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- **ELECTRODIALYSIS: ION EXCHANGE**

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Introduction

Separations with synthetic membranes have become increasingly important; today membrane processes are used in a wide range of applications and their number will certainly increase.

A membrane is a permselective polymer, inorganic or metal phase which restricts the motion of certain species. By controlling the relative rates of transport of various species it gives one product depleted in certain components and a second product concentrated in these components. Membrane performance is characterized by two terms: flux and selectivity. Flux (or permeation rate) is the volumetric mass flow of fluid passing through the membrane per unit area of membrane and unit mass time. Selectivity is a measure of the relative permeation rates of different components through the membrane.

Processes may be classified according to the driving force used: (1) a pressure differential leads to micro-, ultra- and nanofiltration and reverse osmosis; (2) a concentration difference across the membrane leads to diffusion of a species between two solutions (dialysis); (3) a potential field applied to an ion exchange membrane leads to migration of ions through the membrane (electrodialysis, membrane electrolysis and electrochemical devices). This last category and more specifically electrodialysis is the subject of this section. This electrically driven process uses ion exchange membranes, a description of which follows.

Ion Exchange Membranes

Electrodialysis (ED) uses membranes containing fixed charged groups attached to the polymer backbone of its membrane. Two kinds of ion exchange membranes (IEMs) are used in ED: *homopolar membranes* bearing fixed charges of the same sign and *bipolar membranes* bearing positive and negative fixed charges located on each side of the membrane.

IEMs are sheet-shaped materials through which a selective ion transport can be established under a driving force, generally an electric field and/or a concentration gradient.

Most of them are of a polymeric nature. They are constituted of reticulated macromolecular chains forming a tridimensional structure. In this network, ionizable functionalized groups are attached to the polymeric matrix and are at the origin of the membrane selectivity. For example cation exchange membranes (CEMs) contain fixed negative charges and mobile cations which can be exchanged with other cations present in an external phase in contact with the membrane. The ions balancing the fixed exchange sites are called counterions. The concentration of counterions is relatively high and therefore counterions carry most of the electric current through the membrane. The fixed charges attached to the polymer matrix repel ions of the same charges (co-ions). This exclusion, which is a result of electrostatic repulsion, is called Donnan exclusion, named after F. G. Donnan, who first reported the phenomenon in 1910. However, as the membrane selectivity is never ideal, the membrane material can be penetrated by a nonnegligible amount of electrolyte. A schematic structure of such a homopolar CEM is depicted in Figure 1. Under an applied electric field, the CEM bearing sulfonic exchange groups $(-SO_3^-)$ mainly allows the transport of counterions.

A bipolar membrane (BPM) is composed of two layers of ion exchangers joined by a hydrophilic junction. The diffusion of water from both sides of the BPM allows it to dissociate under the electrical field to generate protons and hydroxyl ions, which further migrate from the junction layer through the cation exchange and anion exchange layers of the bipolar membrane. Generally, the cation exchange groups are sulfonic and the anions are trimethyl quaternary

Figure 1 Schematic process of transport of counterion (Na +) through a cation exchange membrane (CEM, bearing sulfonic sites).

ammonium groups $(-N(CH_3)_3^+)$. The principle of this water-splitting phenomenon is depicted in **Figure 2**.

The requirements for suitability of homopolar IEMs for industrial applications are the following:

- 1. high ionic conductivity with a concentration of fixed charges as high as possible;
- 2. high ionic permselectivity combining simultaneously a high conductivity and a moderate water uptake;
- 3. chemical stability of the fixed ions and a good mechanical resistance;
- 4. reasonable price.

Bipolar membranes must have all of these requirements and, in addition, must have an experimental potential to achieve a water-splitting capability as close as possible to the theoretical one, equal to 0.83 V at 25 \degree C.

Nowadays, superior styrene-divinylbenzene copolymer membranes can be easily purchased; perfluorinated membranes with great chemical stability are now being marketed and BPMs with an industrial-scale lifetime are becoming available.

Principles of Electrodialysis

Electrodialysis with Homopolar Ion Exchange Membranes

IEMs can be organized into two-, three- or fourcompartment electrodialysis cells.

Two compartment electrodialysis The principle of ED is depicted in **Figure 3**. Electrically charged membranes are used to remove ions from an aqueous solution. A number of anion exchange membranes (AEMs) and CEMs are placed in an alternative pattern between a cathode and an anode. When an ionic feed solution (for example, a sodium chloride solution) flows through the channels of the electrodialyser, the positively charged sodium ions migrate to the cathode and the negatively charged chloride ions migrate to the anode. As the chloride ions

Figure 2 Schematic principle of water dissociation by a bipolar membrane (BPM).

Figure 3 Schematic of two-compartment electrodialysis. AEM and CEM, anion and cation exchange membranes; (D), diluate; (C), concentrate.

cannot pass the CEM and the sodium ions cannot pass the AEM, the overall effect is a simultaneous ionic concentration increase in alternating compartments and an ionic concentration decrease in the other compartments. Consequently, alternate dilute and concentrated solutions are formed. A set of two compartments (dilute (D) and concentrated (C)) forms a cell pair. In commercial applications several hundreds of cell pairs are assembled in a stack.

Three compartment electrodialysis A three-compartment ED process is depicted in **Figure 4** and concerns the transformation of an electrolyte $M^+X^$ into its acid HX, which is weakly dissociated, according to the reaction:

$$
(H^+A^-)_F + (M^+X^-)_S \to (HX)_S + (M^+A^-)_R
$$

The strong acid H^+A^- (HCl or H_2SO_4) is introduced into the feed compartment (F). Protons migrate to the substitution compartment (S) to transform the salt (M^+X^-) _s into the weak acid (HX)_s. Simultaneously,

Figure 4 Schematic of three-compartment electrodialysis for the conversion of a salt $M + X^-$ into its weak acid HX.

Figure 5 Schematic of four-compartment electrodialysis for the double substitution reaction.

 M^+ ions migrate to the recovery compartment (R) to form the salt $(M+A^{-})_{R}$.

Four-compartment electrodialysis A complex fourcompartment ED process is depicted in **Figure 5**. The elementary cell is composed of four compartments and allows the reaction of double substitution according to

$$
(B+A^-)_{D1} + (C^+D^-)_{D2} \rightarrow (C^+A^-)_{R1} + (B^+D^-)_{R2}
$$

The electrolytes to be substituted, (B^+A^-) and $(C+D^-)$, feed the diluates D1 and D2. In the first recovery compartment R1, A^- combines with C^+ to give $C+A^-$, while simultaneously B^+ combines with D^- to give B^+D^- in the second recovery compartment.

Process parameters and limiting phenomena in electrodialysis The amount of ions transported through the membrane is directly proportional to the electric current (*i*) or current density, which is given by

$$
i = \frac{ZFQ\Delta c}{\eta}
$$

where *z* is the valency, *F* the Faraday constant, *Q* the flow rate, Δc the concentration difference between the feed and the permeate (diluate) and η the current efficiency. Theoretically, 1 faraday of current $(96 500)$ coulombs) will transfer 1 mol of sodium ions to the cathode and 1 mol of chloride ions to the anode. Practically, the permeation of water through the ion exchange membranes and the fact that the membranes are not completely selective slightly reduces the current efficiency to an average of $0.90-0.95$.

Electric current is related to electrical potential *E* by Ohm's law:

 $E = Ri$

where *R* is the resistance of the total membrane stack. Increasing the current density leads to an increase in the number of ions transferred. However, current density cannot be increased by an unlimited amount. In the steady state, the flux of a species through a membrane can never exceed the flux of that species to the surface of the membrane. Concentration polarization is a well-known phenomenon arising at the interface between an IEM and an electrolyte solution when current passes through it. It is due to the difference in transport numbers of the counterion between the membrane and the solution. Gradients of concentration arise in the diffusion layer as depicted in **Figure 6**, and when the concentration of the counterions becomes negligible at the depleted solutionmembrane interface a limiting current appears.

This limiting current density j_L is the current density when the flux of ions through the boundary layers has reached its maximum value and no further increase in ion flux (or current) is possible. It is given by the relation.

$$
j_L = \frac{zDFC}{\delta(t_m - t_s)}
$$

where D is the diffusion coefficient of the counterion in the solution, *C* the concentration of the bulk solution, δ the thickness of the diffusion layer (also named the Nernst layer or unstirred boundary layer), and t_m and t_s are the transport number in the membrane and the solution, respectively. If the current density is allowed to exceed j_L , then the current crossing the membrane must be carried by another ion and dissociation of water occurs at higher current density. The limitations of the rate of ion transport through a membrane can be seen from a current density versus voltage plot for the membrane as depicted in **Figure 7**. This current-voltage plot is composed of three regions: a first, ohmic one in which current is carried

Figure 6 Concentration profile in diffusion layers: depleted and concentrated regions (for a cation exchange membrane).

Figure 7 Current-voltage curve for an ion exchange membrane; limiting current.

by the ions of the electrolyte, a second plateau-shaped one corresponding to the limiting current, and a third region in which water splitting occurs. Because D/δ is equal to k , the mass transfer coefficient, j_L is strongly determined by the hydrodynamics of the system (cross-flow velocity, geometry of the cell). Moreover, the distance between membranes has to be very thin to reduce the ohmic drop due to the electrolyte thickness. Practically, separators of 0.8-1.5 mm thick acting as turbulent promotors are introduced alternately into membranes.

Electrodialysis with Bipolar Membranes

The conventional method for generating H^+ and OH^- ions from water utilizes electrolysis. Electrolysis also generates O_2 and H_2 , and the overvoltage for this generation consumes about half of the electrical energy of the process. Nowadays, special ion exchange membranes are available for splitting water directly into H^+ and OH^- ions without generating gases. Membrane water-splitting technology is a general-purpose unit operation for converting water-soluble salts to their corresponding acids and bases. The process uses BPMs in conjunction with conventional CEMs and/or AEMs, respectively). The separation and rearrangement of ions is effected by a direct current driving force. BPM electrodialysis (EDBM) is therefore an alternative method of electrolysis for the generation of H^+ and OH^- ions which can be used to generate acid and base from salts, without the production of oxygen and hydrogen gases.

The principle of water splitting by a BPM is illustrated in **Figure 8**. The diffusion of water from both sides of the BPM allows its dissociation under the electrical field to generate protons and hydroxyl ions, which further migrate from the junction layer through the cation exchange and anion exchange layers of the BPM.

Figure 8 Diffusion and dissociation of water in a bipolar membrane. AEL and CEL, anion and cation exchange layers.

The application of BPM reduces the energy costs associated with electrode polarization in the more conventional electrolytic approach.

The theoretical potential to achieve the water-splitting capability is 0.83 V at 25° C. The actual potential drop across a BPM is quite close to this, being in the range of $0.9-1.1$ V for current densities between 500 and 1500 A m⁻², which is the general region of practical interest. The value of the membrane potential drops equate to theoretical energy consumptions of the order of 600-700 kWh per ton of NaOH. Of course, the actual energy consumptions are signiRcantly higher because of the ohmic resistances in the other cell stack components, in practical operating units.

The configuration of the EDBM process depends on the application. Typical use of BPM is in the treatment of concentrated salt solutions such as Na2SO4 from the chemical industry to produce $H₂SO₄$ and NaOH. A cell system consists of an AEM, a BPM and a CEM as a repeating unit. In this case the configuration is a *three-compartment EDBM*, illustrated in **Figure 9**. This elementary cell is repeated

Figure 9 Generation of H_2SO_4 and NaOH from Na_2SO_4 solution (three-compartment cell).

and placed between two electrodes. The $Na₂SO₄$ solution flows between the CEM and the AEM. When direct current is applied, water will dissociate in the BPM to form the equivalent amounts of H^+ and OH^- ions. The H^+ ions permeate through the cation exchange side of the BPM and form H_2SO_4 with the sulfate ions provided by the $Na₂SO₄$ solution from the adjacent cell. The OH^- ions permeate the anion exchange side of the BPM and form NaOH with the sodium ions permeating into the cell from the $Na₂SO₄$ solution through the adjacent CEM. The final result is the production of NaOH and H_2SO_4 from $Na₂SO₄$ at a significantly lower cost than by other methods.

There are applications where it is not possible to obtain high purity of both acid and base, or may even generate problems during the process. For example, in the splitting of a salt from a weak acid (sodium acetate), the pure acid is weakly dissociated, so its conductivity is low. It would not therefore be practical to achieve the splitting of sodium acetate in a three-compartment cell. Instead, a two-compartment cell with the acetate solution flowing between a BPM and a CEM is recommended (**Figure 10**A). When the conversion of the salt stream reaches 95%, the conductivity becomes very low. Therefore it is not possible to pursue the EDBM more deeply. The EDBM is then stopped and the residual $Na⁺$ ions are removed using cation exchange resins. In a similar way, an ammonium or amine salt can be treated in a two-compartment cell with an AEM instead of a CEM (**Figure 10**B).

BPM can thus also be used in an alternative twocompartment cell configuration, regenerating only one base or acid. The cation/BPM two-compartment cell is useful for the processing of the salts of weak acids (or organic acids) to give a relatively pure base stream and a mixed acid/salt stream (**Figure 10**A), while the anion/BPM configuration is useful for converting salts of weak bases (e.g. ammonium nitrate) to a salt/base mixture and a relatively pure acid (**Figure 10**B).

Applications of Electrodialysis

Electrodialysis with Homopolar Membranes

Separation electromembrane processes such as ED are being applied to bioindustries and to the treatment of industry of wastewater. ED is a method which is used both for the removal of salts (e.g. to produce drinking water from brackish sources, to remove salts from foodstuffs) and for the concentration of salt solutions (e.g. for the manufacture of table salt from seawater, the concentration of process

Figure 10 Two-compartment bipolar membrane electrodialysis to produce only pure acid or base.

streams and the recovery of salts from effluents). An example of conventional two-compartment ED is depicted in **Figure 11** and some of the many applications of ED are listed in **Table 1**.

The main application of ED is the production of potable water from brackish water whose salt content is close to $5 g L^{-1}$. Beyond this value the reverse osmosis technique is more suitable. A new application of desalination is the reduction of nitrate content in drinking water. AEMs tend to selectively transfer nitrate in preference to other anions common in drinking water. Nowadays, electrodialysis plants produce several hundreds of cubic metres of potable water per day (reduction of nitrates to 5 mg L^{-1} and NaCl to 200 mg L^{-1}).

Another potential increasing area for ED is in the rough desalting of water that will be subjected to subsequent purification for use as boiler feed or rinse water in the electronics industry. Ion exchange has commonly been used for preparing waters with a very low salinity. However, the cost for regenerating and the magnitude of the waste disposal problem are proportional to the salinity of the feed water. A variant of ED which has achieved commercial success is electrodeionization. The depleted compartment is filled with an ion exchange material, generally an ion exchange resin. This material, providing high conductive paths for the ions, prevents the occurrence of the concentration polarization and a drastic increase of the electrical resistance. **Figure 12** illustrates the electrodeionization process with ion exchange resins. It allows the production of high resistivity water (10–15 M Ω cm⁻¹) from water treated by reverse osmosis (50–100 k Ω cm⁻¹). Ion exchange resins can be replaced by ion exchange textiles, which present a higher porosity and allow operation at high flow rates. Moreover, due to their sheet form, ion exchange textiles maintain their shape and dismantling of ED stacks for clearing or repair is easier.

The second historical application of ED is the concentration of recovered salts to high levels. That capa-

Figure 11 Schematic of a conventional two-compartment electrodialysis applied to the reconcentration/diffusion of NaCl solutions. C and D, concentrate and diluate.

Recovery of electrolytes
Pure NaCl from seawater
Ag(I) salts from photographic waste
Ni(II) from electroplating rinse water
Zn(II) from galvanizing rinse water
Salts of organic acids from fermentation broths
Acids from metal pickling baths and rinse
Amino acids from protein hydrolysates
HCI from cellulose
Miscellaneous
Ion substitution

Table 1 Applications of electrodialysis with homopolar membranes

bility has been used for the recovery of crystalline NaCl from seawater. There are several ED plants in Japan with 100000 m^2 of ED membranes being used for NaCl recovery from seawater. Another important field of ED application has been in whey desalting. Whey is a by-product from cheese making containing useful quantities of proteins, lactose and lactic acid. However, the high mineral content makes it unacceptable for human consumption and of marginal value for animal feed. In terms of membrane area installed, this application is the third largest ED process. ED also has important applications in the pharmaceutical and biochemical industries, where gentle processing conditions are required for materials such as human blood plasma. The production of essential amino acids will require various demineralization steps. Certain waste streams in biochemical and pharmaceutical operations contain ammonium sulfate, urea and guanidine hydrochloride which can be recovered by ED. There are several other applications of ED for salt removal which include the production of protein fractions and the separation of amino acids into acidic, basic and neutral groups. Concerning this latter example, amino acids are mainly produced from protein hydrolysates. The solutions obtained contain both natural amino acids and inorganic salts and therefore necessitate a demineralization step. **Figure 13** shows the two-compartment ED configuration for this operation. The hydrolysates to be treated are generally mixtures containing $2-3$ mol L^{-1} of amino acids and 2.5 M NaCl at pH 5-6.

The diluate containing hydrolysate is demineralized from 2.5 M to 0.2 M without significant loss of amino acids. Such a process is running on an industrial scale in Europe. The second step is the obtention of fractions of amino acids. This operation is achieved by a four-compartment ED as depicted in **Figure 14**. Charged amino acid forms are less mobile than the ions of the salts. During this operation pure anionic and cationic amino acid fractions are obtained in the concentrate compartments (C1 and C2, respectively), while the zwitterionic forms remain in the diluate D1. The zwitterionic fraction will then be purified using a BPM.

ED is also applied to the treatment of inorganic media. The metal-finishing industry offers numerous

Figure 12 Schematic of the electrodeionization process. The ion exchange material (resin or textile) fills the diluate compartment.

Figure 13 Schematic of the demineralization of protein hydrolysates by electrodialysis. (Reproduced from Sandeaux et al., 1998, with permission from John Wiley & Sons Limited.)

applications for ED in pollution control and material recovery. The rinse streams from such processes pose pollution problems. They are usually too dilute for direct metal recovery and too concentrated for disposal. For example, ED processing of a rinse stream from a nickel electroplating system allows the production of a dilute stream to be recycled in the rinse tank and a concentrated stream which can be recirculated in the electrodialysis to build up its metal content to a level that is useful for futher recovery or direct return to the plating bath. Other similar applications concern the removal of phosphite from an electroless nickel bath or the recovery of HF and $HNO₃$ used to clean stainless steel.

Industrial countries are increasingly concerned with environment protection issues. The treatment of spent acids containing divalent metallic salts is a problem in several industries where these acids are used in pickling and surface treatment of metals. ED is an attractive technique for treating these waste acids because purified and reconcentrated acids can be obtained and reused. The advantage of this process is not only the possibility of recycling acids but also the production of lower amounts of salt effluents or sludges. For example, the recovery of sulfuric acid from effluents containing metallic salts $(Mg, Zn, Mn,$ 50 g L⁻¹) in an H₂SO₄ solution (200 g L⁻¹) from zinc hydrometallurgy is achieved in a two-compartment ED cell with modified CEMs having high selectivity protons/multivalent cations, and AEMs having a low proton leakage (**Figure 15**). A solution of 150 g L^{-1} H_2SO_4 containing less than 0.5 g L⁻¹ of metals was so obtained.

Electrodialysis with Bipolar Membranes

A large number of applications have been identified. The applications have been classified under the broad categories of pollution control/resource recovery and chemical processing in **Table 2**.

The oldest industrial application of EDBM in pollution/control resource recovery is the recovery of HF and $HNO₃$ from a stream containing KF and $KNO₃$ generated from pickling baths in the steel plant.

Figure 14 Schematic of four-compartment electrodialysis for obtaining anionic forms (in C1), cationic forms (in C2), and zwitterionic amino acids (remaining in D1). (Reproduced from Sandeaux et al., 1998, with permission from John Wiley & Sons Limited.)

Figure 15 Schematic of the recovery of an acid by electrodialysis. Diluate: H_2SO_4 and MSO₄. Pure H_2SO_4 is obtained in the concentrate.

This first commercial use of BPM began operation in 1987 at Washington Steel in Pennsylvania. **Figure 16** illustrates the process. Spent pickling acid is neutralized with KOH to precipitate the heavy metals, which are then removed by filtration. The remaining neutral solution of $KF + KNO₃$ is then treated in a three-compartment EDBM cell in which the salts are split to form KOH, which is directed to the neutralization tank, and the mixed acids $(HF + HNO₃)$, which are directed to the pickling operation. The dilute salt solution from the salt compartment of the EDBM process is then reconcentrated by conventional ED and is then returned to the bipolar stack, while the diluate is used to rinse the filter cake.

The main application of EDBM in chemical processing is the recovery of organic acids which can be recovered from fermentation. The performance of fermentation is better when the pH is slightly higher

Table 2 Some technology applications of water splitting on BPM

Pollution control/resource recovery	
HF/mixed acid recovery	Stainless steel pickle liquor recovery
	HF/NaOH recovery from spent aluminium potlinings
	Fluorosilicic acid conversion to HF, SiO ₂
	Fluoride emission control in chemical processing
Sulfate recovery	Battery acid recovery
	Waste sodium sulfate conversion
	Sodium sulfate conversion in rayon manufacture
Nitrate recovery	Ammonium nitrate conversion from uranium processing
	$KNO3$ conversion
Amine recovery	Recovery of catalyst used to cure epoxy resins in AI coating moulds
Pulp and papers	Sodium alkali recycling in pulping and bleaching operations
Flue gas desulfurization	Soxal [®] process $SO2$ recovery
	Dry sodium scrubbing alkali recovery
Chemical processing	
Organic acid production recovery	Acetic, formic, acetylsalicylic and organic acids
	Amino acids
Ion exchanger regeneration	Production of highly generated ion exchange resins
Potassium and sodium mineral processing	KCI conversion
	Solution mining of trona and subsequent sodium alkali production
	Sodium alkali production from natural brines and solid trona
Sodium methoxide production	EDBM in methanolic solutions
Methanesulfonic acid production	EDBM of sodium methanesulfonate
High purity water production	Continuous electrodeionization

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Figure 16 Process for recycling of HF/HNO₃ steel pickling solution using bipolar membrane electrodialysis. (Reproduced with permission from Davies et al., 1997.)

than the pK_a of the organic acid to be produced. This condition requires addition of a base to maintain this elevated pH. Thus, the product of the fermentation is a dilute salt of the organic acid. For example, in the case of lactic acid production, the conventional process requires many different ion exchange steps, resulting in a high volume of wastewater and organic solvents that have to be recovered. In addition, possible losses of product and a potential contamination of the product have to be taken into account. The recovery of lactic acid from fermentation broth can also be performed by the use of two ED steps. In the first, the dilute sodium lactate solution is concentrated by a conventional two-compartment ED. This step also purifies the product because only the ionized components of the broth are transported by the current through IEMs. The other components of the broth are redirected to the fermentation reactor. In

Figure 17 Schematic of the production of lactic acid from fermentation broth using both conventional electrodialysis and bipolar membrane electrodialysis. (Reproduced with permission from Davies et al., 1997.)

the second step, the concentrated sodium lactate is split in a two-compartment bipolar ED with a CEM (configuration of **Figure 10**A) to generate lactic acid and NaOH. The acid stream, still containing Na⁺ ions, is then purified by a cation exchange resin, while caustic soda is recycled to the fermenter for pH control. For economical reasons in the bipolar ED step, the conversion rate of sodium lactacte is kept at 95%, but almost 100% could be easily achieved. A simplified schema of this process is reported in Figure 17.

Conclusion

ED with homopolar membranes was first developed several years ago, essentially for desalting brackish waters and reconcentrating brine for seawater. Conventional ED is also widely used on a large industrial scale in the dairy industry for demineralization of whey. The technical feasibility of applying ED with BPMs to a variety of commercially interesting processes has been demonstrated. ED techniques are very promising because they can be applied to environmental protection (depollution and recycling of chemicals) and to bioindustries (food, pharmaceuticals and biotechnology). For all these kinds of applications, special membranes have been elaborated showing adapted selectivity in ion transport under an electric driving force. For improvement of most of the other applications of ion exchange membranes, research is mainly focused on the membrane processes themselves rather than on the synthesis of new membranes.

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ENVIRONMENTAL APPLICATIONS

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Introduction

Flotation is the selective separation of solid particles, liquid droplets, chemicals or ions, or biological entities from a bulk liquid, based on their surface properties. In the process two actions occur: the collision between rising bubbles and matter suspended in the liquid, followed by adhesion of the particle to the bubble surface and separation of the resulting bubble–particle aggregate from that liquid. Environmental application of this technology includes the selective separation of specific solids or liquids from solid suspensions, liquids from liquid suspensions or certain dissolved species from solutions.

Separations which are based essentially on the adsorption from solution include colloidal suspensions of solid or liquid products, and the separation of certain dissolved substances and ions. In order to make a separation, there must be a drop in free energy for the removed substance when it attaches to the bubble. For selective separations this drop must significantly exceed those of the competing ions or colloids. In general, this results when the substance to