other polymer-based applications, we envision that physics-based computational simulations and machine learning will play crucial roles in establishing principled and data-driven frameworks that can guide material design and process synthesis.[205,206] Thus, forming a bigger tent of researchers (i.e., to those schooled in data science and computer science) and training students and the future workforce in these key skills will be imperative for the continued success of the field. By adopting this materials genome initiative (MGI) mindset, it is anticipated that high-throughput experiments will soon be coupled to high-throughput computational efforts such that materials discoveries occur in a rapid manner. When coupled with the capabilities of process systems engineering (e.g., superstructure optimization), this approach will lead to faster and less costly deployment of advanced polymeric materials for these critical applications.

For all of these reasons, we view the field of polymer sorbents as one that is extremely bright, and the ceiling on the potential outcomes of efforts is quite high. In particular, we see fundamental science communities and practical industries that are primed to embrace the opportunities described here in a complete and robust manner. In doing so, we anticipate new foundational principles will be developed, tailored macromolecular designs will be had, and advanced sorbent technologies will be implemented. We put forward that this is most likely to occur by bringing teams of scientists and engineers from diverse backgrounds and disciplines to the table. In this way, there is yet again a true opportunity to have polymer science serve as a means to advance the global society.

Acknowledgements

J.A.O., J.X., and C.F.-H contributed equally to this work. This work was kindly support by the National Science Foundation (NSF) through awards 1924714 (Purdue University) and 1924715 (University of Notre Dame). The authors thank the NSF for this generous support.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

advanced separation materials, macromolecular sorbents, analyte-specific chemistry, polymer-based membrane adsorbers

Received: January 25, 2022
Revised: March 31, 2022
Published online:

[1] D. S. Sholl, R. P. Lively, *Nature* **2016**, *532*, 435.
[2] M. Elimelech, WA Phillip, *Science* **2011**, *333*, 712.
[3] EL Cussler, BK Dutta, *AIChE J.* **2012**, *58*, 3825.
[4] A. L. Zydney, *Biotechnol. Bioeng.* **2016**, *113*, 465.
[5] N. Singh, CL Heldt, *Curr. Opin. Chem. Eng.* **2022**, *35*, 100780.
[6] K. Kawka, A. N. Wilton, P. Madadkar, M. F. C. Medina, B. D. Lichty, R. Ghosh, D. R. Latulippe, *Sep. Purif. Technol.* **2021**, *254*, 117503.
[7] National Academies of Sciences, Engineering, and Medicine. *A Research Agenda for Transforming Separation Science*, National Academies Press, Washington, DC **2019**. https://doi.org/10.17226/25421.
[8] P. Suresh, C. E. Duval, *Ind. Eng. Chem. Res.* **2020**, *59*, 12212.
[9] Y. Song, C. Zhu, Q. Sun, B. Aguila, C. W. Abney, L. Wojtas, S. Ma, *ACS Cent. Sci.* **2021**, *7*, 1650.
[10] Q. Sun, Y. Song, B. Aguila, A. S. Ivanov, V. S. Bryantsev, S. Ma, *Adv. Sci.* **2021**, *8*, 2001573.
[11] Q. Sun, B. Aguila, J. Perman, A. S. Ivanov, V. S. Bryantsev, L. D. Earl, C. W. Abney, L. Wojtas, S. Ma, *Nat. Commun.* **2018**, *9*, 1644.
[12] W. Lin, Development of Novel Porous Sorbents for Extraction of Uranium from Seawater, DOE/NEUP–13-5332, 1363745, 2017. https://doi.org/10.2172/1363745 (accessed: January 2022).
[13] K. R. Zodrow, Q. Li, R. M. Buono, W. Chen, G. Daigger, L. Dueñas-Osorio, M. Elimelech, X. Huang, G. Jiang, J.-H. Kim, B. E. Logan, D. L. Sedlak, P. Westerhoff, P. J. J. Alvarez, *Environ. Sci. Technol.* **2017**, *51*, 10274.
[14] Y. Zhang, N. E. Almodovar-Arbelo, J. L. Weidman, D. S. Corti, B. W. Boudouris, W. A. Phillip, *npj Clean Water* **2018**, *1*, 2.
[15] A. Mulchandani, P. Westerhoff, *Bioresour. Technol.* **2016**, *215*, 215.
[16] B. K. Mayer, L. A. Baker, T. H. Boyer, P. Drechsel, M. Gifford, M. A. Hanjra, P. Parameswaran, J. Stoltzfus, P. Westerhoff, B. E. Rittmann, *Environ. Sci. Technol.* **2016**, *50*, 6606.
[17] A. Kumar, H. Fukuda, T. A. Hatton, J. H. Lienhard, *ACS Energy Lett.* **2019**, *4*, 1471.
[18] B. K. Reck, T. E. Graedel, *Science* **2012**, *337*, 690.
[19] X. Zeng, J. Li, N. Singh, *Crit. Rev. Environ. Sci. Technol.* **2014**, *44*, 1129.
[20] A. Kumar, D. G. Madden, M. Lusi, K.-J. Chen, E. A. Daniels, T. Curtin, J. J. Perry IV., M. J. Zaworotko, *Angew. Chem., Int. Ed.* **2015**, *54*, 14372.
[21] National Academies of Sciences, Engineering, and Medicine. *Negative Emissions Technologies and Reliable Sequestration: A Research Agenda*, National Academies Press, Washington DC **2019**. https://doi.org/10.17226/25259.
[22] K. Z. House, A. C. Baclig, M. Ranjan, E. A. Nierop, J. van Wilcox, H. J. Herzog, *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 20428.
[23] Y. Wang, S. B. Darling, J. Chen, *ACS Appl. Mater. Interfaces* **2021**, *13*, 60789.
[24] L Xiao, Y Ling, A Alsbaiee, C Li, DE Helbling, WR Dichtel, *J Am. Chem. Soc.* **2017**, *139*, 7689.
[25] E. L. Cussler, E. L. Cussler, *Diffusion: Mass Transfer in Fluid Systems*, Cambridge University Press, Cambridge **2009**.
[26] M. Yu, J. N. Renner, C. E. Duval, *Front. Chem.* **2021**, 70.
[27] J. L. Weidman, R. A. Mulvenna, B. W. Boudouris, W. A. Phillip, *Langmuir* **2015**, *31*, 11113.
[28] H. Xia, G. Wan, J. Zhao, J. Liu, Q. Bai, *J. Chromatogr. A* **2016**, *1471*, 138.
[29] J. C. Giddings, *Unified Separation Science Wiley*, Wiley, New York, Toronto **1991**.
[30] D. T. T. Nguyen, D. Guillarme, S. Rudaz, J. L. Veuthey, *J. Sep. Sci.* **2006**, *29*, 1836.
[31] L. C. Advancing, *Anal. Chem.* **2005**, *77*, 460.
[32] J. Heinonen, Q. Sanlaville, H. Niskakoski, T. Saino, *Sep. Purif. Technol.* **2018**, *193*, 317.
[33] G. Liu, D. M. Dotzauer, M. L. Bruening, *J. Membr. Sci.* **2010**, *354*, 198.
[34] S. Wijeratne, M. L. Bruening, G. L. Baker, *Langmuir* **2013**, *29*, 12720.
[35] Y. Jiang, W.-C. Wang, *Polym. Adv. Technol.* **2011**, *22*, 2509.
[36] C. Magnenet, F. E. Jurin, S. Lakard, C. C. Buron, B. Lakard, *Colloids Surf. A* **2013**, *435*, 170.
[37] B. Gao, F. An, Y. Zhu, *Polymer* **2007**, *48*, 2288.

 © 2022 The Authors. Macromolecular Chemistry and Physics published by Wiley-VCH GmbH

[38] F. Zhang, B. Wang, S. He, R. Man, *J. Chem. Eng. Data* **2014**, *59*, 1719.
[39] HCS Chenette, JR Robinson, E. Hobley, SM Husson, *J. Membr. Science.* **2012**, *423–424*, 43.
[40] J. Chen, R. Peng, X. Chen, *Front. Mater. Sci.* **2017**, *11*, 197.
[41] P. He, X. Tang, L. Chen, P. Xie, L. He, H. Zhou, D. Zhang, T. Fan, *Adv. Funct. Mater.* **2018**, *28*, 1801121.
[42] Y.-X. Huang, Z. Wang, D. Hou, S. Lin, *J. Membr. Sci.* **2017**, *531*, 122.
[43] A. K. Hołda, I. F. J. Vankelecom, *J. Appl. Polym. Sci.* **2015**, *132*, 1.
[44] M. Müller, V. Abetz, *Chem. Rev.* **2021**, *121*, 14189.
[45] T.Ishigami, K. Nakatsuka, Y.Ohmukai, E.Kamio, T. Maruyama, H. Matsuyama, *J. Membr. Sci.* **2013**, *438*, 77.
[46] Y. Zhang, J. L. Sargent, B. W. Boudouris, W. A. Phillip, *J. Appl. Polym. Sci.* **2014**, *132*, 4.
[47] H. Hu, S. Rangou, M. Kim, P. Gopalan, V. Filiz, A. Avgeropoulos, CO Osuji, *ACS Nano* **2013**, *7*, 2960.
[48] T. M. Burt, S. Monemian, A. M. Jordan, L. T. J. Korley, *Soft Matter* **2013**, *9*, 4381.
[49] L. J. Tan, W. Zhu, K. Zhou, *Adv. Funct. Mater.* **2020**, *30*, 2003062.
[50] I. R. Woodward, C. A. S. Fromen, *Addit. Manuf.* **2021**, *48*, 102386.
[51] S. Lawson, X. Li, H. Thakkar, A. A. Rownaghi, F. R. Rezaei, *Chem. Rev.* **2021**, *121*, 6246.
[52] M. R. Hartings, Z. Ahmed, *Nat. Rev. Chem.* **2019**, *3*, 305.
[53] A. Al-Shimmery, S. Mazinani, J. Flynn, J. Chew, D. Mattia, *J. Membr. Sci.* **2019**, *590*, 117274.
[54] V. A. Beck, A. N. Ivanovskaya, S. Chandrasekaran, J.-B. Forien, S. E. Baker, E. B. Duoss, M. A. Worsley, *Proc. Natl. Acad. Sci. USA* **2021**, *118*, e2025562118.
[55] M. D. Saikia, N. N. Dutta, *React. Funct. Polym.* **2008**, *68*, 33.
[56] A. Z. M. Badruddoza, Z. B. Z. Shawon, W. J. D. Tay, K. Hidajat, M. S. Uddin, *Carbohydr. Polym.* **2013**, *91*, 322.
[57] M. Zhang, Y. Zhang, R. Helleur, *Chem. Eng. J.* **2015**, *264*, 56.
[58] R. Molinari, P. Argurio, T. Poerio, *Desalination* **2004**, *162*, 217.
[59] T. Miyajima, M. Mori, S. Ishiguro, K. H. Chung, C. H. Moon, *J. Colloid Interface Sci.* **1996**, *184*, 279.
[60] P. R. Andres, U. S. Schubert, *Adv. Mater.* **2004**, *16*, 1043.
[61] B. Bibel, The Bohr Effect: Hemoglobin Oxygen-Carrying Molecular Magic. The Bumbling Biochemist, 2020, https://thebumblingbiochemist.com/365-days-of-science/the-bohr-effect-hemoglobin-oxygen-carrying-molecular-magic/.
[62] C. L. Peacock, D. M. Sherman, *Geochim. Cosmochim. Acta* **2005**, *69*, 3733.
[63] AM Ramos-de-la-Peña, J. González-Valdez, O. Aguilar, *J. Sep. Sci.* **2019**, *42*, 1816.
[64] A. R. Mazzer, X. Perraud, J. Halley, J. O'Hara, D. G. Bracewell, *J. Chromatogr. A* **2015**, *1415*, 83.
[65] MC Martos - Maldonado, CT Hjuler, KK Sørensen, MB Thygesen, JE Rasmussen, K. Villadsen, SR Midtgaard, S. Kol, S. Schoffelen, KJ Jensen, *Nat. Commun.* **2018**, *9*, 3307.
[66] L. Yang, L. Bui, D. Hanjaya-Putra, ML Bruening, *Anal. Chem.* **2020**, *92*, 11912.
[67] Y. Çanak, S. Özkara, S. Akgöl, A. Denizli, *React. funct. polym.* **2004**, *61*, 369.
[68] S. Özkara, H. Yavuz, S. Patır, MY Arıca, A. Denizli, *Sep. sci. Technol.* **2002**, *37*, 717.
[69] N. J. Alves, N. Mustafaoglu, B. Bilgicer, *Biosens. Bioelectron.* **2013**, *49*, 387.
[70] N. Mustafaoglu, N. J. Alves, B. Bilgicer, *Langmuir* **2015**, *31*, 9728.
[71] D. L. Nelson, M. M. Cox, *Lehninger Principles of Biochemistry*, MacMillan, New York, NY **2021**.
[72] V. Pichon, A. Combès, *Anal. Bioanal. Chem.* **2016**, *408*, 6983.
[73] S. Akgöl, D. Türkmen, A. Denizli, *J. Appl. Polym. Sci.* **2004**, *93*, 2669.
[74] BJ Fuhr, DL Rabenstein, *J. Am. Chem. Soc.* **1973**, *95*, 6944.
[75] LK Müller, I. Duznovic, D. Tietze, W. Weber, M. Ali, V. Stein, W. Ensinger, AA Tietze, *Chemistry* **2020**, *26*, 8511.
[76] A. Torrado, G. K. Walkup, B. Imperiali, *J. Am. Chem. Soc.* **1998**, *120*, 609.
[77] J. L. Weidman, R. A. Mulvenna, B. W. Boudouris, W. A. Phillip, *ACS Appl. Mater. Interfaces* **2017**, *9*, 19152.
[78] T. Komikawa, M. Tanaka, K. Yanai, BRG Johnson, K. Critchley, T. Onodera, SD Evans, K. Toko, M. Okochi, *Biosens. Bioelectron.* **2020**, *153*, 112030.
[79] M. Okochi, M. Muto, K. Yanai, M. Tanaka, T. Onodera, J. Wang, H. Ueda, K. Toko, *ACS Comb. Sci.* **2017**, *19*, 625.
[80] J. Wang, M. Muto, R. Yatabe, Y. Tahara, T. Onodera, M. Tanaka, M. Okochi, K. Toko, *Sens. Actuators, B* **2018**, *264*, 279.
[81] J. Berwanger, H. Y. Tan, G. Jokhadze, M. Bruening, *Anal. Chem.* **2021**, *93*, 7562.
[82] W. Liu, L. Bennett, W. Ning, H. Y. Tan, J. Berwanger, X. Zeng, M. Bruening, *Anal. Chem.* **2018**, *90*, 12161.
[83] M. McKeague, M. C. DeRosa, *J. Nucleic Acids* **2012**, *2012*, e748913.
[84] V.-T. Nguyen, Y. S. Kwon, M. B. Gu, *Curr. Opin. Biotechnol.* **2017**, *45*, 15.
[85] M. A. Romero-Reyes, J. M. Heemstra, *ACS Mater. Lett.* **2019**, *1*, 568.
[86] M. R. Berwick, L. N. Slope, C. F. Smith, S. M. King, S. L. Newton, R. B. Gillis, G. G. Adams, A. J. Rowe, S. E. Harding, M. M. Britton, A. F. A. Peacock, *Chem. Sci.* **2016**, *7*, 2207.
[87] D. Baker, *Protein Sci.* **2019**, *28*, 678.
[88] RK Wierenga, *FEBS Lett.* **2001**, *492*, 193.
[89] S. J. Caldwell, I. C. Haydon, N. Piperidou, P.-S. Huang, M. J. Bick, H. S. Sjöström, D. Hilvert, D. Baker, C. Zeymer, *Proc. Natl. Acad. Sci. USA* **2020**, *117*, 30362.
[90] S. Vukovic, BP Hay, *Inorg. Chem.* **2013**, *52*, 7805.
[91] C. Kip, K. O. Hamaloglu, C. Demir, A. Tuncel, *J. Sep. sci.* **2021**, *44*, 1273.
[92] X. Wu, B. Wang, Z. Yang, L. Chen, *J. Mater. Chem. A* **2019**, *7*, 5650.
[93] H. Singh, M. Devi, N. Jena, M. M. Iqbal, Y. Nailwal, A. De Sarkar, S. K. Pal, *ACS Appl. Mater. Interfaces* **2020**, *12*, 13248.
[94] L. Wang, M. Deng, H. Xu, W. Li, W. Huang, N. Yan, Y. Zhou, J. Chen, Z. Qu, *ACS Appl. Mater. Interfaces* **2020**, *12*, 37619.
[95] MN Yazdi, Y. Yamini, H. Asiabi, A. Alizadeh, *Microchim. Acta* **2018**, *185*, 525.
[96] S. Safaei, H. Kazemian, P. C. Junk, *J. Solid State Chem.* **2021**, *300*, 122267.
[97] M. R. Sohrabi, *Microchim. Acta* **2014**, *181*, 435.
[98] S. Mukherjee, B. Manna, AV Desai, Y. Yin, R. Krishna, R. Babarao, SK Ghosh, *Chem. Commun.* **2016**, *52*, 8215.
[99] S. D. Harvey, A. D. Eckberg, P. K. Thallapally, *J. Sep. Sci.* **2011**, *34*, 2418.
[100] N. Tang, J. Liang, C. Niu, H. Wang, Y. Luo, W. Xing, S. Ye, C. Liang, H. Guo, J. Guo, Y. Zhang, G. Zeng, *J. Mater. Chem. A* **2020**, *8*, 7588.
[101] B. Yu, L. Zhang, G. Ye, Q. Liu, J. Li, X. Wang, J. Chen, S. Xu, S. Ma, *Nano Res.* **2021**, *14*, 788.
[102] SD Alexandratos, X. Zhu, M. Florent, R. Sellin, *Ind. Eng. Chem. Res.* **2016**, *55*, 4208.
[103] H. Gu, P. Ju, Q. Liu, G. Sun, J. Liu, R. Chen, J. Yu, J. Zhu, J. Wang, *J. Colloid Interface Sci.* **2022**, *610*, 1015.
[104] L. Merí - Bofí, S. Royuela, F. Zamora, ML Ruiz - González, JL Segura, R. Muñoz - Olivas, MJ Mancheño, *J. Mater. Chem. A* **2017**, *5*, 17973.
[105] Q. Sun, B. Aguila, J. Perman, LD Earl, CW Abney, Y. Cheng, H. Wei, N. Nguyen, L. Wojtas, S. Ma, *J. Am. Chem. Soc.* **2017**, *139*, 2786.
[106] S. Mondal, S. Chatterjee, S. Mondal, A. Bhaumik, *ACS Sustainable Chem. Eng.* **2019**, *7*, 7353.
[107] J. Wang, S. Zhuang, *Coord. Chem. Rev.* **2019**, *400*, 213046.
[108] L. Lv, N. Chen, C. Feng, J. Zhang, M. Li, *RSC Adv.* **2017**, *7*, 27992.
[109] H Ren, B Li, M Neckenig, D Wu, Y Li, Y Ma, X Li, N Zhang, *Carbohydr. polym.* **2019**, *207*, 737.
[110] S. Venkateswarlu, A. Panda, E. Kim, M. Yoon, *Nano Mater.* **2018**, *1*, 4198.

© 2022 The Authors. Macromolecular Chemistry and Physics published by Wiley-VCH GmbH

[111] K. Ziach, M. Karbarz, J. Romanski, *Dalton Trans.* **2016**, *45*, 11639.
[112] D. Jagleńc, S. Siennicka, Ł. Dobrzycki, M. Karbarz, J. Romański, *Inorg. Chem.* **2018**, *57*, 12941.
[113] M. Zaleskaya, M. Karbarz, M. Wilczek, Ł. Dobrzycki, J. Romański, *Inorg. Chem.* **2020**, *59*, 13749.
[114] S. Lin, W. Wei, X. Wu, T. Zhou, J. Mao, Y.-S. Yun, *J. Hazard. Mater.* **2015**, *299*, 10.
[115] A. Abbas, M. A. Hussain, M. Sher, M. I. Irfan, M. N. Tahir, W. Tremel, S. Z. Hussain, I. D. Hussain, *Int. J. Biol. Macromol.* **2017**, *102*, 170.
[116] X. Zhou, H. A. Essawy, M. F. Mohamed, H. S. Ibrahim, N. S. Ammar, *J. Environ. Chem. Eng.* **2018**, *6*, 2137.
[117] J. Filley, M. A. Ibrahim, M. R. Nimlos, A. S. Watt, D. M. Blake, *J. Photochem. Photobiol., A* **1998**, *117*, 193.
[118] L. Qin, W. Liu, S. Zhou, Y. Qu, B. Qian, Y. Yang, X. Zhang, H. Wang, L. Zhang, X. Liu, *Chem. Eng. J.* **2021**, *421*, 129549.
[119] G. Sharma, B. Kandasubramanian, *J. Chem. eng. Data* **2020**, *65*, 396.
[120] Y. Ruan, L. Gao, D. Yao, K. Zhang, B. Zhang, Y. Chen, C.-Y. Liu, *ACS Macro Lett.* **2015**, *4*, 1067.
[121] B. Soman, Y. K. Go, C. Shen, C. Leal, C. M. Evans, *Soft Matter* **2022**, *18*, 293.
[122] M. E. Seitz, C. D. Chan, K. L. Opper, T. W. Baughman, K. B. Wagener, K. I. Winey, *J. Am. Chem. Soc.* **2010**, *132*, 8165.
[123] T. Kashiwagi, J. Fagan, J. F. Douglas, K. Yamamoto, A. N. Heckert, S. D. Leigh, J. Obrzut, F. Du, S. Lin-Gibson, M. Mu, K. I. Winey, R. Haggenmueller, *Polymer* **2007**, *48*, 4855.
[124] A. Rizzi, T. Jensen, D. R. Slochower, M. Aldeghi, V. Gapsys, D. Ntekoumes, S. Bosisio, M. Papadourakis, N. M. Henriksen, B. L. from Groot, Z. Cournia, A. Dickson, J. Michel, MK Gilson, MR Shirts, DL Mobley, JD Chodera, *J. Comput. Aided Mol. From.* **2020**, *34*, 601.
[125] A. Radu, R. Byrne, N. Alhashimy, M. Fusaro, S. Scarmagnani, D. Diamond, *J. Photochem. Photobiol., A* **2009**, *206*, 109.
[126] H. Cui, H. Liu, S. Chen, R. Wang, *Dyes Pigm.* **2015**, *115*, 50.
[127] Z. Yang, F. Wang, H. Liu, *J. Polym. Res.* **2019**, *26*, 89.
[128] S. Zhang, R. Ou, H. Ma, J. Lu, MM Banaszak Holl, H. Wang, *Chem. Eng. J.* **2021**, *405*, 127037.
[129] L. X. Dang, *J. Am. Chem. Soc.* **1995**, *117*, 6954.
[130] Y. Zhang, J. R. Vallin, J. K. Sahoo, F. Gao, B. W. Boudouris, M. J. Webber, W. A. Phillip, *ACS Cent. Sci.* **2018**, *4*, 1697.
[131] D Kumar Das, P Goswami, C Barman, B Das, *Environ. Closely. Res.* **2012**, 75.
[132] H. Shao, D. Yin, D. Li, Q. Ma, W. Yu, X. Dong, *ACS Appl. Mater. Interfaces* **2021**, *13*, 49288.
[133] K. H. Fries, J. D. Driskell, G. R. Sheppard, J. Locklin, *Langmuir* **2011**, *27*, 12253.
[134] A. Zürn, H. Müller, *Fresenius' J. Anal. Chem.* **1993**, *346*, 589.
[135] L. Mitchell, E. J. New, C. S. Mahon, *ACS Appl. Polym. Mater.* **2021**, *3*, 506.
[136] A. L. Zydney, *J. Membr. Sci.* **2021**, *620*, 118804.
[137] B. Belhalfaoui, A. Aziz, EH Elandaloussi, MS Ouali, LC De Ménorval, *J. Hazard. Mater.* **2009**, *169*, 831.
[138] Z. Qu, X. Meng, H. Duan, D. Qin, L. Wang, *Sci. Rep.* **2020**, *10*, 7723.
[139] T. Oymak, E. Bağda, *Clean: Soil, Air, Water* **2018**, *46*, 1700186.
[140] S. Girdthep, O. Hanmeng, N. Triamnak, N. Chailek, N. Wanichacheva, *Polym. Test.* **2021**, *97*, 107151.
[141] K. Zhang, Z. Dai, W. Zhang, Q. Gao, Y. Dai, F. Xia, X. Zhang, *Coord. Chem. Rev.* **2021**, *434*, 213809.
[142] S. Boija, A. Almesåker, E. Hedenström, D. Bylund, H. Edlund, M. Norgren, *J. Mass Spectrom.* **2014**, *49*, 550.
[143] R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, R. G. Wilkins, *Inorg. Chem.* **1966**, *5*, 622.
[144] Z. Wang, F. Cui, Y. Pan, L. Hou, B. Zhang, Y. Li, L. Zhu, *Carbohydr. Polym.* **2019**, *213*, 352.
[145] R. Zhao, T. Ma, S. Li, Y. Tian, G. Zhu, *ACS Appl. Mater. Interfaces* **2019**, *11*, 16662.
[146] L. Han, Y. He, R. An, X. Wang, Y. Zhang, L. Shi, R. Ran, *Colloids Surf. A* **2019**, *569*, 18.
[147] S. Şenel, A. Kara, G. Alsancak, A. Denizli, *J. Hazard. mater.* **2006**, *138*, 317.
[148] M. V. Gonzalez, Y. Tang, G. J. Phillips, A. W. Lloyd, B. Hall, P. W. Stratford, A. L. Lewis, *J. Mater. Sci. Mater. Med.* **2008**, *19*, 767.
[149] G. Naidu, S. Jeong, MAH Johir, AG Fane, J. Kandasamy, S. Vigneswaran, *Water Res.* **2017**, *123*, 321.
[150] G. Naidu, T. Nur, P. Loganathan, J. Kandasamy, S. Vigneswaran, *Sep. Purif. Technol.* **2016**, *163*, 238.
[151] M. P. Dugas, G. V. Every, B. Park, J. R. Hoffman, R. J. LaRue, A. M. Bush, Y. Zhang, J. L. Schaefer, D. R. Latulippe, W. A. Phillip, *Mol. Syst. Des. Eng.* **2020**, *5*, 943.
[152] MAC Stuart, WTS Huck, J. Genzer, M. Müller, C. Ober, M. Stamm, GB Sukhorukov, I. Szleifer, VV Tsukruk, M. Urban, F. Winnik, S. Zauscher, I. Luzinov, S. Minko, *Nat. Mater.* **2010**, *9*, 101.
[153] D. Wang, RJ Nap, I. Lagzi, B. Kowalczyk, S. Han, BA Grzybowski, *J. Am. Chem. Soc.* **2011**, *133*, 2192.
[154] P. Gong, T. Wu, J. Genzer, I. Szleifer, *Macromolecules* **2007**, *40*, 8765.
[155] T. Wu, P. Gong, I. Szleifer, P. Vlček, V. Šubr, J. Genzer, *Macromolecules* **2007**, *40*, 8756.
[156] S. Angelos, Y.-W. Yang, N. M. Khashab, J. F. Stoddart, J. I. Zinnk, *J. Am. Chem. Soc.* **2009**, *131*, 12912.
[157] B. Lee, S. Hyun, G. Jeon, E. Y. Kim, J. Kim, W. J. Kim, J. K. Kim, *ACS Appl. Mater. Interfaces* **2016**, *8*, 11758.
[158] S. Benavides, S. Qu, F. Gao, W. A. Phillip, *Langmuir* **2018**, *34*, 4503.
[159] E. Aznar, M. Oroval, L. Pascual, JR Murguía, R. Martínez - Máñez, F. Sancenón, *Chem. Rev.* **2016**, *116*, 561.
[160] J. Liu, G. Liu, W. Liu, *Chem. Eng. J.* **2014**, *257*, 299.
[161] Z. Yuan, J. Wang, Y. Wang, Q. Liu, Y. Zhong, Y. Wang, L. Li, S. F. Lincoln, X. Guo, *RSC Adv.* **2019**, *9*, 21075.
[162] H. A. Essawy, M. F. Mohamed, N. S. Ammar, H. S. Ibrahim, *RSC Adv.* **2017**, *7*, 20178.
[163] X. Zhao, K. Ma, T. Jiao, R. Xing, X. Ma, J. Hu, H. Huang, L. Zhang, X. Yan, *Sci. Rep.* **2017**, *7*, 44076.
[164] T. S. Anirudhan, S. S. Gopal, S. R. Rejeena, *Int. J. Polym. Mater. Polym. Biomater.* **2015**, *64*, 772.
[165] R. Zhao, X. Li, B. Sun, M. Shen, X. Tan, Y. Ding, Z. Jiang, C. Wang, *Chem. Eng. J.* **2015**, *268*, 290.
[166] P. Bhunia, S. Chatterjee, P. Rudra, S. De, *Sep. Purif. Technol.* **2018**, *193*, 202.
[167] P. Viel, S. Palacin, F. Descours, C. Bureau, F. Le Derf, J. Lyskawa, M. Sallé, *Appl. Surf. Sci.* **2003**, *212–213*, 792.
[168] A. Duran, M. Soylak, S. A. Tuncel, *J. Hazard. Mater.* **2008**, *155*, 114.
[169] Y. Chen, W. Zhao, J. Zhang, *RSC Adv.* **2017**, *7*, 4226.
[170] H. El-Hamshary, M. El-Garawany, F. N. Assubaie, M. Al-Eed, *J. Appl. Polym. Sci.* **2003**, *89*, 2522.
[171] Y. Fan, R. P. Lively, Y. Labreche, F. Rezaei, W. J. Koros, C. W. Jones, *Int. J. Greenhouse Gas Control* **2014**, *21*, 61.
[172] A. H. Berger, J. A. Horowitz, T. Machalek, A. Wang, A. S. Bhown, *Energy Procedia* **2017**, *114*, 2193.
[173] S. Huang, X. Liu, Q. Hu, T. Wei, J. Wang, H. Chen, C. Wu, *ACS Appl. Mater. Interfaces* **2020**, *12*, 2991.
[174] Y. Jiang, S.-F. Shan, W. Liu, J. Zhu, Q.-X. He, P. Tan, L. Cheng, X.-Q. Liu, L.-B. Sun, *Chem. Commun.* **2017**, *53*, 9538.
[175] S. Tan, R. I. Boysen, K. Saito, M. T. W. Hearn, *Sep. Purif. Technol.* **2021**, *259*, 118173.
[176] P. Maharjan, M. T. W. Hearn, W. R. Jackson, K. De Silva, B. W. Woonton, *J. Chromatogr. A* **2009**, *1216*, 8722.
[177] R. P. Lively, M. J. Realff, *AIChE J.* **2016**, *62*, 3699.
[178] E. Pantuso, G. De Filpo, FP Nicoletta, *Adv. Opt. Mater.* **2019**, *7*, 1900252.
[179] FP Nicoletta, D. Cupelli, P. Formoso, G. De Filpo, V. Colella, A. Gugliuzza, *Membranes* **2012**, *2*, 134.

 © 2022 The Authors. Macromolecular Chemistry and Physics published by Wiley-VCH GmbH

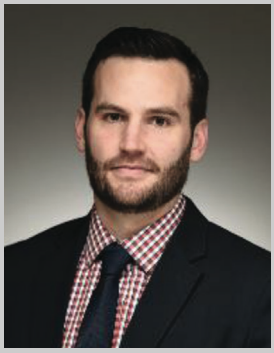
[180] S. Sun, S. Liang, W.-C. Xu, G. Xu, S. Wu, *Polym. Chem.* **2019**, *10*, 4389.
[181] L. Zou, C. J. Addonizio, B. Su, M. J. Sis, A. S. Braegelman, D. Liu, M. J. Webber, *Biomacromolecules* **2021**, *22*, 171.
[182] L. Cheng, Y. Jiang, S.-C. Qi, W. Liu, S.-F. Shan, P. Tan, X.-Q. Liu, L.-B. Sun, *Chem. Mater* **2018**, *30*, 3429.
[183] M. Irie, M. Kato, *J. Am. Chem. Soc.* **1985**, *107*, 1024.
[184] S. Shinkai, T. Nakaji, T. Ogawa, K. Shigematsu, O. Manabe, *J. Am. Chem. Soc.* **1981**, *103*, 111.
[185] R. Ou, H. Zhang, V. X. Truong, L. Zhang, H. M. Hegab, L. Han, J. Hou, X. Zhang, A. Deletic, L. Jiang, G. P. Simon, H. Wang, *Nat. Sustain.* **2020**, *3*, 1052.
[186] R. Chen, T. Sheehan, J. Lian Ng, M. Brucks, X. Su, *Environ. Sci.: Water Res. Technol.* **2020**, *6*, 258.
[187] P. Formoso, E. Pantuso, G. De Filpo, FP Nicoletta, *Membranes* **2017**, *7*, 39.
[188] K.-J. Tan, X. Su, T. A. Hatton, *Adv. Funct. Mater.* **2020**, *30*, 1910363.
[189] W. Duan, G. Chen, C. Chen, R. Sanghvi, A. Iddya, S. Walker, H. Liu, A. Ronen, D. Jassby, *J. Membr. Sci.* **2017**, *531*, 160.
[190] B. S. Lalia, F. E. Ahmed, T. Shah, N. Hilal, R. Hashaikeh, *Desalination* **2015**, *360*, 8.
[191] C. Liu, P.-C. Hsu, J. Xie, J. Zhao, T. Wu, H. Wang, W. Liu, J. Zhang, S. Chu, Y. Cui, *Nat. Energy* **2017**, *2*, 1.
[192] P. B. Medina, K. Kim, J. Elbert, X. Su, *ECS Meet. Abstr.* **2021**, *MA2021-02*, 1531.
[193] K. Kim, S. Cotty, J. Elbert, R. Chen, C.-H. Hou, X. Su, *Adv. Mater.* **2020**, *32*, 1906877.
[194] R. Chen, J. Feng, J. Jeon, T. Sheehan, C. Rüttiger, M. Gallei, D. Shukla, X. Su, *Adv. Funct. Mater.* **2021**, *31*, 2009307.
[195] H. Vapnik, J. Elbert, X. Su, *J. Mater. Chem. A* **2021**, *9*, 20068.
[196] M.-L. Liu, L. Li, Y.-X. Sun, Z.-J. Fu, X.-L. Cao, S.-P. Sun, *J. Membr. Sci.* **2021**, *617*, 118644.
[197] L. Fan, C. Luo, M. Sun, H. Qiu, X. Li, *Colloids Surf., B* **2013**, *103*, 601.
[198] E. Santala, M. Kemell, M. Leskelä, M. Ritala, *Nanotechnology* **2008**, *20*, 035602.
[199] S. Xu, J. Liang, M. I. B. Mohammad, D. Lv, Y. Cao, J. Qi, K. Liang, J. Ma, *Chem. Eng. J.* **2021**, *426*, 131861.
[200] F. Lassouane, H. Aït-Amar, S. Amrani, S. Rodriguez-Couto, *Bioresour. Technology.* **2019**, *271*, 360.
[201] F. M. Olajuyigbe, O. Y. Adetuyi, C. O. Fatokun, *Int. J. Biol. Macromol.* **2019**, *125*, 856.
[202] T. K. Sherwood, *Mass Transfer between Phases*, University Park, Pennsylvania **1959**.
[203] A. M. K. Nambiar, Y. Li, A. L. Zydney, *Biotechnol. Bioeng. 115*, 139.
[204] B. Napadensky, O. Shinkazh, A. Teella, A. L. Zydney, *Sep. Sci. Technol.* **2013**, *48*, 1289.
[205] E. A. Eugene, W. A. Phillip, A. W. Dowling, *ACS ES&T Eng.* **2021**, *1*, 1171.
[206] E. A. Eugene, W. A. Phillip, A. W. Dowling, *Curr. Opin. Chem. Eng.* **2019**, *26*, 122.

Jonathan Aubuchon Ouimet received his bachelor's degree in Chemical Engineering from Miami University in 2019. Following graduation, He then began his doctoral studies in the Department of Chemical and Biomolecular Engineering at the University of Notre Dame. Jonathan is a recipient of the NSF GRFP Honorable Mention. Broadly, he is interested in utilizing high-throughput characterization techniques to study the thermodynamic and transport phenomena that govern membrane-based separations. In particular, his doctoral research aims to mimic the facilitated transport mechanisms of biological ion pumps using polymer membranes that undergo distinct conformational changes.

Jialing Xu received her bachelor's degree in Chemical Engineering from Beijing University of Chemical Technology and completed her master's degree under the guidance of Dr. Christine Duval at Case Western Reserve University in 2019. She is now a Ph.D. candidate at the University of Notre Dame under the supervision of Dr. William Phillip. She is interested in the development of polymer membranes and sorbents for water treatment. In particular, her research focuses on the design and fabrication of structured sorbents with high capacity and permeability for the removal of emerging contaminants and recovery of resources.

© 2022 The Authors. Macromolecular Chemistry and Physics published by Wiley-VCH GmbH

Carsten Flores-Hansen received his bachelor's degree in Multidisciplinary Science from the University of Texas at San Antonio in 2019. He continued his education with the doctoral program in the Department of Chemistry at Purdue University under the mentorship of Professor Bryan Boudouris. His research interests include the application of polymeric materials for water purification, high-fidelity gas sensing, and the development of conducting macromolecules for defense applications. Upon graduation, he intends to use his scientific background within the context of industrial consulting and entrepreneurial projects.



William Phillip is the Rooney Family Collegiate Professor of Engineering in the Department of Chemical and Biomolecular Engineering at the University of Notre Dame. He received his Ph.D. from the University of Minnesota in 2009 and his B.S. from the University of Notre Dame in 2004. His group seeks to develop polymer membranes and sorbents that provide more precise control over mass transfer to enable energy-efficient separation processes at the water-energy nexus. Dr. Phillip and his team have been recognized with the FRI/John G. Kunesh Award from the American Institute of Chemical Engineers and the College of Engineering Outstanding Teaching Award.

Bryan W. Boudouris is a professor in the Charles D. Davidson School of Chemical Engineering and a professor (by courtesy) in the Department of Chemistry at Purdue University. He received his B.S. in Chemical Engineering from the University of Illinois at Urbana-Champaign in 2004. After receiving his Ph.D. in Chemical Engineering from the University of Minnesota in 2009, he conducted postdoctoral research from 2009 to 2011 at the University of California, Berkeley. His group's current research interests include the design, nanostructural characterization, and implementation of soft materials in multiple end-use applications that include electronic materials and polymers for water purification.

© 2022 The Authors. Macromolecular Chemistry and Physics published by Wiley-VCH GmbH