Chapter

A New Approach for Membrane Process Concentrate Management: Electrodialysis Bipolar Membrane Systems-A Short Communication

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Abstract

In most cases traditional and advanced treatment technologies transfers and concentrates the pollutants from one phase to other phase. However, nowadays, these concentrated flows containing heavy pollution are rapidly moving away from being manageable. In particular, membrane concentrate flows await immediate solutions to this issue. Electrodialysis Bipolar Membrane (EDBM) Processes are becoming a serious and potential solution technique for similar concentrate streams. In this chapter, principles and potentials of EDBM processes for the recycling or recovery of membrane concentrates are discussed.

Keywords: electrodialysis, electrodialysis bipolar membrane, concentrate, reuse, recovery

1. Introduction

Membrane processes, including Ultrafiltration, Nanofiltration and Reverse Osmosis, are widely used for the treatment of water and wastewater. Main advantage of these processes are well known operational conditions and wide application areas. But, main disadvantage of these processes is concentrate management. Mainly high amount of salt content in concentrate stream is limiting the discharge of these streams to water bodies.

Starting from evaporation to ion exchange, most of these processes transfer the pollutants from one phase to other phase. It means more concentrated streams can be created from these processes. Therefore, applicable and valuable product production techniques are urgently needed for membrane concentrates. Electrodialysis Bipolar Membrane (EDBM) Processes are promising technique for the disposal of membrane concentrates.

EDBM technique has too many advantages against other techniques such as, valuable product formation and low cost operation. On the other hand, there is still great limitations on application point such as limited company production, alkali element fouling on membranes, high capital cost etc.,

Briefly, technological opportunities may solve the application disadvantages of EDBM processes in near future. In this chapter, principles and potentials of EDBM processes are discussed.

2. Electrodialysis bipolar membrane: principles and definitions

Industrial wastewater differs in industrial pollutant components depending on the types of industries in which they are formed. This difference plays a major role in the selection of wastewater treatment technologies.

Treatment technologies applied for wastewater recycling; Secondary Treatment (IA), Nutrient Removal, Filtration, Surface Filtration, Microfiltration (MF), Ultrafiltration (UF), Flotation, Nanofiltration (NF), Reverse Osmosis (TO), Electrodialysis (ED), Carbon Adsorption, Ion Exchange, Advanced Oxidation and Disinfection [1]. **Figure 1** shows the corresponding pore sizes of the pressure-operated membranes and their ability to hold specific wastewater components.

Membrane Processes (mainly reverse osmosis (RO) systems) and desalination plants are increasing day by day. In last two decades, over 10.000 membrane treatment plants have been established in most countries [3]. Daily treatment capacity of these plants may access 100 million m3/day in 2020.

With the introduction of low cost membrane modules in the 1960s and 1970s, membranes were widely used in industrial areas [4]. RO process (pore diameter < 0.0001 μm) can remove dissolved solids, bacteria, viruses and other microorganisms present in water [5]. By operating RO systems, which is one of the wastewater recycling processes, both high quality process water (filtrate flow) production is provided, and concentrate flow with high pollution load but low flow (silk) is formed. In RO systems with flow and concentrate modifications, approximately almost 90% filtrate and 10% concentrate can be formed from the inlet flow at high pressure [3].

The disposal of the concentrate from Membrane systems is still the main focus of most scientific research. This is an important issue for most country for the protection of water bodies and soil. As well known, discharged wastewater streams are still being used for irrigation. High salt content in concentrate streams means desertification of most valuable agricultural areas. The concentrate originating from membrane processes should be disposed or treated with feasible system.

Bipolar membranes are a type of ion-selective membranes first introduced in the 1950s (**Figure 2**). Bipolar membranes are composite membranes consisting of a Cation exchange membrane and an Anion exchange membrane [7]. Cation exchange membrane and anion exchange membranes, which are among ion exchange membranes, are heterogeneous, while bipolar membranes are homogeneous. Homogeneous bipolar membranes can be prepared from many different

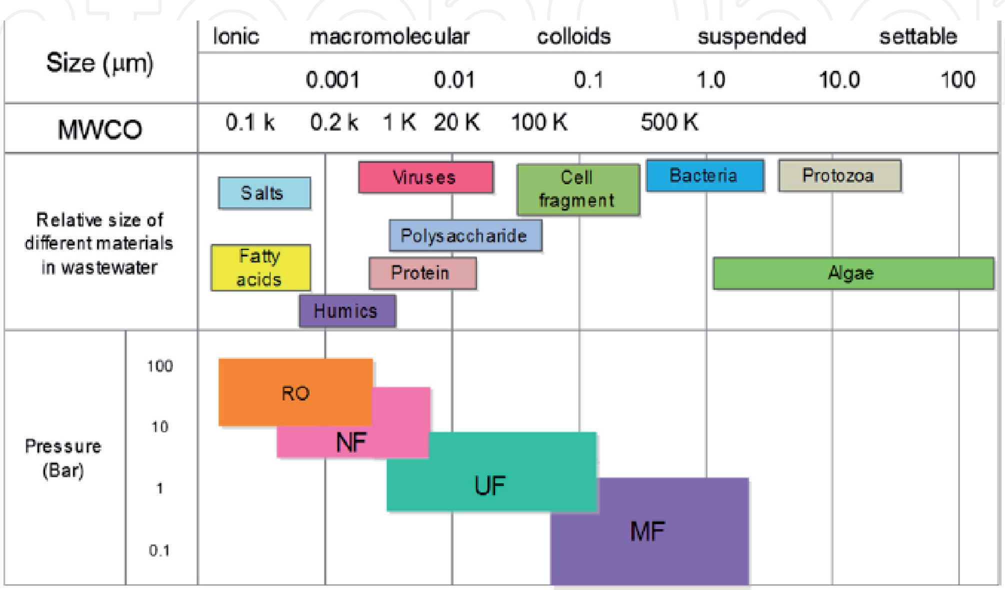

Figure 1.
Pressure operated membrane technology [2].

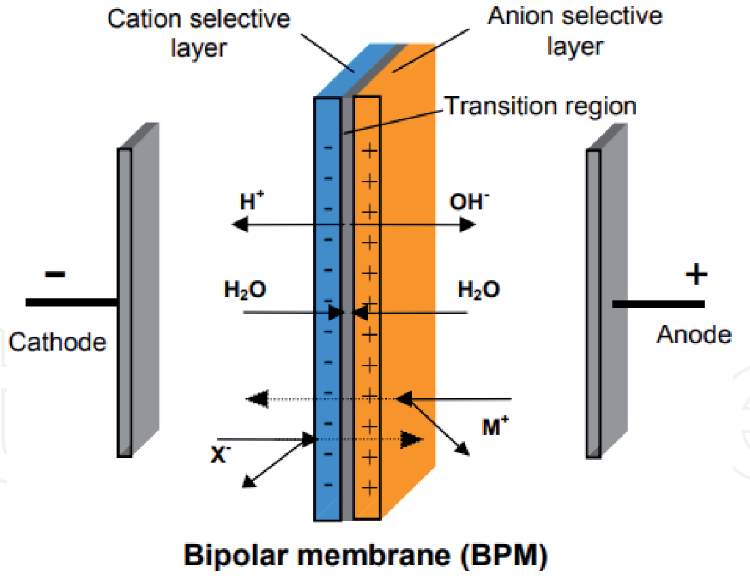

Figure 2.
Water splitting function of a bipolar membrane [6].

materials. The properties of bipolar membranes formed from different materials are given in the table below (**Table 1**).

Earlier studies on electrodialysis began before the World War II in Germany. Industrial and pilot scale applications have been developed since 1950. The first applications were about obtaining drinking water from sea water. Later, in applications in the food industry, it was tried to produce demineralized sugarcane sugar. If we consider the electrodialysis system as a black box, as a result of natural brine feeding, acid and base are formed at the output of the system, this picture is shown in the picture below [8] (**Figure 3**).

Electrodialysis processes is one of the membrane process that the driving force is an electrical field. EDBM system consist of anionic, cationic and bipolar membranes. [9] EDBM systems are widely used in chemical industry, in food industry, biochemistry industry and environmental protection technologies. [9].

Using bipolar membranes together with ion exchange membranes in electrodialysis processes, high quality process water production can be possible and EDBM may become a more viable method for industrial wastewater treatment applications [10].

In the EDBM process, direct current (DC) is supplied to the electrodes to electrolyse the water molecules. Electrical potential between anode and cathode works as a driving force for the movement of electrons in electrolyte solution. [8]. In EDBM process, bipolar membranes realizes the acid and base production in electrolyte solution.

Organic acids such as lactic acid, ascorbic acid, salicylic acid, amino acid and inorganic acids such as hydrofluoric (HF) acid, sulfuric acid (H_2SO_4), hydrochloric acid (HCl) can be produced using EDBM systems. Alkali bases potassium hydroxide (KOH), Sodium Methoxide (CH_3NaO) can also be produced in this systems [11].

In electrodialysis systems that separate water with bipolar membranes, an acid - base is formed from a very efficient energy-related salt concentration due to the accumulation of hundreds of cell units between 2 electrodes, such as conventional electrodialysis processes [7].

Some catalytic reactions take place in electrodialysis systems using bipolar membranes. Reactions between water molecules and functional chemical groups occur as Eq. (1), (2), (3), (4) [12]. The catalytic mechanism is underlined by chemical reaction model of water dissociation, that is, the water splitting could be considered as some type of proton-transfer reaction between water molecules and the functional groups or chemicals [7]:

Polymer(s)	İon exchange group	Remarks
Anion exchange layer		
Poly-styrene-co- divinylbenzene	Tertiary and quaternary amines	Crosslinked resin, heterogeneous
Poly-sulfone	Di-amines	Crosslinked homogeneous
Poly-sulfone	Quaternary amines	Homogeneous
Poly-vinylidene fluoride blend with poly-vinyl benzyl chloride	Different diamines	Crosslinked
Anion exchange resin	Not specified	PVC binder
Poly-ether sulfone	Quaternary amines	Homogeneous
Poly-divinylbenzene-codimethylamino propyl methacrylamide		
Poly-methyl methacylate-coglycidyl methacrylate	Quaternary amines	
Cation exchange layer		
Poly-styrene-co- divinylbenzene	Sulfonic acid	Heterogeneous (polyvinylchloride binder)
Poly-styrene-co- divinylbenzene	Phosphoric acid	Poly-ethylene binder
Nafion	Sulfonic acid	Homogeneous
Grafted perfluorinated polymer membranes	Sulfonic acid	
Poly-butadiene-co-styrene	Sulfonic acid	
Poly-phenylene oxide or poly-styrene	Sulfonic acid	Homogeneous
Poly-ether sulfone	Sulfonic acid	Homogeneous
Poly-sulfone	Sulfonic acid	Homogeneous
Poly-ether ether ketone	Sulfonic acid	Homogeneous
Separate contact layer		
Poly-vinyl amine		
Poly-viylbenzylchrloride-co-divinylbenzene resin	Sulfonic acid	Heterogeneous (polyvinyl benzyl chlorideco-styrene binder)
Poly-sulfone	Aminated	

Table 1.
Ion exchange polymers of bipolar membrane layers [8].

$$B + H_2O \leftrightarrow BH^+ \ldots OH^- \leftrightarrow BH^+ + OH^- \quad (1)$$

$$BH^+ + H_2O \leftrightarrow B \ldots H_3O \leftrightarrow B + H_3O \quad (2)$$

$$A^- + H_2O \leftrightarrow AH \ldots OH^- \leftrightarrow AH + OH^- \quad (3)$$

$$AH + H_2O \leftrightarrow A^- \ldots H_3O^+ \leftrightarrow A^- + H_3O \quad (4)$$

where BH^+ and A^- refer to the catalytic centers. The catalytic sites provide an alternative path with low effective activation energy for water splitting into hydrogen and hydroxyl ions [7]. EDBM configurations including acid base production schematic diagrams are given in **Figure 4** [12].

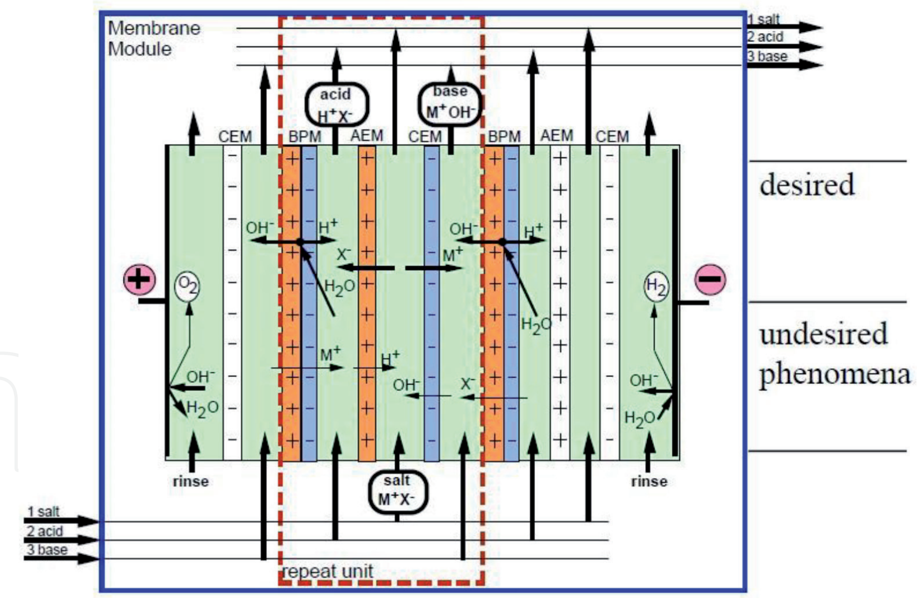

Figure 3.
Schematic illustration of EDBM process as a black-box [8].

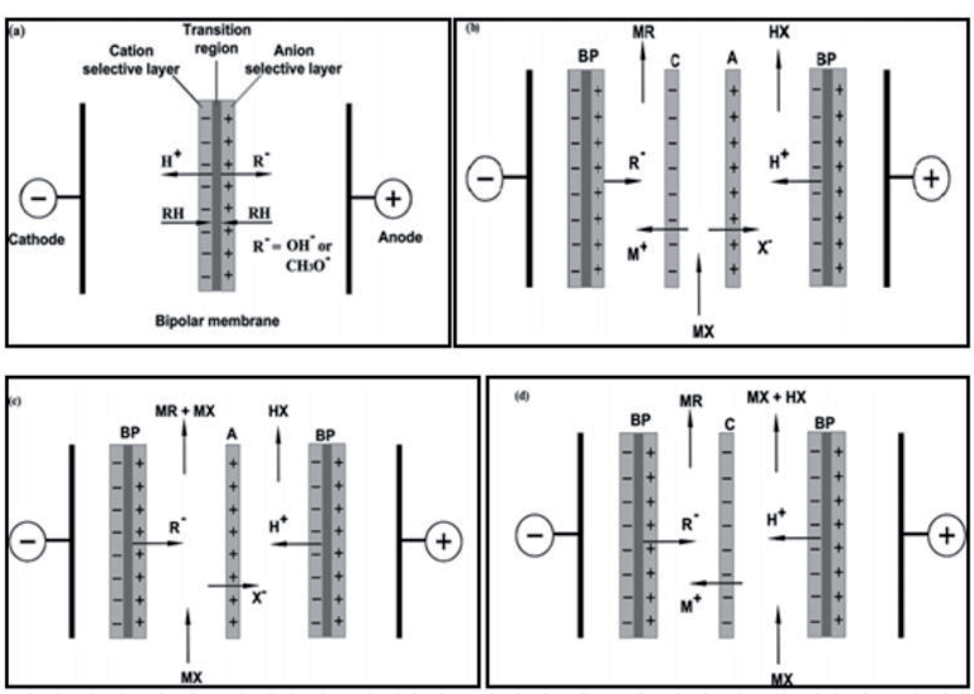

Figure 4.
Bipolar membrane and EDBM: BP, bipolar membrane; A, anion selective membrane; C, cation selective membrane; M +, cation; X- anion; H +, hydrogen ion; R, OH^- or CH_3O. (a) Bipolar membrane and its functions; (b) acid and base production; (c) acid production; (d) base production [12].

3. Usage areas of EDBM process

The bipolar membrane electrodialysis process is used in the latest technological way as an integrated process for the supply of potable water and industrial salt water and recovery of industrial effluent. On the other hand, both in chemical processes and environmental protection processes, they have been successfully applying in recent years. Another field of use of bipolar membrane is the chemical industry, where new products such as H_2SO_4 and NaOH are produced from a salt such as Na_2SO_4. Indeed, this method has become widespread recently and is used successfully. Especially, the production of acid and base without producing waste and the production of organic - inorganic acids increased the interest in this method. Many researchers have worked on this subject. It is possible to find many studies especially on acetic acid, propionic acid, gluconic acid, citric acid and lactic acid. In fact, some model studies have started to be carried out recently. Biotechnological research is ongoing to reduce costs in the electrodialysis process in order to reduce the cost in order to ensure acid recovery.

When ED and EDBM processes are compared with other treatment methods, it is an important advantage that it provides recovery from pollutants in wastewater and salt water. Studies show that it is possible to recover pollutants from solutions with one or more contaminants. In addition to this, the process of making acid and base production possible with EDBM process takes another step forward. [13]

4. Recovery of concentrated wastes by EDBM process

An important advantage of the electrodialysis process over other processes is the possibility of recovery of concentrated waste. When the electrodialysis studies in the literature are taken into consideration, recovery has been proved possible. Electrodialysis studies are mainly in the form of recovery of those pollutants from aqueous solutions with single or multiple pollutants.

The process characteristics and economic evaluations of some studies in the literature are given in **Table 2**.

Application	Scale	Process characteristics	Economic evaluations	References
HF and HNO_3 Recovery	Industrial Scale	3 compartments, M. Area; $3x10^5$ m^2, BM Service Life; 2 years, Efficiency 90–95%	Total $ 2,950,000 Annual Business Administration Cost: $ 870,000	Pourcelly and Gavach [15]
NaOH Recovery	Semi Industrial Pilot Scale	M. Area: 0.5 m^2 Feed Speed 5 L / h Initial conc. 22 g / L Current Density 900 A/ m^2 Efficiency 82% (1 M)	5.0kWh/kg NaOH	[15]
NH_3 and HNO_3 Recovery GmbH, Germany	Semi Industrial Pilot Scale	M. Area: 120 m^2 Initial conc. 250 g / L Current Density 1000 A / m^2 Efficiency 97%	0.34 $/kg NaNO3	Pourcelly and Gavach [15], Graillon and Persin [16]
Dimethylisopropylamine recovery	Semi Industrial Pilot Scale	M. Area: 0,3 m^2 Initial conc 110 g / L Current Density 800 A / m^2 Efficiency 30–70%	$ 2.5–5.0 / kg amine	Pourcelly and Gavach [15], Graillon and Persin [16]
Gluconic Acid Recovery	Lab. scale	2 compartments, M. Area; 0,19 m^2, 2.2 V – 415 A/m^2 Efficiency 95%	—	Pourcelly and Gavach [15]
Methanesulfonic Acid Recovery	Industrial Scale	3 compartments, M. Area; 64 m^2, 2.26 V – 800 A/m^2 Initial conc 80–250 g / L Efficiency 95%	Total Expense: $ 700,000 Oper. Goods. $ 354 / ton MTA Sales fee: $ 5500 / ton MTA	Pourcelly and Gavach [15]

Application	Scale	Process characteristics	Economic evaluations	References
Amino Acid Recovery	Industrial Scale	3 compartments, M. Area; 540 m^2, BM Service Life; 2 years, Efficiency 4–6 M Org. Asit	—	Pourcelly and Gavach [15]
Lactic Acid Production	Industrial Scale	2 compartments, M. Area; 280 m^2, Efficiency 60–96%	UN Cost 0,12 $ / kg 1kWh / kg Acid	Pourcelly and Gavach [15], Aritomi [17]
Camphorsulfonic Acid Regeneration	Pilot Scale	3 compartments, BM. Area; 0,14m^2, Acid Conc. 0,8 M Current Density 500 A / m^2 Efficiency 98,5%	300 kWh/ton Acid	Pourcelly and Gavach [15]
Ascorbic acid Production	Lab. Scale - Semi End. Pilot Scale	2 Compartments Current Density 1000 A / m^2 Acid Conc. 1 M	1,4–2,3kWh/kg Acid	Pourcelly and Gavach [15], ve Novalic and Kulbe [18], Yu et al. [19]
Citric Acid Production	Pilot Scale	2 compartments, BM. Area; 0,004 m^2, Acid Conc. 30 M Current Density 1000 A / m^2	2–5 kWh/kg Acid	Wakamatsu [20], Xu [21], ve Novalic and Kulbe [18]
Salicylic Acid Production	Lab. - Pilot Scale	3 Compartments 30 V - 750 A / m^2 Acid Conc. 4.5 g / L	15–20 kWh / kg product	Alvarez et al. [22]
Sodium Acetate conversions	Pilot Scale	5 Compartments BM. Area; 0,008 m^2, Product 0.5 M Acetate	1.3–2.0 kWh / kg product	Yu et al. [19], Trivedi et al. [23]
Toluenesulphonic Acid regeneration	Lab. Scale	2 Compartments	1,2kWh / kg Acid	[19]
Formic Acid regeneration	Lab. Scale	3 compartments, M. Area; 540 m^2, Acid Conc. 7 M	2.6kWh / kg Acid	Ferrer and Laborie [24]
Sulfuric Acid recovery	Lab. Scale	6 compartments 3 compartments	3.3kWh / kg Acid 2.4kWh / kg Acid	Cifuentes [25]
Magnesium and Protein recovery	Lab. Scale	Bipolar Membrane electrodialysis	1.7kWh / kg Mg^{+2} 0.6kWh / kg protein	Pourcelly and Bazinet [26]

Table 2.
Recovery of concentrated wastes by EDBM process [14].

In addition to treatment and recovery, it is frequently encountered that electrodialysis method is used directly in acid and base production.

5. Advantages and disadvantages of EDBM process

Main advantage of EDBM systems is energy efficiency. In most cases high energy needed for most treatment processes mainly for pumping. But in EDBM process, system works with low pressure pumps (0.5–0.8 Bar). On the other hand direct current usage makes the EDBM systems advantageous against the other advanced treatment processes. Beside the most treatment processes, by products of EDBM are valuable materials such as acids and bases. Additionally, the inlet concentrated stream with a high salt content is deionized and water can be recovered. Briefly, salt content can be converted to valuable materials and water content can be reduced and recovered. Actually, it turns out that the EDBM system is a process capable of very high approach to zero waste practice.

The biggest advantages of using bipolar membranes in EDBM processes is that BPMs increase ionization by 50 million times compared to the self-hydrolysis of water. In addition, the anionic and cationic membranes inside the EDBM systems prevent the OH^- and H^+ ions formed in the system from reaching the anodes and cathodes, and no O_2 and H_2 gas output is observed in the BPMs. [3]

The first disadvantage of EDBM systems meets the mark in acid and base production from membrane process concentrates. Concentrates consisting of membrane processes from wastewater treatment processes, generally contain mixed ion groups instead of single ion groups. This is due to the type and variety of wastewater they treat. Mixed acids and bases may remain low in commercial value. Another problem is the permanent damage left in the membrane structure of the multivalent ions in the concentrated stream. For this, +2 and + 3 valence cations can be removed from the water by nanofiltration, ion exchange, evaporation etc., before reverse osmosis process. Or + 2-valued (especially calcium compounds) ions can be removed from the reverse osmosis concentrate content by processes such as precipitation. However, in both cases, the operating costs of the processes will increase and will lead to reductions in acid and base concentrations resulting from the decrease in ion concentration in the feed water to EDBM systems.

Another problem to be encountered in EDBM systems may be the locking of the system at low acid and base concentrations (1–2%) with the increase of osmotic pressure in the system due to the increasing ion content. As it is known, high acid and base levels are important in these systems both commercially and in terms of water recovery. The most important solution related to this lies in the separate collection and purification of the salt content in the wastewater source. In other words, these systems can be paved with clean production. In other words, the disadvantages of the EDBM system in mixed wastewater streams can be prevented by interventions at the source. Thus, the operating life of EDBM systems is preserved and operating costs and product quality are increased.

It is certain that the advantages mentioned so far will lead the EDBM systems to attract more attention in the future. However, the biggest obstacle to the implementation of EDBM systems is the high cost of the membranes used in the system. This is thought to be in favor of the price decrease of the balances in the market due to the widespread use of EDBM and increased membrane production over time. Because the vast majority of existing wastewater treatment systems transfer existing pollutants to another phase or make them more concentrated and present them as an even bigger problem. However, EDBM systems promise us to use new products from our waste. This; It plays an important role in the solution of many environmental problems from efficient use of resources to global warming.

6. Conclusions

For further usage of membrane processes without any problematic concrete flows on environment, new concentrate disposal technologies will be needed such as EDBM process. The main advantage of the EDBM process is the commercially obtaining precious product from environmentally problematic products. However, the most important problem at the moment is high initial investment costs. But, similar high investment problems are valid for many processes that are widely used today, and with the spread of manufacturing, this problem has disappeared and the possibility of widespread use has increased. Finally, membrane concentrate flows are waiting an urgent solution, and the spread of EDBM or similar technologies will not take too long.

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