CADMIUM REMOVAL FROM WASTEWATER: A COMPARATIVE STUDY BETWEEN ELECTROLYTIC AND MEMBRANE SEPARATION PROCESSES

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ABSTRACT

To minimize the effects of pollution caused by toxic metals, the environmental laws of the various countries of the world have become increasingly restrictive with regard to the emission of industrial waste. On the other hand, technological development has driven the creation of new processes and techniques that are extremely efficient in the removal of toxic metal contaminants from wastewater. In the literature review, several techniques for removing toxic metals such as cadmium are evaluated. The main objective of this work is to carry out a comparative laboratory study between electrolytic and membrane separation techniques (reverse osmosis) for the removal of cadmium ions (Cd2+) from wastewater. The electrolytic process, because it is simple and does not require chemical additives, has the advantage of enabling the recovery of cadmium in its metallic form and in high concentrations present in wastewater. However, at low concentrations of Cd2+ ions, the process is not efficient. Finally, it can be proposed to use the two processes in a complementary way. At first, the electrolytic process is applied to remove the highest concentration of cadmium, followed by reverse osmosis to reach values acceptable by environmental legislation.

Keywords: Cadmium. Electroplating. Reverse osmosis. Contamination. Environment.

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INTRODUCTION

The pollution of water bodies is a chronic problem for society, which has been progressively aggravated by urban, agricultural and industrial growth. If, on the one hand, there is a growing demand for water, on the other hand, the increase in the pollutant load discarded in rivers, lakes and seas reduces their quality, often making them unavailable to the noblest uses, reducing the supply of water.

As a way to minimize the effects of pollution, the environmental laws of the various nations have become increasingly restrictive with regard to the launching of dumps. In parallel, technological development has been driving the emergence of new processes and extremely efficient techniques for the removal of contaminants from water.

Among the main contaminants associated with the pollution of natural waters, toxic metals stand out, a class of compounds of high toxicity and that are bioaccumulated in organisms. Because they are not biodegradable, the traditional process of biological treatment of wastewater (activated sludge) is not efficient in removing these contaminants, which requires investments in the development of physical-chemical processes, with emphasis on electrolytic processes and membrane separation processes.

Electrolytic processes are based on the use of electrical energy for the occurrence of chemical reactions. In the case of an aqueous phase, heavy metals are dissolved in the form of cations. When the electric current is applied in the aqueous phase, in the cathode of the electrolytic reactor, these cations will react with electrons, reducing their metallic form. The metallic form is deposited in a solid phase on the surface of the cathode, thus being removed from the aqueous phase.

The use of membrane separation processes has shown extremely satisfactory results in the removal of heavy metals from aqueous solution. From the second half of the twentieth century, the use of membranes in separation processes was incorporated in different areas, which include the desalination of brackish and salt waters, hemodialysis and various industrial applications, such as gas separation and beverage clarification. Recently, these processes have also started to be used in the environmental area, providing the removal of contaminants from industrial effluents, in order to meet the limits of effluent disposal imposed by environmental legislation and provide water reuse.

The main objective of this book chapter is to carry out a comparative study between electrolytic and membrane separation techniques for the removal of cadmium ions from wastewater.

LITERATURE REVIEW

DISPOSAL OF HEAVY METALS IN WATER BODIES

Metals play important roles in the metabolism of living beings. Its properties are fundamental in maintaining the three-dimensional structure of biomolecules. Some metals are necessary in minimal amounts for the maintenance of cellular metabolism, while others have no relevant biological function, which can cause damage to metabolism. From a physiological point of view, metals can be classified into three categories: essential (calcium and magnesium), essential metals that can become harmful in high concentrations (iron, manganese, zinc, copper, cobalt, nickel and molybdenum) and toxic (mercury, lead and cadmium). However, it is important to highlight that the interactions of the organism with the metal do not depend only on the element, but on its chemical speciation [1].

The most toxic form of a metal is not free, but when it is found as a cation or bound in carbon chains. The main mechanism of toxic action of these elements derives from their affinity for sulfur. Thus, they react with the sulfhydryl radical (-SH) present in protein molecules, altering their properties, which can result in harmful consequences to the metabolism of living beings [2, 3].

Within this context, a group of metals has taken a particular position in relation to their impacts on the environment: heavy metals. According to Hawkes [4], in general, the literature classifies as a toxic metal that has a specific mass greater than 5 g/cm3. However, this author highlighted the importance of defining these elements in relation to their chemical properties and cites them as elements that form insoluble sulfides and hydroxides, whose salts form colored aqueous solutions and originate colored complexes.

All metals, to a greater or lesser extent, in the form of soluble salts or hydroxides are solubilized in water, and can affect aquatic ecosystems in two basic ways: the metal can be toxic to the body or it can be bioaccumulated, having its effect enhanced along the food chain. Thus, even at low concentrations, a dump with toxic metals can be dangerous.

Toxic metals correspond to a class of compounds commonly present in dumps from different types of industries, such as mining, electroplating, tanneries, and electronics manufacturing. Table 1 presents the limits established by Brazilian legislation for the discharge of effluents and the potability of water for the main toxic metals.

Table 1 – Limits of effluent discharge and water potability.

Inorganic contaminants	**Effluent discharge, mg/L**	**Limits for potability of water, mg/L**
Arsenic, As3+	0,5	0,01
Barium, Ba2+	5,0	0,7
Cadmium, CD2+	0,2	0,005
Lead, Pb2+	0,5	0,01
Copper, Cu2+	1,0	2,0
Mercury, Hg2+	0,01	0,001
Manganese, Mn2+	0,5	0.05
Nickel, Ni2+	2,0	-
Zinc, Zn2+	5,0	-

CADMIUM

Cadmium was discovered in 1817 by chemist Friedrich Strohmeyer, professor of chemistry and pharmacy at the University of Göttingen, Germany, while working with zinc carbonate (ZnCO3), this scientist noticed the presence of an unexpected substance. Later, he concluded that it was a new element, still unknown. The element was baptized as cadmium because it was extracted from cadmium, the designation used for the ore rich in zinc carbonate [5, 6].

Cadmium is a transition metal of light gray color. Its most stable ion is the divalent species. This element occupies the 67th place in the order of abundance of chemical elements that make up the Earth's crust, having no biological function and being highly toxic to men, plants and animals, however the natural levels of cadmium found do not cause acute toxicity.

Cadmium is a rare element and does not occur in nature in pure form. The common concentration of this element in the earth's crust is approximately 0.15 - 0.2 mg/kg. The main cadmium mineral is greenochite, the cadmium sulfide that is found in small amounts in the soil, usually associated with zinc ores, especially sphalerite and galena [7, 8].

Cadmium is found in mines for zinc (constituting more than 1% of the metal content of such mines), lead and copper. The anthropogenic origin of cadmium contamination is typically 3 to 10 times higher than natural contamination.

Due to its low boiling point and high vapor pressure in relation to the metals with which it is found, cadmium volatilizes during fusion and condenses into fine particles that react immediately with oxygen, transforming into cadmium oxide, an inhalable and extremely toxic form. This element emits vapors even when at temperatures below its boiling point. In its solid state it is insoluble in water and in the usual organic solvents, undergoing oxidation in the presence of air and humidity [9].

Cadmium is not normally present in the environment as a pure metal, but as a mineral combined with other elements, such as oxygen in the form of oxide, chlorine in the form of chlorides, and sulfur in the form of sulfates and sulfides. It also comes in complexed form, with oxides, sulfides and carbonates of zinc, lead and copper. The most soluble structures found are sulfates and chlorides [10].

Natural sources of contamination of this element are the emissions of gases from volcanic activities, burning of forests and wind transport of soot particles and soil [11]. The main sources of contamination are due to anthropogenic activities, such as: burning of coal, improper disposal of industrial and domestic waste, mining processes and metal refining. Another important source of contamination is the incorporation of fertilizers that contain cadmium as an impurity. Studies on cadmium tailings show that about 30 thousand tons of the element are released into the environment per year [10].

Cadmium consumption and use have varied greatly, especially in recent years. Its use in batteries has surpassed more traditional uses, such as pigments, stabilizers and coatings. One of the main industrial uses of cadmium is due to its low melting point (320.9 ºC), being used in metal alloys that require this characteristic, offering low melting point, low coefficient of friction and high fatigue resistance. It is also used in electroplating and battery construction, along with nickel. It is in the battery sector that most of the cadmium used in the industry is used. However, changes are being noticed in this field [11-13].

Nickel-cadmium (Ni/Cd) batteries are gradually being replaced by nickel metal hydride (NiHM) batteries, mainly due to the high toxicity of cadmium and the risk presented in the final disposal, which, being within the reach of the majority of the population, ends up not having an adequate destination, being placed most of the time in household garbage [11-13].

Because it is considered a persistent element, cadmium can accumulate in plants and animals, reaching humans and, similar to what happens in the food chain, accumulate in the human body for a long time, mainly in the kidneys and liver, where it has been detected that its biological half-life is approximately 10 years. Other studies show that the half-life of this element can vary even more, reaching 40 years in organisms [14-19].

REMOVAL OF HEAVY METALS FROM WASTEWATER

Because they are not biodegradable, heavy metals are not removed in conventional biological treatments, so that in the treatment of effluents containing these contaminants, physicochemical processes are used, the most common being: chemical precipitation, coagulation-flocculation, flotation, ion exchange, electrochemical processes and membrane processes.

Physicochemical processes have operational advantages over conventional effluent treatment processes, such as: low residence time, ease of operation and control, the systems are compact, the possibility of associating two or more techniques and the ability to operate in different temperature ranges. However, there are still limitations, mainly the high operating costs resulting from the use of additives and energy expenditure and the need to dispose of the formed sludge [20-22].

In addition to these factors, each technique has its particularities, so that the choice of the process to be employed depends on operational parameters (contaminant concentration, desired removal efficiency, pH, etc.) and economic parameters. The main techniques for the removal of heavy metals from wastewater are: chemical precipitation, coagulation-flocculation, flotation, ion exchange, adsorption, biosorption, electrochemical techniques and membrane processes.

Chemical precipitation is a widely used technique in the removal of heavy metals from industrial effluents. The principle of this technique consists of raising the pH of the medium, around 11, which leads to the precipitation of metal hydroxides. This technique is suitable for the removal of metals in concentrations in the range between 100 and 1000 mg/L. The main advantages provided are the simplicity of the process and the low operating costs involved. However, the total removal of the dissolved metal species in the aqueous phase is not achieved. Consequently, in certain cases, the residual concentration of metal may be higher than the limits imposed by environmental legislation, which would require further complementary treatment [20].

Although they have different principles, because they are complementary, coagulation and flocculation techniques are usually addressed together. Coagulation consists of the destabilization of charged colloidal particles, through the use of coagulating agents, causing their coalescence and formation of flakes. In turn, in flocculation, with the help of flocculating agents, there is the growth of these flocs and their consequent sedimentation. Depending on the system, a single compound can be used that will play the role of coagulant and flocculant, or different compounds for each of the stages.

Compared to chemical precipitation, coagulation-flocculation allows the removal of metals at concentrations lower than 100 mg/L or higher than 1000mg/L. In addition, there is better stability and decantability of the particulate matter, with the formation of sludge with lower water content. However, coagulation-flocculation has disadvantages, such as higher operating costs, due to the use of chemical additives [20].

Depending on the characteristics of the effluent, flotation can be used after the coagulation-flocculation process, so that, in contact with the air, the formed flocs ascend to the surface of the liquid. Another possibility is the use of adsorbent materials, on the surface of which the adsorption of metals occurs. Among the adsorbents used, there are zeolites, biosurfactants and activated carbon. The main advantages of using flotation are: low cost of adsorbent material, high efficiency of removal in effluents with initial concentrations of metals in the range between 50 and 500 mg/L, possibility of separation at pH lower than that of chemical precipitation, low hydraulic retention time and low operational cost [20-22].

In the ion exchange process, there is a reversible exchange of ions between a solid phase and a liquid phase. In this way, as heavy metal ions are removed to the solid phase, other cations such as H+ and Na+ are transferred to the effluent [23]. In general, ion exchange is efficient in removing metals at concentrations below 10 mg/L, and can extend this efficiency to concentrations above 100 mg/L.

When compared to other heavy metal removal techniques, ion exchange has the following advantages: there is no sludge (solid waste) production, shorter operating times and the systems are compact. However, this process has some limitations, such as: the importance of efficient effluent pretreatment for particulate matter removal and the high costs of resins and operating costs. In view of the high costs of ion exchange resins, an alternative lies in the use of low-cost, high-availability natural ion exchangers [23, 24].

Adsorption is a mass transfer process in which the species to be removed is transferred from the liquid phase (effluent) to the surface of a solid, to which it is bound by physical and/or chemical interactions. Due to its high surface area and high adsorption capacity, activated carbon is the most used adsorbent in the removal of heavy metals. However, activated carbon is a relatively high-cost material, especially the best quality types, a characteristic that does not make it attractive for industrial use. In addition, the techniques of regeneration of activated carbon (chemical and thermal) are costly, cause a considerable loss of adsorbent capacity and generate effluents [20, 25, 26].

In order to develop processes with high efficiency and low cost, in the removal of heavy metals, the use of agricultural waste (orange, hazelnut and soybean peels), industrial by-products (lees, sludge and furnace slag) and clays have already been reported. so that large quantities of these are needed in the treatment of effluents [20, 25, 26].

Biosorption consists of adsorption on biomass (live or dead) and uses everything from microorganisms to aquatic plants. In a generic way, the term biosorption encompasses different independent metabolic processes that occur in the cell wall, such as: physical and chemical adsorption, electrostatic interactions, ion exchange, complexation, chelation and microprecipitation. Thus, these processes differ from oxidative metabolism (biodegradation). The main advantages of biosorption are high selectivity and efficiency and low cost [26].

Electrochemical techniques, such as electrolysis and electrochemical precipitation, also deserve the attention of researchers. Despite the high energy costs involved, these techniques emerge as alternatives for the removal of heavy metals, especially in view of the large volume of sludge generated with a significant toxic load in the processes of chemical precipitation and coagulation-flocculation. Electrolysis is a process that uses electric current for the occurrence of oxy-reduction reactions, so that in the cathodic region there is a reduction of metal ions in solution. Despite the energy expenditure, an advantage of this process is the possibility of removing metals in a wide concentration range, from values below 10 mg/L to concentrations greater than 2000 mg/L [27-29].

Electroflocculation combines the application of electric potential and chemical precipitation. The advantage of this process lies in the fact that heavy metals are removed through oxy-reduction reactions in an electrochemical cell without the need for continuous addition of chemical reagents, minimizing reagent costs. Depending on the characteristics of the electrodes, electrochemical precipitation can be performed in acidic medium or in basic medium [30-32].

MEMBRANE SEPARATION PROCESSES FOR CADMIUM REMOVAL FROM WASTEWATER

A membrane can be defined as a selective barrier, solid or liquid, that separates two phases and restricts the transport of one or several chemical species in a specific way. This transport can occur either by diffusion or convection, induced by a gradient of pressure, concentration, temperature or electric potential [33].

According to Londsdale [34] the first studies using membranes date from 1748, having been carried out by Nollet and Dutrochet. Since then, several other researchers have contributed to the development of these processes. As a result, at the beginning of the twentieth century, the production of microporous cellulose nitrate membranes began on a commercial scale, but with initial use limited to laboratory applications.

The main advantages associated with these processes are: low energy consumption, absence of chemical additives, the systems are compact, easy scale expansion, use in continuous or batch systems and the possibility of combining with other processes. However, this technology still has some drawbacks to be overcome, such as: low permeate flow, short membrane life and low selectivity for certain separations. In this sense, there is a large investment in research and development of new membrane-forming materials.

On a commercial scale, the most commonly used membranes are made up of synthetic polymers, which are called polymeric membranes. These can be classified in numerous ways, and the classification according to their structure (morphology) is the most used, since the separation mechanism and, consequently, its application are a function of morphology. According to this classification, membranes are subdivided into: porous and dense. In porous membranes, the transport of substances takes place through the pores. These can be classified as symmetrical and asymmetric. Symmetrical membranes do not show significant variation in pore size over the thickness of the membrane. In turn, asymmetric membranes have a porosity gradient throughout their thickness.

Dense membranes have no pores. The transport of substances through the polymeric matrix is carried out by a sorption-diffusion mechanism, and its selectivity is a function of the mobility of the permeants and their chemical affinity with the membrane-forming material. These can be classified as: homogeneous (the membrane is made up of the same material), integral (a thin dense layer that is responsible for the selectivity supported on the porous structure that gives mechanical resistance to the membrane) and composite (formed by a porous membrane covered by a dense film of another polymer).

Table 2 presents the main processes with membranes, the respective morphological structures of the membranes employed and the basic separation mechanisms. Of these processes, three are used in the removal of heavy metals from wastewater: electrodialysis, nanofiltration and reverse osmosis.

Table 2 - Characteristics of the main membrane separation processes.

Process	**Membrane structure**	**Driving force**	**Separation factor**
Microfiltration	Porous	Pressure difference (0.5 – 2 atm)	Retention by size
Ultrafiltration	Porous	Pressure difference (1 – 7 atm)	Retention by size
Nanofiltration	Porous	Pressure difference (5 – 25 atm)	Retention by size
Reverse Osmose	Dense	Pressure difference (15 - 80 atm)	Sorption-diffusion
Dialysis	Porous	Concentration difference	Diffusion in pores
Electrodialysis	Porous	Electric Potential Difference	Electric Charge
Gas permeation	Dense	Partial pressure difference	Sorption-diffusion
Pervaporation	Dense	Partial pressure difference	Sorption-diffusion

Electrodialysis is a membrane technique in which species ionized in solution permeate ion exchange membranes (cationic and anionic) under the action of an electric field. The main advantage of this process lies in the production of an aqueous stream that is virtually free of heavy metals and an extremely concentrated disposal stream. However, this technique has limitations, such as the need for a supply stream without the presence of particulate matter, equipment and operational costs, and low efficiency for solutions with concentrations higher than 100 mg/L [35].

Nanofiltration is a process that employs porous membranes, in which separation occurs basically by the rejection of the heavy metal cation due to its size. The diameter of the ion is larger than the average diameter of the pores. In reverse osmosis, the separation occurs by a mechanism of sorption-diffusion of the solvent through the membrane and rejection of the metal cation. Operationally, the only difference between these processes is in the applied pressure range. According to Qdais and Moussa [36], research has indicated that the application of reverse osmosis and nanofiltration in the treatment of effluents is extremely promising in terms of reducing operating costs, conserving natural resources and increasing the efficiency of pollutant removal.

In addition, it should be noted that reverse osmosis and nanofiltration processes do not require the use of chemical additives, which end up becoming a source of secondary contaminants [37]. In the same way, the sludge generated, in processes such as chemical precipitation, requires the investment of resources for its treatment and final disposal. Another advantage associated with nanofiltration and reverse osmosis is the possibility of recovering the metals at the end of the process.

Qdais & Moussa [36] conducted a comparative study with solutions of cadmium sulfate, copper sulfate and the mixture of cadmium sulfate and copper sulfate, using reverse osmosis and nanofiltration membranes. The results showed that both membranes were efficient in removing cadmium and copper. The average percentage of copper removal was around 97% in the reverse osmosis system and the rejection in the nanofiltration system was 84% and 96%.

Zuo *et al.* [38] studied multiple processes with membranes combined with physicochemical pretreatment in the galvanizing industry with the objective of selectively separating the heavy metals present in the effluent and reducing costs, in addition to reducing the effects caused by the presence of these contaminants in the environment. The processes were divided into three stages: the microfiltration and ultrafiltration processes were applied to separate possible organic suspensions, then the electrodialysis process was used to remove the salts, and finally the nanofiltration and reverse osmosis processes, carried out separately to increase the water recovery rate. Electrodialysis demonstrated excellent performance, achieving rejections above 97%. The permeate obtained from electrodialysis was used as feed in the nanofiltration and reverse osmosis processes. The results showed that nanofiltration was more effective in terms of selective separation between univalent and bivalent ions, with greater flow at lower pressures. In general, reverse osmosis showed better performance on salt rejection.

Table 3 presents more research relating the removal of some toxic metals from wastewater in relation to the processes mentioned above.

Table 3 – Removal of toxic metals using membrane processes

Referenced authors	Processes	Metals removed
Lohokare *et. al*., 2008 [39]	Ultrafiltration	AS3+
Huang *et al*., 2019 [40]	Ultrafiltration	CD2+
Garba *et al*., 2019 [41]	Ultrafiltration	Cd2+, Cu2+
Koli & Singh, 2023 [42]	Ultrafiltration/nanofiltration	Cd2+, Cu2+
Wang *et al*., 2020 [43].	Nanofiltration	Cu2+
Trus *et al*., 2020 [44]	Nanofiltration	Cu2+,
Pezeshki *et al*., 2023 [45]	Nanofiltration/Reverse Osmosis	AS3+
Caprarescu *et al*.,2014 [46]	Electrodialysis	Cu2+
Omran *et al*., 2024 [47]	Electrodialysis	Cu2+
Nthwane *et al*, 2024 [48]	Reverse Osmose	Ni2+, Cu2+, Nd2+
Kheriji *et al*., 2015 [49]	Reverse Osmose	CD2+
Sahebjamee *et al*. 2019 [50]	Reverse Osmose	Ni2+, Cu2+ ,Nd2+
Momtazan *et al*., 2018 [51]	Reverse Osmose	CD2+
Lumani Kapepula *et al*., 2022 [52]	Reverse Osmose	Cr3+, Pb2+, Cd2+, As3+ Ni2+, Sb+3

ELECTROLYTIC PROCESSES IN THE REMOVAL OF CADMIUM FROM WASTEWATER

An electrochemical cell is a device that uses oxide-reduction reactions to produce the interconversion of chemical and electrical energy. It is called an electrolytic cell when electrical energy from an external source is used to produce chemical reactions. Electrochemical processes are widely used for metal removal. The electrochemical cell is the basis of the process, consisting of an anode and a cathode, immersed in a solution. When the current is applied to the cell, the metals are deposited on the cathode, thus obtaining separation. Electrochemical recovery of metals basically involves two steps: electrodeposition of the metal, followed by some form of re-extraction to remove them from the cathode. The reextraction process can be carried out by chemical or electrochemical dissolution, by extractive electrolysis or reversal of the polarity of the electrode [53].

Dutra *et al*. [54] used a cross-linked vitreous carbon cathode in flux for the treatment of aqueous solutions containing cadmium at the usual concentration found in wastewater from metallurgical industries (15 to 100 ppm). It was possible to treat 2 liters of solution with an initial concentration of 210 mg/L, reaching a final concentration of 0.1 mg/L. Elsherief [28] describes the removal of cadmium from synthetic liquid residues by electrodeposition of cadmium on three-dimensional spiral steel electrodes. In this work, a cadmium removal of 30% of a dilute acidic solution was achieved.

Grau and Bisang [55] conducted a study on cadmium removal in dilute aqueous solutions. The authors cite three factors for the efficiency of metal removal: good mass transfer condition of the rotating cylinder electrode; large surface area of expanded structures; promotion of turbulence, however, as a disadvantage of the process is the high energy consumption.

MATERIALS AND METHODS

MATERIAL

The synthetic effluents evaluated consisted of aqueous solutions of cadmium chloride (CdCl2) for the electrodeposition tests and cadmium sulfate (CdSO4) for the reverse osmosis tests.

TANGENTIAL FILTRATION SYSTEM

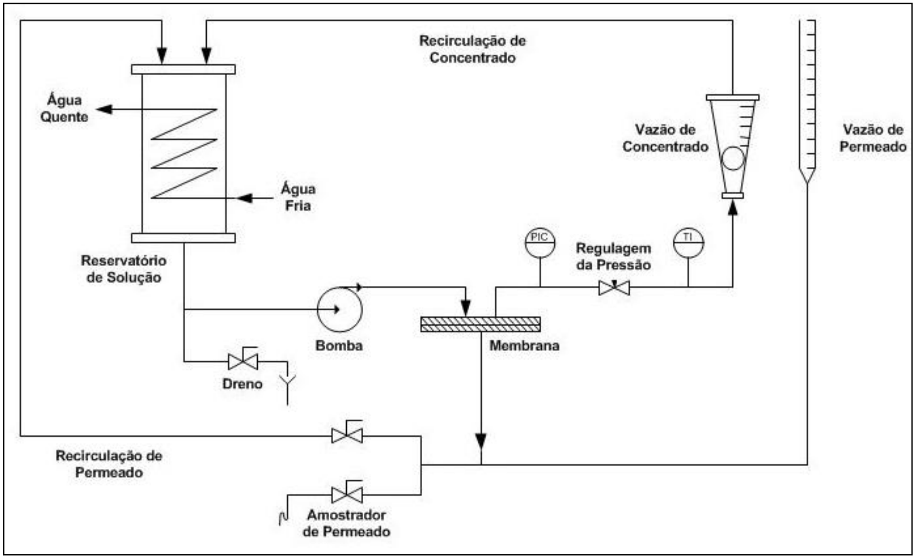
The commercial membrane used is composed of polyamide, model 4040-X201-TSA, manufactured by TriSep Corporation. The manufacturer's recommended operating conditions are: operating pressure from 7 to 21 bar, operating temperature from 2 to 45 ºC, and operating pH from 2 to 11. Figure 1 shows the tangential filtration system used in the experiments. The system has a tangential filtration module for a flat membrane, and the effective permeation area is 77.2 cm2.

Figure 1 – Tangential filtration system used

Figure 2 shows the flow chart of the filtration system, which consists of a feeding tank (capacity of five liters), current rectifier, rotameter, pressure gauge, thermometer, permeate flow indicator and centrifugal pump.

During the operation of the system, the system is pressurized gradually. The rotation speed of the pump is adjusted by the current rectifier. With the help of a back pressure valve, the pressure is regulated in the system. From the control of the current rectifier and the back pressure valve, it is possible to regulate the supply flow rate and the operating pressure.

Figure 2 - Flowchart of membrane systems



The maintenance of the temperature of the system was done through water circulation and during the operation, it was sought to control the temperature increase, which occurs due to pumping and friction, so there is cooling with water flow in a stainless steel coil in the feeding tank, thus preventing temperature fluctuations from interfering with the separation process. The system allows batch operation (with recirculation of the concentrate current) and continuous (with disposal of the concentrate current). In the operation of the system, it is possible to collect a permeate sample and measure its flow.

The analytical methods for determining the concentrations of metals both in the feed and in the permeate and concentrate were conductivity measurements, pH and atomic absorption and ion chromatography analyses.

The membrane performance effect was evaluated through metal rejection calculations and permeate flow determination. Rejection was calculated according to the following equation, which indicates the percentage of solute retained by the membrane.

$$R(\%) = \left[1 - \frac{C_p}{C_f}\right].100$$

Where:

R(%) = percentage solute rejection (%),

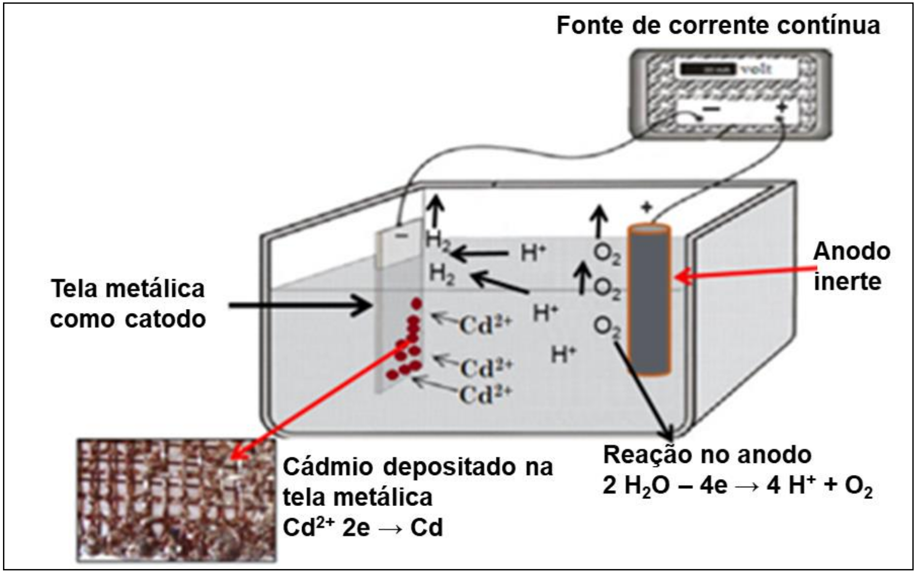
Cf = solute concentration in the feed (mg/L),

Cp = the concentration of solute in the permeate (mg/L).

ELECTROLYTIC SYSTEM

The electrolytic cell assembled in this study is formed by a platinum anode and a carbon steel cathode in the form of a wire mesh. Agitation was used in this process, for which a magnetic stirrer was used. For the application of voltage in the cell, a direct current power supply was used. The procedure was performed at room temperature and pressure, and no temperature or pH control of the solutions was performed during the removal process. The container where the electrochemical process took place has a volume of 280 mL, and the volumes of solution used were 250 mL. The cell schema is shown in Figure 3.

Figure 3 - Electrolytic cell schematic.



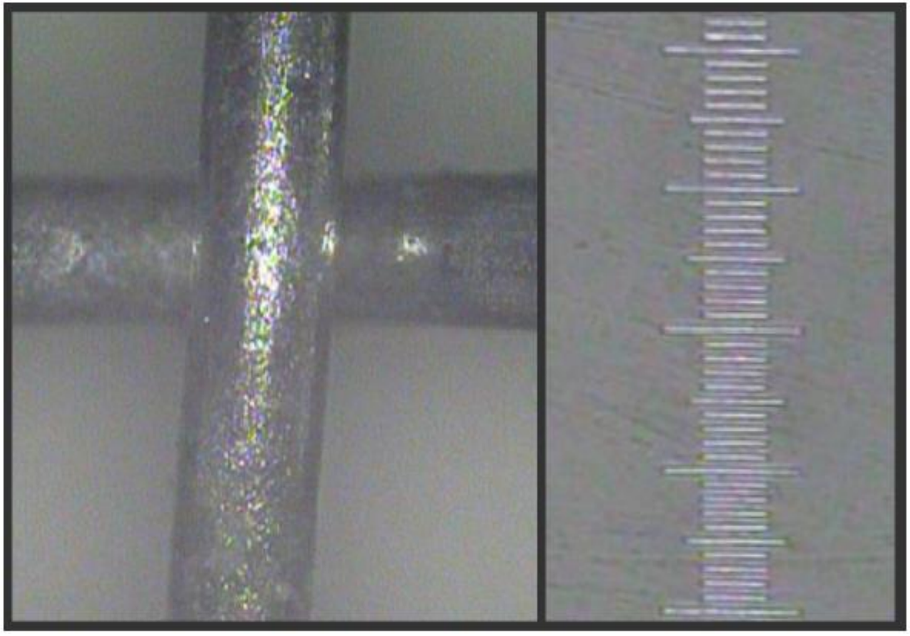
RESULTS AND DISCUSSION

CADMIUM REMOVAL BY ELECTRODEPOSITION

In the electrodeposition experiments, solutions with a volume of 250 mL and cadmium concentrations equal to 500, 250 and 50 mg/L were tested. The experimental results used in this item were obtained through a previous study carried out by Fernandes [6, 56].

The electrolytic system used a platinum plate with a surface area of 7 cm2 as anode. Carbon steel electrodes were used as cathodes, which corresponded to screens with braided wires, whose diameters varied between 0.10 and 0.15 mm. Figure 4 shows the image of the wires that make up the screen with microscopic magnification. In all experiments, the potential difference applied was 20 V.

Figure 4 - Image of the wires that form the screen with magnification under the optical microscope.



The main electrochemical reactions involved in electrodeposition are:

Anodic reaction: H_2O (l) → 1/2 O_2 (g) + 2 H^+ (aq) + 2 e;

Cathodic reaction: Cd^{2+} (aq) + 2 e^- → Cd (s)

In Figure 5 it is possible to observe the results of the electrochemical process the deposition of cadmium in the cathode.

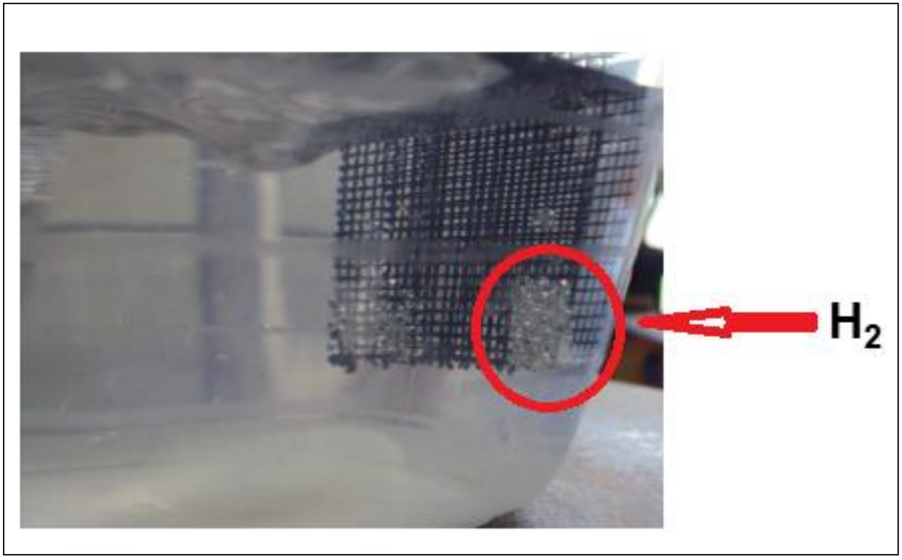
Figure 5 - Visual observations of the electrolytic process.

In addition to the main reactions, during the electrolytic process the formation of hydrogen gas is also observed in the cathode, according to the chemical reaction:

$2 H_2O (l) + 2 e^- \rightarrow H_2 (g) + 2 OH^- (aq)$.

This reaction, although secondary, occurred due to the low concentration of ions in solution, which led to a low electrodeposition speed, thus allowing the electrodeposition of the metal. In Figure 6, the formation of hydrogen gas in the cathode can be seen.

Figure 6 - H2 formation in the cathode.



In the experiments, the difference in applied potential (20 V) was fixed. Thus, as a function of the concentrations of the solutions, different values of electric current intensity are observed. This fact was due to the presence of ions in solution, since the intensity of electric current is a function of the electrical conductivity of the medium. The experiments aimed to analyze the influences of the applied current intensity, the electrodeposition time and the cathode area for the different cadmium ion solutions.

Table 4 presents the results obtained for the solution with an initial concentration of 500 mg/L. When comparing the results obtained in experiments 1 to 4, it is observed that the increase in the surface area of the cathode led to an increase in cadmium deposition, keeping the other parameters constant. These results can be seen in the graph in Figure 7.

When comparing the results obtained between the pairs of experiments 1-5 and 2-6, it is verified that the increase in the intensity of the electric current applied led to an increase in the percentage removal of cadmium. Likewise, when comparing the results obtained between experiments 5 and 7, it was observed that the increase in the deposition time led to a greater cadmium deposition. The results of the influence of time and intensity of applied electric current are in accordance with those predicted by Faraday's Law, from which the mass of metal deposited is directly proportional to the applied current and the electrodeposition time.

Table 4 - Results obtained for the initial concentration of CD2+ equal to 500 mg/L.

Tests	Area cm^2	Time Min	Tension V	Current A	Final concentration, mg/L	Removal, %
1	36,44	90	20	0,08	159,83	69,1
2	27,33	90	20	0,08	180,15	65,1
3	21,86	90	20	0,08	184,29	63,5
4	16,78	90	20	0,08	197,47	60,9
5	36,44	95	30	0,15	16,52	96,7
6	27,33	95	30	0,15	67,05	86,5
7	36,44	120	30	0,15	10,03	98,0

Figure 7 - Influence of cathode area on the percentage removal of cadmium ions in solution.

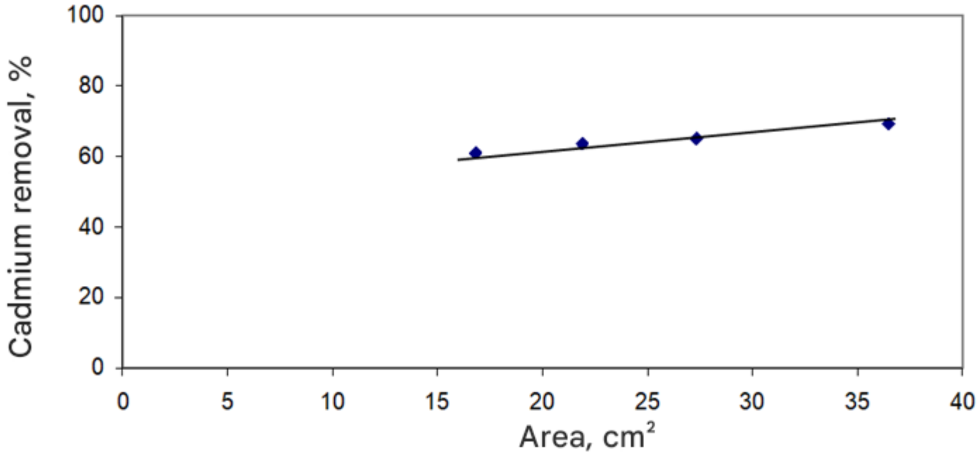


Table 5 presents the results obtained for the initial concentration solution of 250 mg/L. When comparing the results obtained in the pairs of experiments 1-2 and 3-4, it is observed that the increase in the cathode area led to a greater electrodeposition of cadmium, keeping the time and intensity of the current constant. The influence of time can be seen when comparing experiments 3 and 5, in which the increase in time led to the greater formation of cadmium metal.

Table 5 - Results obtained for the initial concentration of Cd2+ equal to 250mg/L.

Tests	Area cm2	Time min	Tension V	Current A	Final concentration, mg/L	Removal, %
1	36,44	90	20	0,06	45,00	82,5
2	27,33	90	20	0,06	65,27	74,6
3	36,44	80	30	0,09	69,26	71,1
4	27,33	80	30	0,09	74,96	68,7
5	36,44	120	30	0,09	48,15	79,9

Table 6 presents the results obtained for the solution with an initial concentration of 50 mg/L. When comparing the results obtained, it is observed that the increase in the cathode area led to a greater electrodeposition of cadmium, keeping the time and intensity of the current constant.

Table 6 - Results obtained for the initial concentration of Cd2+ equal to 50mg/L.

Tests	Area cm2	Time min	Tension V	Current A	Final concentration, mg/L	Removal, %
1	36,44	90	20	0,04	15,57	66,3
2	27,33	90	20	0,04	20,73	55,1

Due to the limitations of the experimental apparatus used and the concentration of the solution, it is observed that as the concentration of cadmium in solution is reduced, there is a reduction in the removal achieved. Thus, the electrolytic system allowed better results for the tests with a concentration of 500 mg/L, in which it was possible to achieve the highest values of current intensity (0.15 A) and removal, reaching 98%. The experiment with a concentration of 50 mg/L, on the other hand, led to the lowest values of applied current intensity (0.04 A) and a maximum removal of 66.3%.

CADMIUM REMOVAL BY REVERSE OSMOSIS

The reverse osmosis experiments were carried out in the tangential filtration system. In this system, three liters of the feed solution were processed in batch, with recycle of the concentrate and collection of the permeate. The aim was to evaluate a range of initial concentrations from 5 to 1500 mg/L. In all experiments, the system was operated with a feed flow rate of 1 L/min and a pressure of 10 bar.

Table 7 presents the results of permeate current concentration and rejection (removal) for the different initial concentrations evaluated.

Table 7 - Results obtained in the reverse osmosis experiments.

Initial concentration (mg/L)	Permeate concentration (mg/L)	Rejection (%)
4,49	0,17	96,1
15,77	0,39	97,5
153,6	0,70	99,5
490	1,43	99,7
680	2,25	99,6
1430	5,30	99,7

In the graphs of Figures 8 and 9, the permeate concentration and rejection profiles are observed as a function of the initial concentration. From the analysis of these graphs, it can be seen that the concentration of the permeate increases as a function of the increase in the concentration of feed. However, when observing the rejection profile, it is verified that for feed concentrations lower than 100 mg/L, the rejection increases as a function of the feed concentration. From 100 mg/L, rejection remains practically constant, ranging from 99.5 to 99.7.

Figure 8 - Permeate concentration as a function of feed concentration.

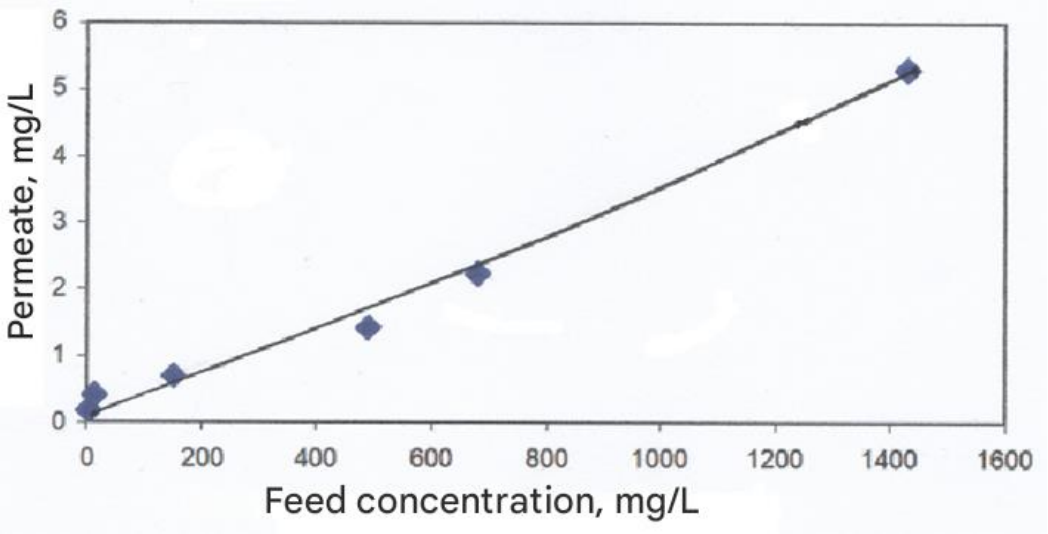
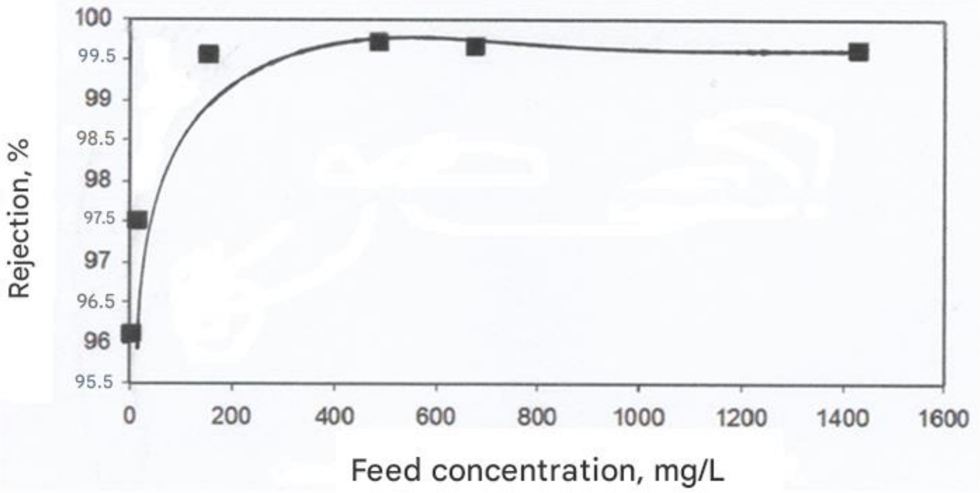


Figure 9 - Rejection as a function of feeding concentration.



CONCLUSIONS

From the analysis of the results obtained, it can be seen that the electrolytic process allowed high values of cadmium removal for concentrations of around 500 mg/L. This process, in addition to being simple and not requiring the use of chemical additives, has the advantage of enabling the recovery of cadmium in its metallic form. The biggest drawback is that its efficiency is directly proportional to the electrical conductivity of the medium and for solutions of low concentrations of metals, the reduced conductivity proves to be an impediment.

The reverse osmosis process proved to be extremely efficient for low concentrations of cadmium in solution, reaching removals above 96% for concentrations of the order of 5 mg/L. The main advantage of this process is to obtain a treated stream with concentrations lower than 0.2 mg/L, thus adapting to the disposal limits required by environmental legislation.

By analyzing the two processes, it is possible to propose their use in a complementary way. In a first step, the electrolytic process to remove the highest concentration of cadmium, followed by reverse osmosis to reach values acceptable by legislation.

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