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NOVEL SEPARATION PROCESSES AND THEIR APPLICATIONS

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Abstract

Separation processes are an integral part of any process flow sheet. Various techniques can beused to separate the mixture depending on the raw mix. Sometimes, two or more methods must be used to get the desired product. Differences in chemical and physical properties also help decide the separation technique that must be used. An external agent, any form of energyor matter, can act as the driving force for the separation. Some of these techniques are conventional processes like distillation, filtration, adsorption, and absorption, which have already been well-studied and extensively used. These days newer separation processes called novel separation processes, such as membrane separation, gas separation, supercritical fluid extraction, use of ultrasonics, chromatographic separation, magnetic projection, and liquid- liquid extraction, among many others, are gaining importance in the area of research and implementation. Novel processes were first implemented as analytical tools in laboratories.

However, they developed rapidly to become significant commercially and technically. The development in gas separation techniques has led to using Liquified Natural Gas in Air Separation Units to produce high-purity nitrogen and oxygen[4]. Novel separation methods also include ultrasound to enhance separation processes like extraction, demulsification, and crystallisation. Pressure-driven processes are a subset of membrane separation techniques where pressure is utilised as a driving force for separation, with a semipermeable membrane acting as a barrier. This method has various applications ranging from wastewater treatment to dairy processing. Chiral chromatography is used for enantiomeric separations by the use ofHPLC. A new magnetic separation process proposes the separation of plastics by submergingthem in a paramagnetic medium and attaching a magnet. This results in moving the particles inside the medium with different trajectories, thereby separating them.

This article will scrutinise and briefly describe the essential aspects and developments of novel separation processes and their applications.

Keywords - Novel, separation, driving force, commercial, applications

1. Introduction to Separation Processes

Separation processes are used to isolate substances from a mixture into various products. The specific design of the operations may depend on the separated chemicals and their physical and chemical properties. Still, the rudiments of designing for a given separation process remain the same.

Figure 1-1. Typical chemical plant layout

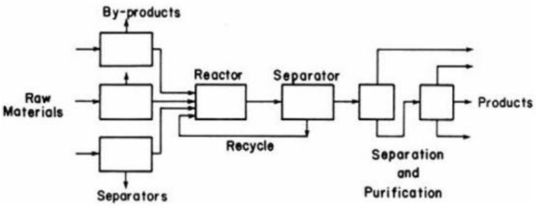


Figure 1.1 shows the layout of a typical chemical plant consisting of a reactor surrounded byseparators.[32]
Chemical plants invest 50-90 percent of their capital in separation equipment.

In Chemical process industries (CPI), separation processes play a critical role as they are used essentially for removing contaminants from the feed along with effluent water and air streams, recovery and purification of primary products. A separator can also recycle the excess reagent, which can help effectively utilise reactants.

The second law of Thermodynamics states that entropy always increases. Substances mix spontaneously, and these spontaneous processes tend to increase the universe's entropy. Hence, to separate the mixture into components, we must supply equivalent energy in heat or work. This is the driving force for the separation process to take place.

The separation rate can be governed by mass transfer, and thermodynamics limits the extent of separation.

Molecular properties such as molecular weight, molecular shape (acentric factor), dipole moment, polarizability, dielectric constant, and electric charge, along with thermodynamic and transport properties such as vapour pressure, solubility, absorptivity, diffusivity, are some of the properties that help decide the separation process that needs to be used.[11]

1.1 General separation techniques

a. By phase creation: Requires production of a phase by either adding or removing work, heat or any other required factor. Examples: Distillation, Evaporation

b. By barrier: Separation, which depends on the penetration of molecules through asemi-permeable membrane.Examples: Membrane filtration, Ultrafiltration

c. By Solid agent: Uses solid-mass separating agents. The solid is in the form of a granular material or packing material such as activated carbon, silica gel, and zeolites.

   Examples: Chromatography, Ion Exchange, Adsorption

d. By force field or gradient: Examples- Centrifugation, Thermal diffusion, Electrophoresis, Electrodialysis

2. Novel separation processes

Conventional separation processes such as distillation, filtration, and absorption havebecome quite common and have been well-studied and extensively used. Newer separation processes have become quite popular in research and are gaining importance in today's modern plants. Newer separation processes are gaining importance for several reasons, reflecting advancements in technology, sustainability concerns, and the evolving needs of various industries.

Separation processes can be classified as follows:

a. Equilibrium Separation- When two immiscible phases come in contact with each other, the two phases will get separated when equilibrium is reached. Heat transfer and mass transfer operations on a large scale follow the mechanism of equilibriumseparation.

b. Rate governed Separation- Separation, which involves the transfer of species through a medium, is under the influence of a driving force mainly due to concentration, pressure or electric field gradient.[10]

Some equilibrium and rate-defined separations are defined as novel separation processes. Membrane-based separation processes, Chromatographic separation processes, Ion exchange processes, and Gas separation are a few examples among many.

2.1 Significance of Novel Separation processes

Separation and purification processes conventionally follow multistep, batch-type systems where a sample undergoes distillation in batches meaning a mixture is distilled into its components repeatedly. In Large scale processes, separation and purification techniques are costly and usually follow batch-type mechanisms. The medium of separation to be used, the cost of energy-intensive separation columns, volumes of solvent needed for refurbishing the columns make the overall process quite expensive.[16]

These separation processes also require much energy, making them energy inefficient. As we venture into preserving our environment and focusing on sustainability and other green principles, energy conservation nowadays has become crucial. For decades, separation processes such as distillation have been preferably used in CPIs. Using energy-efficient separation processes will make the gain and contribution to sustainability significant. Novel separation processes are likely to use distributed, digitalised energy systems, giving them an advantage over conventional methods as when integrated with digital energy systems, they can be optimized for energy efficiency. Advanced control systems and real-time monitoring enable better management of energy consumption, leading to overall lower energy costs compared to conventional methods. CPIs also need better separation methods to remove VOCs and other non-volatile components from effluent streams. Environmental issues contribute to deciding the process design. Waste production, water use, effluent streams, and raw materials substantially impact the designing of better separation processes and generate a new set of constraints.[14]

In conclusion, Novel Separation processes follow a continuous mode mechanism and are target specific, which differentiates them from conventional methods as they contribute significantly to reduced costs and overall purification time by reducing the number of purification steps, input costs and high purity at capture.

Membrane processes today are one of the premier technologies used for industrial separations and play an essential role in shifting from conventional techniques to better sustainable systems in the future.

2.2 Membrane separation processes

In membrane separation processes, the membrane acts as a selective barrier, separating the components of a mixture by allowing the passage of one component, rejecting unwanted substances, and retaining other components under a pressure or a concentration gradient depending on the type of membrane separation. The role of the membrane is to act as a barrier between two phases and not to control the rate at which the components move across the membrane—for example, the membrane's usage to deoxygenate water.[5]

Based on pore size and utilisation of pressure as a driving force, membrane processes can be classified as-Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF), and Reverse Osmosis (RO).

a. Microfiltration: Functions while separating solids in the range 0.1-10µm and because MF membranes have a larger pore size, processes can run at lower pressures. Applications include the removal of bacteria from cellular broth and the removal of fat in the dairy industry.[46]

b. Nanofiltration: In Nanofiltration, both size and charge play an essential role. NF membranes have a pore size of 0.1-10nm and can retain low molecular weight uncharged organic molecules. These membranes can also control charged species, but smaller monovalent ions can escape. Applications include the removal of organic matter from wastewater, reducing the hardness of water and demineralisation.[7]

c. Ultrafiltration: Lies between Microfiltration and Nanofiltration, and the membranes have a pore size range from 1-100nm. They can retain high molecular weight particles such as macromolecules and are analysed based on their retention power rather than the size of the pores. Applications include recovery of the undeposited element in the electrocoating process and the food and beverage industries.[9]

d. Reverse Osmosis: Capable of retaining all the particles, even the monovalent ions. Its mechanism uses filtration based on pore size along with diffusion. Due to tiny pore size and to overcome osmotic pressure, RO processes need high pressure. Applications include the purification of water and beverage concentration.[2]

Membrane separations include not only the separation of liquid phase components but the separation of gaseous mixtures and solid concentrates from solutions.

Gas separation processes are critical in oil and gas-related industries. Distillation is the most common process for separating gases, but it could be more energy efficient. Ionic liquids have good stability and are non-volatile, which can be considered an alternative medium for the absorption of gases. Hence, distillation, along with I-L-based gas absorption, can be used for the energy-efficient separation of gases. This is known as a hybrid gas separation process and is used to intensify operations. [5] Gas separation membranes (see fig 2.1) work on selective permeation, with the difference in partial pressures being the driving force. As the difference increases, more gas molecules which are small and highly soluble can pass through the membrane. Most gas separation techniques are used to separate non-condensable gases such as carbon dioxide from methane, nitrogen from the air, and hydrogen. However, with new gas separation can be used to separate mixtures containing condensable gases, which has higher market potential.

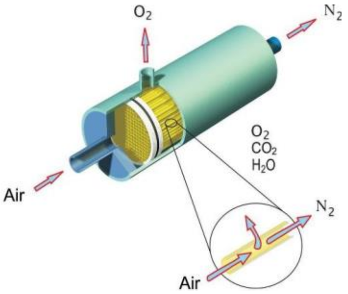


Figure 2.1 depicts a gas separation membrane.[34]

Membrane distillation: Membrane distillation has a temperature gradient inducing partial pressure difference as the driving force wherein the vapours from a hot aqueous solution selectively permeate through a hydrophobic membrane from the high to the low-temperature side (see fig 2.2). The separation efficiency depends on the volatile nature of the separating agent and the construction of the porous membrane. The most crucial applications of Membrane Distillation involve the desalination of seawater and industrial wastewater treatment. The most undesirable problem in MD is where the liquid bulk temperature decreases after the vaporisation of a component, and the vapour temperature increases. This leads to a reduction in the temperature gradient and, thus, permeate selectivity. The concentration of contaminations on membrane surfaces, however less in MD than in other pressure-driven membrane processes, can reduce the separation's efficiency. MD can prove to be highly beneficial if these disadvantages can be overcome. When combined with other membrane technologies such as RO, nanofiltration and even standard distillation, MD can offer high-quality products and be energy efficient[7]

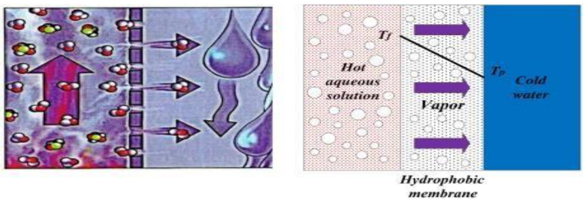


Figure 2.2 depicts the mechanism of Membrane Distillation.[1]

Membrane separation processes operate without the use of heat and therefore are less energy extensive as compared to conventional methods. They can even perform separation that would be impossible to take place by choosing a traditional approach, such as separating the constituents of azeotropic liquids and producing advanced thin-layer materials at a larger scale.

The critical challenge of Membrane Separation includes the need for a highly permeable membrane with high selectivity. Large-scale production of membranes needs to be done with zero faults. The membrane process needs to be set up at the most appropriate location of the process flow with effective pre-treatment units to ensure a long lifespan of the membranes[3] Hence, a combination of high selectivity and performance membranes, process engineering and technology and appropriate conditions and structured flow of the process can lead to the development of membrane processes.

2.3 Chromatographic and Ion exchange separation process:

The Chromatographic or Ion exchange chromatographic process is a sanctification techniquepredicated on the electrostatic commerce of charged shells. It separates ions and polar motes grounded on their charges to the ion exchanger. It applies to any charged patch, including large proteins, small nucleotides, and amino acids[17] . The ion exchange chromatography extraction principle is the reversible commerce of charged species with the ion exchange matrix.

Ion exchange chromatography can be distinguished into two types on the base of chargedions:

1. Cationic exchange chromatography:

The Cationic exchanger retains a positively charged ions and have negatively charged functional groups. It separates cations analogous to protonated essential proteins with different amino groups on their face.

2. Anionic exchange chromatography:

The anionic exchangers have positively charged functional groups that will attract negatively charged anions. It is used to separate anions with different carboxylic acid groups on their face, similar to deprotonated or acidic protein molecules[18]. The setup consists of a channel placed on top of a narrow column. The column is packed with charged gel droplets. The droplets can be positively or negatively charged depending on the proteins that are supposed to separate.

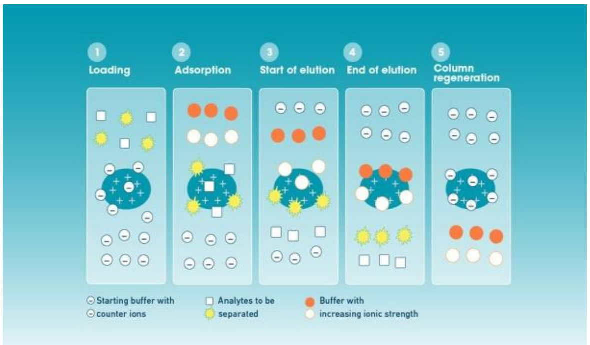


Figure 2.3 Schematic of separation of analytes by increasing the ionic strength of elution buffer. [19]

Droplets are made of some sugar polymers similar to cellulose. As the proteins descend the column, those proteins with the topmost net positive charge will move slowest down thecolumn because they will be attracted to the negative mote[19].

The primary ion exchange trials involve conducting equilibrium, sample handling and rinsing, elution, and rejuvenation (refer to fig. 2.3). The initial phase entails standardizing the stationary phase to the required starting condition. Once equilibrium is attained, all charged groups on the stationary phase become associated with interchangeable counter ions such as chloride or sodium. The subsequent phase is sample handling and wetland; its purpose is to bind the target particles and eliminate any free material. To ensure the proper desorption of proteins, the sample buffer should match the pH and ionic strength of the initial buffer, securing all the appropriately charged protons. In the third phase, biomolecules are liberated from the ion exchanger by altering the buffer composition. A common approach involves elevating the ionic strength using sodium chloride or another uncomplicated solution to desorb the attached proteins. The proteins are desorbed based on the number of charged groups on their surface. The concluding phase eliminates all still-bound particles, ensuring that the total capacity of the stationary phase is ready for the next run.

2.4. Principles of supercritical separation processes:

Supercritical fluid extraction is an advanced method in solvent extraction, is employed for sample preparation, analyte purification and concentration. Supercritical fluid is used to extract the desired compounds from the mixture. Supercritical fluids have unique density, diffusivity, viscosity, solubility, and polarity between liquid and gas. *Supercritical fluid separation* is a technique that uses these unique properties of supercritical fluid for extraction. [23] (see fig.2.4).

The CO2 is stored and passes into cold exchangers to maintain its liquid state before entering the high-pressure pump. The pressure and temperature are raised to 300 bars and 33°C, respectively.

At this condition, CO2 becomes supercritical. CO2 supercritical is used as a solvent to extract active plant ingredients without denaturing them. Lowering the pressure and, thus, the return of the CO_2 to the gas state allows the separation of the extract of CO_2.

Moreover, the temp is maintained at an atmospheric condition.

CO_2 is extracted with the help of gravity in the first separation stage. Later the sample is placed in a stainless-steel vessel in a heated oven. It is pressurized with CO_2, the extract is transferred to a fraction chamber, it is depressurized to precipitate the material. Recycle CO_2 gas and extract the precipitate with a small amount of solvent.

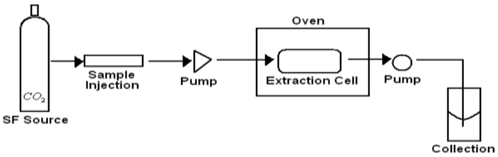


Figure 2.4 Scheme of Idealized Supercritical fluid extraction[46]

2.5 Ultrasonic-assisted separation:

Ultrasound-assisted extraction is an effective and swift technique used to extract various mixture ingredients by enacting them through ultrasound. It is preferred to isolate the bioactive compounds from botanicals. It provides high extraction and better qualitative yield. Ultrasound separation works on the principle of ultrasonic cavitation.[21](see fig.2.5).

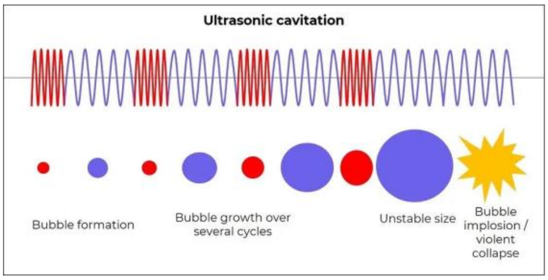


Figure 2.5. Ultrasonic Cavitation[28]

The simultaneous compression and rarefaction of ultrasonic waves can eliminate unwanted gases in the mixture as they cause an implosion of a micro-bubble present in the solvent. A sample is placed in an open vessel (see fig.2.6), and an extraction sample is added. As soon as the ultrasound probe or sonotrode is placed in contact with the sample, ultrasound cavities start propagating, resulting in the extraction of constituents that are ready for further cleanupprocesses.

It improves the overall efficiency of extraction. The main benefit of this process is that it requires less energy and does not promote CO2 emission, making it a green and sustainable alternative to conventional techniques.

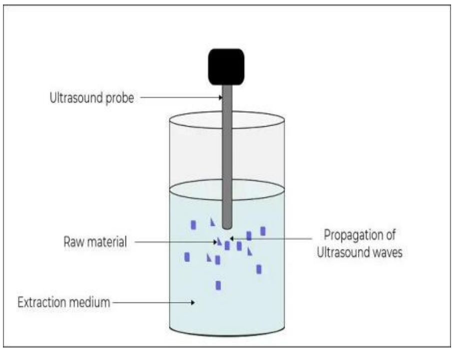


Figure 2.6. Working of ultrasound-assisted extraction [22]

2.6 Liquid-Liquid extraction:

Liquid-Liquid Extraction is associated with mass transfer that separates components of a liquid mixture by contacting them with another liquid. This technique isolates the desired compound from the mixture by driving it from one solvent to another.[31] In this technique, a solvent has added to the solution that dissolves and isolates one compound from the mixture. The solvent used is immiscible with the first solvent, so separate layers will form, making it relatively easy to separate them.

To do this, we need a separatory funnel, a tool to separate two immiscible liquids of different consistency. Two liquids will be an organic solvent with any compound dissolved in it and then water with any compounds dissolved in it. It is generally the case that the aqueous subcaste has a greater density than the organic subcaste, so it goes to the bottom; in discrepancy, the organic subcaste stays on top. The separatory funnel is a distinctive apparatus used in Extraction, it has a stopper at the top and a stopcock at the bottom, and in the middle region, separation takes place. This process also operates at low temperatures, making it suitable for separating heat-sensitive products. A ring stand is attached to support, and a separatory funnel is placed in the ring, ensuring everything is secure. To verify that the stopcock works, add some water and ensure there are no leakages when the stopcock is closed. Open the valve to see how the water flows, and the water is removed once satisfied. Now, this setup is ready for the extraction process. The post-reaction mixture is quenched with water and added to the separatory funnel (see fig.2.7). Two phases are mixed and are allowed to separate. The lower phase is drained into a clean container, leaving the top phase in the funnel. The rectification process follows extraction to obtain the purest possible transition component.[32]

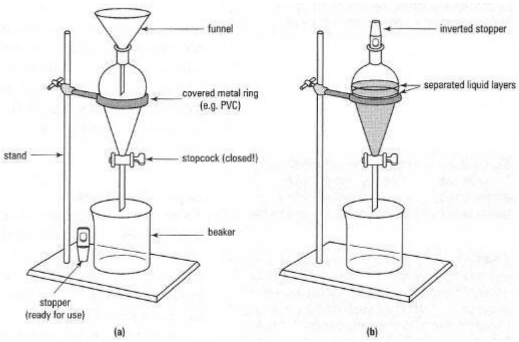


Figure 2.7. Laboratory Setup of LLE.

3. Recent Development in Novel Separation Processes

3.1. Olefin Gas Purification

Olefins, such as propylene, are vital raw materials used in the petrochemical industry to produce polypropylene, HDPE, LDPE, and styrene. Olefin gas purification is a critical step in this process. Earlier, this was carried out by cryogenic distillation, which required high energy, and the distillation columns were almost 300ft tall with 200 trays. These required high capital investment. Alternatively, a facilitated transport membrane for olefin gas separation is a novel process. There are two types of facilitated transport membranes- Immobilized Liquid Membrane (ILM) and a solvent swollen fixed site carrier ILM known as a Supported Liquid Membrane (SLM). [35]

3.1.1. Mechanism

The facilitated transport mechanism works on how the transition metal reacts with the olefins present in the solution. The transition metals react reversibly and selectively with the olefins, depending on the lattice energy and the metal electronegativity of the given salt. From research values, it was found that when the lattice energy was lower than 2500 kJ/mol, there was less interaction between the anion and the cation. It is also preferred to have the electronegativity of the metal salt between 1.6-2.3 because if the electronegativity is too high, there is a chance of an irreversible reaction of the metal salt with the pi electrons.[36]

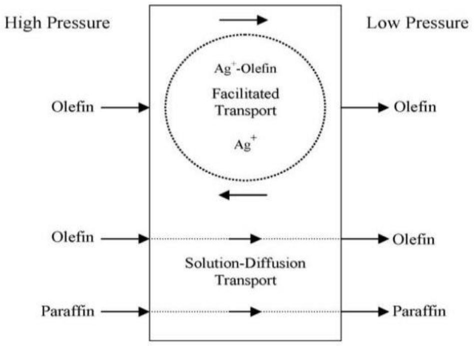


Figure. 3.1. Facilitated transport mechanism in membrane separation[47]

In Fig. 3.1, the Enhanced transfer of olefin is depicted by introducing the olefin with a complexing agent in the membrane at the high-pressure side. The olefin is liberated when decomplexation occurs as the complex diffuses because of the concentration disparity across the membrane to the low-pressure side. The complexing agents re-diffuse to the high-pressure side due to the concentration difference, and this cycle repeats. Paraffin does not form a complex with the agent, resulting in its low concentration and transport rate in the membrane. This leads to a high purity separation of olefin/paraffin mixtures, such as a propylene-propane mixture. Hence, the metal salt employed for this procedure is AgNO3[36], which aligns with the electronegativity and lattice energy requirements and is economically viable.

3.1.2 Taguchi Method for analysis

The analysis of the membrane pressure and carrier concentration was done by the Taguchi method, which administrates the experiments where multiple factors are involved in finding asystematic approach to increase product quality [39]. Here, the crucial aspects, such as the transmembrane pressure and carrier concentration, were chosen, as shown in Table 3.1.

Factor	Unit	Level 1	Level 2	Level 3
Trans-membrane pressure	kPa	50	100	120
Carrier concentration	wt.%	5	10	20

Table 3.1 Separation Factors and their levels

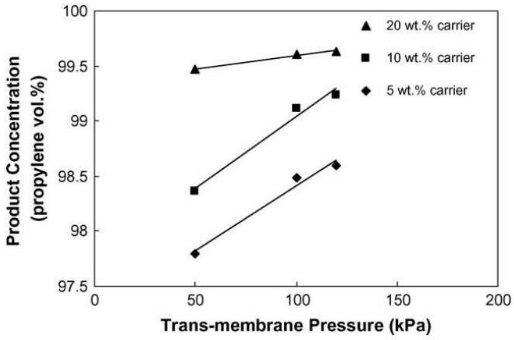


Figure 3.2. Effect of trans-membrane pressure on product concentration with carrier concentration as parameter (experimental results)[47]

The Taguchi examination anticipates optimal circumstances where the maximum product concentration is achieved when trans-membrane pressure and carrier concentration are at their peak levels (i.e., 120 kPa and 20 wt.% respectively). According to this assessment, under optimal conditions, the propylene concentration in the product will be 99.801 vol.%, as illustrated in Fig. 3.2. [35]

3.2 Janus nanofibrous membrane for water-in-diesel emulsion separation

[40]With the growing automobile industry, there is an increase in demand for diesel engines. This requires a more streamlined and effective separation method of water from diesel. Primarily, the presence of water leads to microbial growth and acid formation due to the sulfur present in the fuel. This acid leads to the corrosion of the engine and the blocking of the filters and the orifices, thereby resulting in the emission of pollutants. This makes removing water from diesel fuels a vital step in environmental protection and better engine working. Earlier methods, such as chemical adsorption and precipitation filtration, have separated water from diesel emulsion. Recently, a membrane with Superhydrophobic-oleophilic properties has been employed due to its elevated specific surface area and porosity. The attainment of superhydrophobicity typically involves electrospinning the low-surface-energy polymer solution directly. This nanofibrous membrane operates on the principle that hydrophilicity causes water droplets to adhere to the nanofibers, resulting in water separation as the droplets are intercepted on the hydrophobic surface. In addition to water, diesel contains surfactants, and the water content is typically minimal (~1 vol% water in diesel).

A design for a surfactant-stabilized water-in-diesel emulsion (1 vol% water) was formulated, incorporating a Janus nanofibrous membrane made of deacetylated cellulose/acetate polyvinylidene fluoride (dCA/PVDF) with under-diesel super hydrophilic/superhydrophobic asymmetric wettability. This demonstrated an efficacy of 96% even after undergoing 50 cycles of reuse. The Janus nanofibrous membrane provides exceptional resistance to acids/alkalis and exhibits high efficiency. The Janus dCA/PVDF membrane, illustrated in Fig. 3.3, is produced by electrospinning the PVDF nanofibrous membrane onto a supporting membrane layer. Simultaneously, the CA nanofibrous membrane is electrospun onto the previously prepared PVDF membrane. To create the Janus dCA/PVDF membrane, this CA/PVDF membrane is immersed in a NaOH solution and dried using deionized water. [45]

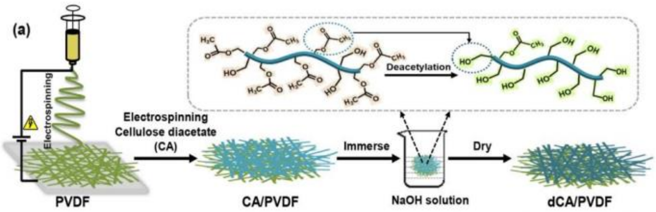
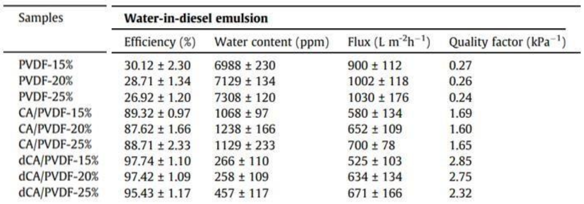


Figure 3.3. Preparation of Janus dCA/PVDF membrane[14]

From experimental results, it was observed that when only PVDF was used, the efficiency was around 30%. When electrospun with CA, the efficiency increased significantly to approximately 88%. When the CA was deacetylated into dCA, the separation efficiency was 97% for a water-in-diesel emulsion. The results with different concentrations are shown in Table 3.2. [44]



Samples	Water-in-diesel emulsion			
	Efficiency (%)	Water content (ppm)	Flux (L $m^{-2}h^{-1}$)	Quality factor (kPa^{-1})
PVDF-15%	30.12 ± 2.30	6988 ± 230	900 ± 112	0.27
PVDF-20%	28.71 ± 1.34	7129 ± 134	1002 ± 118	0.26
PVDF-25%	26.92 ± 1.20	7308 ± 120	1030 ± 176	0.24
CA/PVDF-15%	89.32 ± 0.97	1068 ± 97	580 ± 134	1.69
CA/PVDF-20%	87.62 ± 1.66	1238 ± 166	652 ± 109	1.60
CA/PVDF-25%	88.71 ± 2.33	1129 ± 233	700 ± 78	1.65
dCA/PVDF-15%	97.74 ± 1.10	266 ± 110	525 ± 103	2.85
dCA/PVDF-20%	97.42 ± 1.09	258 ± 109	634 ± 134	2.75
dCA/PVDF-25%	95.43 ± 1.17	457 ± 117	671 ± 166	2.32

Table 3.2. Separation properties of PVDF, CA/PVDF, and dCA/PVDF membranes.

3.2.1 Separation mechanism for water-in-diesel emulsion

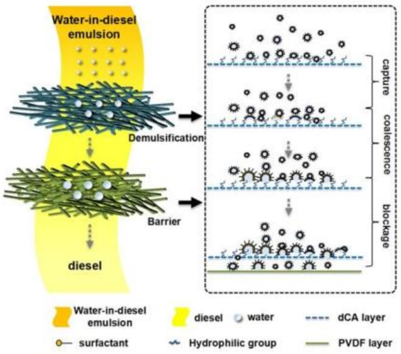


Fig. 3.4. Separation mechanism of dCA/PVDF membrane for water-in-diesel emulsion[30]

Due to the under-diesel super hydrophilicity of the dCA membrane, it can interact with surfactants and droplets. First, the water-in-diesel emulsion comes in contact with the dCA membrane, and the water droplet gets captured in the membrane layer due to its hydrophilicity and porous nature. These tiny water droplets aggregate to form bigger water droplets leading to demulsification. These giant water droplets, diesel and the remaining water-in-diesel emulsion now go into the PVDF membrane layer under-diesel superhydrophobic. This makes it difficult for water to permeate through the membrane. In contrast, diesel passes through it due to its superoleophilic nature [46], separating dieseland water, as shown in Fig. 3.4.

Discussions

Emerging separation processes hold significant potential for introducing innovative separation methods and their applications. What sets them apart from traditional approaches is their specificity to targets and their energy efficiency. Ion exchange chromatography, recognized for its efficiency in water treatment, emerges as an optimal solution

amid evolving standards and current global circumstances. In sectors like petrochemicals and automobiles, these processes represent a progressive pathway, curbing operational costs and yielding superior outcomes. In a more direct sense, they can widen the scope of the purification process, delivering high-quality products. Addressing one of the initial unexplored challenges in this domain involves embracing improved technologies and investing in enhanced purification procedures. Despite the considerable involvement of numerous research groups, the field is in urgent need of well-designed, scientifically-grounded studies to delve into the fundamentals of these innovative techniques. It is crucial to venture beyond the conventional methods, pushing the boundaries of the "comfort zone." Exploring alternatives to the standard separation processes opens up a realm of boundless possibilities in this field.

Conclusions

This article touched upon the basic and essential theories of Novel Separation Processes. It acknowledged their fundamentals, types, mechanisms, significance, and applications as they have become a prominent and emerging research topic. Novel Separation processes have been receiving high recognition. They are subjugating the conventional methods, and many kinds of research are being carried out on their development and selectivity for high-quality products and highly efficient and energy-intensive separation processes.

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