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MEMBRANE TECHNOLOGY

Engineering, design, and optimization of membrane processes for industry and research.

Adsorption

1 Adsorption

In membrane technology, adsorption describes the attachment of ions, molecules, or particles to the membrane surface.

This process can occur on both the outer and inner surface of the membrane. Adsorption leads to specific effects at the membrane surface that can influence the transport properties of the membrane.

Adsorption-related effects can either increase or decrease flux and can affect the retention of specific substances.

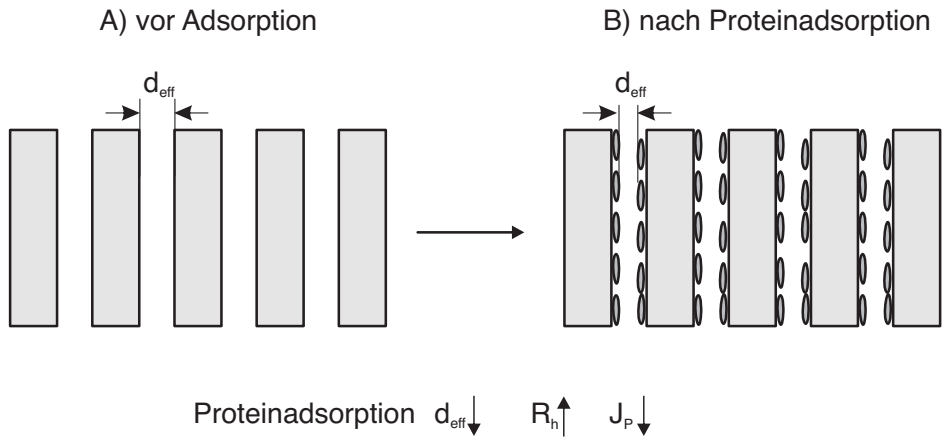

Figure 1. When applied correctly, membrane technology puts this principle into practice: what is waste for one process can become a raw material for another.

1.1 Ultrafiltration with Polymeric Membranes

Polymeric ultrafiltration membranes are semipermeable membranes made of polymeric materials that retain molecules and particles above a certain size, while allowing water and low-molecular-weight substances to pass through.

The surface properties of the materials used strongly influence adsorption processes.

Hydrophobic materials such as polysulfone (PSU), polyethersulfone (PES), and polyvinylidene fluoride (PVDF) show increased adsorption of organic substances, whereas hydrophilic cellulose acetate membranes tend to have lower adsorption affinity.

The surface charge of polymeric ultrafiltration membranes is usually pH-dependent. This is caused by protolytically active functionalities on the membrane surface. These include acidic groups (e.g., carboxyl or sulfonic groups), which deprotonate as pH increases and thereby generate negative surface charges, as well as basic groups (e.g., amine functionalities), which are protonated at low pH and create positive charges. The pH therefore determines the equilibrium between protonated and deprotonated surface sites and thus the resulting net charge.

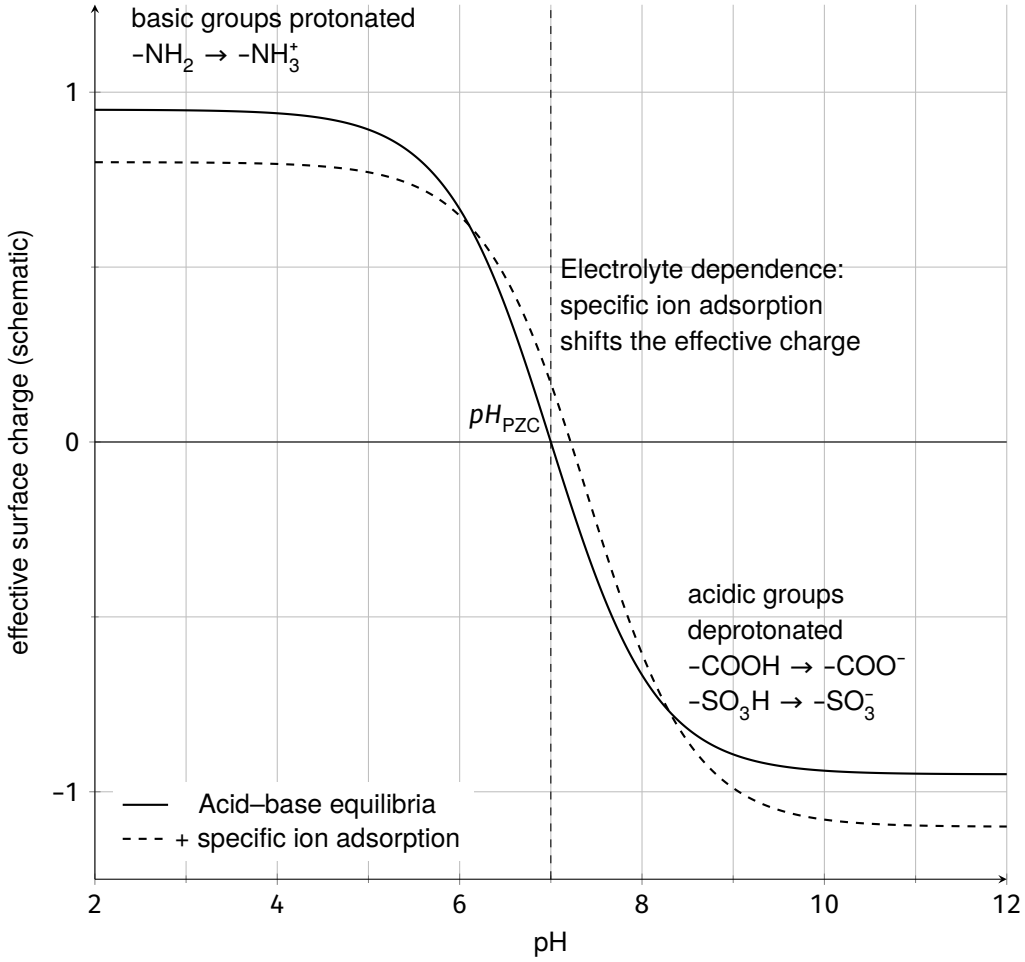

Figure 2. Schematic illustration of the pH dependence of membrane surface charge due to protonation/deprotonation of functional groups, as well as the possible shift caused by specific ion adsorption from the aqueous phase.

The pH of a solution indicates how many protons (H^+) are present in the solution. At low pH, the proton concentration is high and the solution is acidic. Under these conditions, particles or functional groups tend to become protonated, meaning they take up a proton. At high pH, the proton concentration is low and the solution is basic. In this case, particles or functional groups are more likely to release a proton, which is referred to as deprotonation. Protonation and deprotonation are therefore directly linked to the pH of the solution and determine the electrical charge of many dissolved substances and surfaces.

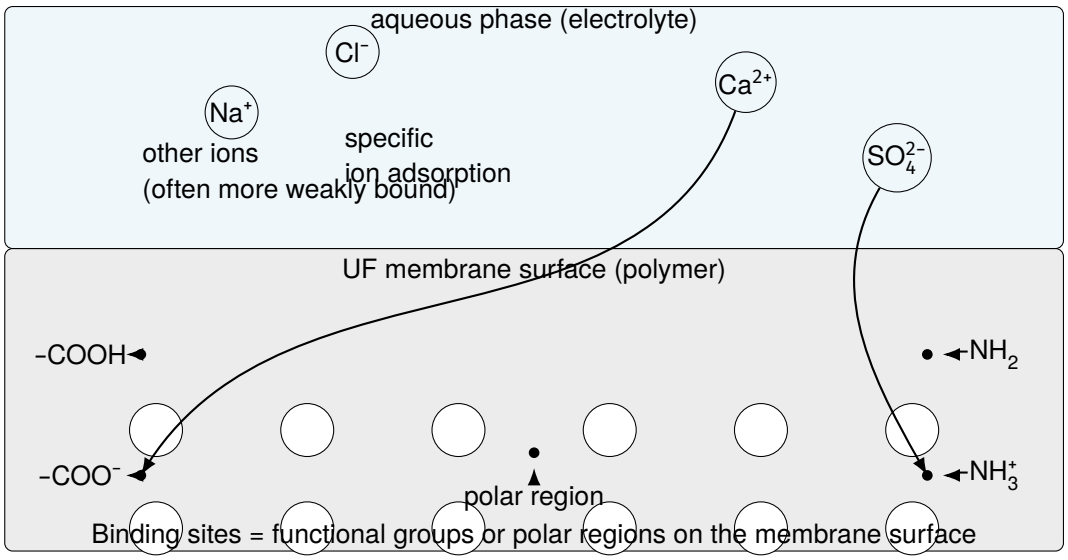

Figure 3. Schematic illustration of binding sites on a polymeric UF membrane and the specific adsorption of selected ions from the aqueous phase.

Binding sites on polymeric ultrafiltration membranes refer to specific regions on the membrane surface where particles from the water can attach or interact with the surface. These are mainly functional groups of the polymer material, for example carboxyl, sulfonic, or amino groups, as well as polar regions of the surface. These binding sites can attract charged or uncharged particles such as ions, molecules, or proteins. Depending on the type of binding site, the pH, and the substances dissolved in the water, adsorption, protonation, or specific ion binding can occur there. As a result, binding sites influence the surface charge, mass transport, and fouling behavior of the membrane.

The isoelectric point of a polymeric ultrafiltration membrane is defined as the pH at which the net charge of the membrane surface is zero. At this point, positive and negative surface charges balance each other, so that the electrokinetic potential of the membrane disappears. The isoelectric point can be determined experimentally as the pH at which the measured zeta potential or streaming potential reaches zero.

At the isoelectric point, electrostatic interactions between the membrane surface and charged dissolved substances are minimized. This can lead to increased adsorption of amphoteric substances, especially proteins, as well as an increased fouling risk. At the same time, charge-based retention of charged species is reduced in this pH range.

In contrast to the isoelectric point of individual molecules, the isoelectric point of a membrane is not a fixed material constant. It can shift due to chemical pretreatment, aging, adsorption of process chemicals, as well as the use of chemical cleaning agents.

The isoelectric point should therefore be understood as a state-dependent property of the membrane surface and represents an important parameter for the design and operation of ultrafiltration processes.

1.2 Influence of the Membrane Surface on Adsorption

The tendency to form an adsorbed layer on the membrane surface depends to a large extent on the physicochemical properties of the membrane.

Adsorption effects can occur very rapidly. The characteristic time for protein adsorption on solid surfaces is often only a few seconds.

Surface energy, chemical composition, and the micro- and nanostructure of the membrane surface play a decisive role. Hydrophobic membrane surfaces typically show stronger adsorption of organic substances than hydrophilic surfaces. This is because hydrophobic interactions favor the displacement of water molecules at the interface and thereby facilitate the attachment of organic molecules.

In particular, nonpolar or weakly polar components such as proteins, lipids, or other organic macromolecules show a high affinity for hydrophobic surfaces. Hydrophilic membranes, in contrast, are often covered by a stable hydration layer that acts as an energetic barrier to adsorption. This hydration layer reduces direct interaction between the membrane surface and dissolved substances and can therefore significantly reduce fouling tendency.

In addition to hydrophilicity, membrane surface charge also strongly influences adsorption behavior. Charged membrane surfaces can interact electrostatically with ionic or polar functional groups of dissolved molecules. Depending on the pH and ionic strength of the solution, either attractive or repulsive forces may occur. Opposite charges on membrane and solute promote adsorption, whereas like charges can inhibit adsorptive attachment.

In addition, local charge inhomogeneities and functional groups on the membrane surface can lead to specific binding mechanisms. The interplay of hydrophobic effects, electrostatic forces, and other physical interactions ultimately determines the strength and stability of the adsorbed layer.

1.3 Surface Charge and Isoelectric Point

In aqueous solutions, membranes and macrosolutes essentially acquire a net surface charge through the adsorption of specific positive or negative ions from the solution and/or through the ionization of certain chemical groups at their surface.

At neutral pH, most membranes (as well as many macromolecules) carry a negative net charge due to the preferential adsorption of negative ions. In alkaline solutions, the strength of this negative charge increases, which can be attributed to enhanced anion adsorption, increased ionization of acidic groups (e.g., $-COOH \rightarrow -COO^-$) and/or the deionization (deprotonation) of basic groups (e.g., $-NH_3^+ \rightarrow -NH_2$). In acidic solutions, the opposite effects occur accordingly.

When the pH of the solution is lowered, most amphoteric species pass through a state in which they no longer carry any net charge. The pH at which this occurs is called the *isoelectric point* or *pI*.

> Amphoteric substances play a special role in this context because they contain both acidic and basic functional groups and change their charge state depending on the pH of the solution. Adsorption of amphoteric substances can change the surface charge and hydrophilicity of the membrane and thereby influence both the effective pore diameter and the separation and fouling behavior.

2 Protein Adsorption in Ultra- and Microfiltration

During ultra- and microfiltration of protein-rich solutions, adsorption of proteins at the membrane is particularly common and pronounced. This effect is due to the complex molecular structure of proteins and their many possible interactions with the membrane surface. Proteins can accumulate both on the outer membrane surface and within the pores and membrane matrix. In particular, intrapore adsorption is critical because it can lead to irreversible pore blockage.

Many materials used in membrane technology, such as polyethersulfone, polysulfone, or polyvinylidene fluoride, have hydrophobic or charged surfaces. These surface properties promote interaction with proteins, which contain both hydrophobic amino acid residues and charged functional groups. Adsorption occurs through various physical and physicochemical mechanisms.

The dominant interactions include van der Waals forces, which cause short-range attraction between protein molecules and the membrane surface. In addition, hydrogen bonds can form between polar groups of the proteins and functional groups of the membrane. Another major contribution to protein adsorption arises from electrostatic interactions. These depend strongly on the pH of the solution, the isoelectric point of the proteins, and the surface charge of the membrane.

If the protein and membrane carry opposite charges, adsorption is enhanced by electrostatic attraction.

Protein adsorption leads to the formation of a fouling layer on the membrane.

If the charges are the same, adsorption may be partially inhibited, although local charge inhomogeneities can still result in attachment. Furthermore, conformational changes in the proteins may occur during adsorption, further stabilizing their binding to the membrane.

Protein adsorption inside the membrane matrix leads to a reduction in the effective pore diameter, an increase in hydraulic resistance, and thus a reduction in permeate flux.

At more advanced stages, the adsorbed protein layer can serve as a starting point for additional deposits and further intensify fouling.

2.1 Adsorption of Amphoteric Substances on Polymeric UF Membranes

Amphoteric substances contain both acidic and basic functional groups and can therefore exist in positively charged, negatively charged, or uncharged form depending on the pH of the solution. Typical examples include proteins, peptides, and certain polymers that commonly occur in aqueous membrane systems.

Adsorption of amphoteric substances on polymeric ultrafiltration (UF) membranes occurs through a combination of different interactions, including electrostatic attraction or repulsion, hydrophobic interactions, hydrogen bonding, and van der Waals forces. The type and strength of these interactions depend both on the surface properties of the membrane and on the charge state of the amphoteric substances, which in turn is determined by the pH and ionic strength of the solution.

Near the isoelectric point of amphoteric substances, electrostatic repulsion is reduced, which promotes adsorption at the membrane surface. If amphoteric molecules adsorb on the membrane surface or within the pores, they can significantly alter the membrane surface properties. This affects the surface charge, hydrophilicity, and effective pore size.

These adsorption-induced changes affect the separation performance of the membrane and can lead to increased retention of dissolved substances as well as a decrease in permeate flux. Especially in polymeric UF membranes, amphoteric substances therefore represent a major factor in adsorption and fouling processes.

The surface properties of polymeric membranes can be influenced through the targeted use of amphoteric substances. Amphoteric molecules contain both acidic and basic functional groups and can therefore assume different charge states depending on the pH of the surrounding solution. This property enables controlled modification of the membrane surface, especially with respect to surface charge, hydrophilicity, and interaction behavior toward dissolved substances.

One possible method of modification is the physical adsorption of amphoteric substances on the membrane surface or inside the pores. This adsorption occurs via electrostatic, hydrophobic, and hydrogen-bond-based interactions. Near the isoelectric point of amphoteric substances, electrostatic repulsion is minimized, which favors stronger adsorption. The resulting adsorption layers can significantly alter the effective surface charge and wettability of the membrane, but they are usually reversible and sensitive to changes in pH, ionic strength, and hydrodynamic conditions.

In addition, amphoteric substances can be permanently incorporated into the membrane surface by chemical fixation or coating. Such functionalized membranes often exhibit a pH-dependent charge

reversal and improved antifouling properties. Targeted adjustment of the surface chemistry allows the separation behavior to be tailored, but if poorly controlled it can also lead to a reduction in permeate flux due to pore blockage.

3 Chemical Cleaning Agents

Chemical cleaning agents are used in membrane technology to remove fouling and adsorbed deposits. In addition to the desired cleaning effect, however, these chemicals can also cause unintended changes to the membrane surface. With polymeric membranes, there is a risk that chemical cleaning not only removes reversible adsorption layers but also affects the surface properties of the membrane.

Depending on the type, concentration, and contact time of the cleaning agents used, functional groups on the membrane surface may be protonated, deprotonated, or chemically altered.

Strongly acidic or alkaline conditions can lead to a shift in the surface charge and the isoelectric point of the membrane.

In addition, oxidizing cleaning agents are capable of degrading polymeric membrane material and thereby permanently changing hydrophilicity, mechanical stability, and effective pore size.

Another critical aspect is the interaction between cleaning chemicals and previously adsorbed or intentionally fixed amphoteric substances. Chemical cleaning can partially or completely remove such layers, change the charge state of amphoteric groups, or damage their structure. As a result, previously adjusted membrane surface functionality may be lost or only be reproducible to a limited extent.

Consequently, the separation behavior of the membrane may change significantly after repeated cleaning cycles, even if the permeate flux appears to have been restored. For a reliable assessment of adsorption and surface modification effects, it is therefore necessary to systematically account for and control the influence of chemical cleaning agents.

Cleaning agent	Influence on the membrane surface
Acidic solutions	Typical conditions: pH < 4 Effects: protonation of functional groups, shift of surface charge and isoelectric point, partial desorption of amphoteric substances Reversibility: usually reversible under moderate conditions
Alkaline solutions	Typical conditions: pH > 10 Effects: deprotonation of acidic and basic groups, increased negative surface charge, possible hydrolysis of polymer chains and change in hydrophilicity Reversibility: partly irreversible after prolonged exposure
Oxidizing agents	Typical conditions: low to moderate concentrations Effects: oxidative damage to the polymer structure, irreversible change in surface chemistry, possible pore modification Reversibility: predominantly irreversible
Surfactant-containing cleaners	Typical conditions: variable pH Effects: removal of hydrophobic deposits, possible adsorption of surfactants, change in wettability Reversibility: usually reversible after thorough rinsing
Enzymatic cleaners	Typical conditions: mild pH and temperature conditions Effects: selective removal of biological fouling layers with minimal impact on membrane structure Reversibility: largely reversible

Table 1. Influence of chemical cleaning agents on the surface properties of polymeric membranes

3.1 Water Flux after Cleaning

The water flux of a membrane is often used as an indicator to assess cleaning success. However, an increased water flux after chemical cleaning is not necessarily an indicator of a fully cleaned membrane. In addition to fouling removal, water flux is strongly influenced by the surface properties of the membrane, especially its hydrophilicity.

Chemical cleaning agents can increase the hydrophilicity of the membrane surface by activating or generating polar functional groups or by chemically modifying hydrophobic deposits. Improved wetting of the membrane pores reduces the hydraulic entry resistance for water and can therefore lead to increased water flux, even if fouling-related deposits are still present.

In many cases, fouling is not completely removed by chemical cleaning but instead altered in its chemical structure. For example, proteins may denature and adopt a flatter conformation, or polymer-like deposits may exhibit reduced hydraulic resistance as a result of swelling. These effects lead to a reduction in flow resistance without significantly reducing the fouling mass.

For a reliable assessment of cleaning performance, it is therefore necessary to supplement water flux measurements with additional characterization methods. These include, for example, determining the retention of characteristic solutes, analyzing surface hydrophilicity, or comparing with the original pure water permeability of the membrane.

4 Affinity Membranes

Adsorption of dissolved substances on membrane surfaces is a frequently observed effect in membrane-based separation processes. In conventional ultrafiltration membranes, adsorption often occurs nonspecifically and leads to undesirable effects such as fouling, flux decline, or changes in solute retention. These interactions are caused by the chemical and physical properties of the membrane surface, in particular surface charge, hydrophilicity, and the presence of specific functional groups.

At the same time, these effects show that membrane surfaces are fundamentally capable of selectively binding dissolved substances. This insight forms the basis for the concept of affinity membranes. In contrast to conventional membranes, affinity membranes contain deliberately defined binding sites integrated into the membrane or immobilized on its surface. In this way, adsorption is transformed from a nonspecific, often undesirable side effect into a controlled and selective separation mechanism. Affinity membranes therefore make targeted use of adsorptive interactions to selectively retain or enrich specific target substances.

Affinity ultrafiltration represents an extension of classical ultrafiltration in which, in addition to size exclusion effects, specific interactions between the membrane and dissolved substances are utilized.

Whereas in conventional ultrafiltration processes separation is determined primarily by the pore size of the membrane, affinity ultrafiltration additionally relies on specific binding mechanisms. These bindings arise from defined docking sites (in English, *binding sites*) on or within the membrane matrix.

Such docking sites may consist of functional groups, immobilized ligands, or biochemically active molecules. The goal is to selectively retain or enrich specific substances. The separation performance of affinity ultrafiltration therefore does not depend exclusively on the physical properties of the membrane. Instead, chemical and biochemical interactions play a central role. Selective binding makes it possible to achieve greater selectivity between structurally similar substances. This process offers decisive advantages, especially in complex liquids.

Affinity ultrafiltration is therefore used in biotechnology and process engineering. Typical applications include the purification of proteins, enzymes, and biomolecules. The process is also becoming increasingly important in pharmaceutical and medical research.

Binding between the target substance and the membrane is generally designed to be reversible. This allows the bound substance to be selectively released again, for example by changing pH or ionic strength. The process therefore enables not only separation but also controlled recovery of the target substance. At the same time, targeted surface functionalization places high demands on membrane manufacturing. Stability and reproducibility of the binding sites are of great importance. In addition, nonspecific adsorption effects must be minimized.

Overall, affinity ultrafiltration combines membrane-based separation with molecular selectivity.

Commercial manufacturers and suppliers:

- Sartorius Sartorius offers a broad portfolio of membrane-based separation and purification solutions, including functionalized chromatography membranes (e.g., Sartobind®) for protein and biomolecule purification, as well as membrane adsorbers and UF modules for biotechnological applications.

- Merck Millipore Merck Millipore (part of the Merck Group) is a leading supplier of filtration and purification technologies and provides membranes and membrane adsorbers for bioprocessing, affinity- and chromatography-based separations, as well as tools for protein purification.
- Pall Corporation Pall Corporation is an international manufacturer of filtration, separation, and purification products. Its life sciences portfolio includes membrane adsorbers, chromatography membranes, and filtration solutions for biopharmaceutical and analytical applications.
- Cytiva Cytiva (formerly GE Healthcare Life Sciences) offers membrane-based chromatography and purification solutions, including membrane adsorbers and membranes for protein and biomolecule purification, as well as a wide range of downstream technologies for biotechnological processes.

Manufacturer	Example product	Link
Sartorius	Sartobind® Rapid A (Protein A affinity membrane adsorber for the selective purification of monoclonal antibodies)	https://www.sartorius.com
Merck Millipore	Natrix® Q (chromatography membrane with strong anion-exchange groups for biotechnological applications)	https://www.merckmillipore.com
Pall Corporation	Mustang™ Chromatography Membrane Capsules (membrane adsorbers for ion-exchange and polishing steps)	https://www.pall.com
Cytiva	Mustang Q XT5 Chromatography Membrane (chromatography membrane with quaternary ammonium groups for biomolecule purification)	https://www.cytivalifesciences.com

Table 2. Examples of commercial membrane products with affinity or chromatographic properties.