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REVIEW OF METHODS FOR GREENING WASTEWATER FROM ELECTROPLATING INDUSTRIES

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Ion-exchange treatment is a process used to remove heavy metals, salts of alkaline and alkaline earth metals, free mineral acids, alkalis, and some organic substances from the wastewater of electroplating plants. This method of purification is widely used to make valuable solutions from electroplating plants suitable for reuse and to produce clean process water that can be used in cleaning processes. Ion exchange is reversible, so saturated ionite can be regenerated and reused.

The process of removing suspended particles from a liquid using bubbles generated during electrolysis is called electroflotation. During electroflotation, gas bubbles generated by electrolysis and suspended in the liquid interact with the contaminant particles, causing the particles and gas bubbles to adhere to each other due to the low surface energy at the liquid-gas interface. The resulting flocculant has a lower density than water, which facilitates its transport to the surface of the liquid, where it accumulates a suspended sediment that is periodically removed from the equipment.

Wastewater treatment by electrodialysis involves the removal of dissolved mineral salts, acids, alkalis, and radioactive substances in a multi-chamber device (electrodialyzer) under the influence of direct current. This method is also widely used for brine desalination. It is used to treat wastewater from fluorine and chromium compounds with a desalination rate of 75–80 %.

Impurities can be removed from wastewater by arranging several membranes through which positively or negatively charged ions alternately pass. These membranes form a concentration chamber and a desalination chamber. Ions are concentrated in one chamber and removed in the other.

Ultrafiltration is a membrane separation process designed to purify water from impurities up to 0.01–0.1 microns in size. The average operating pressure for this technology is 2–3 MPa. The average pore size of an ultrafiltration membrane is 0.01–0.03 microns. The driving force behind ultrafiltration is the pressure difference between the two sides of the membrane (operating pressure and atmospheric pressure). *Key words:* ion-exchange treatment, electroplating, electroflotation, electrodialyzer, ultrafiltration.

Огляд методів екологізації стічних вод гальванічних виробництв. Феденко Ю.М., Косенко К.О.
Іонообмінне очищення – це процес, який використовується для видалення важких металів, солей лужних і лужноземельних металів, вільних мінеральних кислот, лугів і деяких органічних речовин зі стічних вод гальванічних виробництв. Цей метод очищення широко використовується для того, щоб зробити цінні розчини, отримані на гальванічних виробництвах, придатними для повторного використання, а також для отримання чистої технічної води, яка може бути використана в процесах очищення. Іонний обмін є оборотним, тому насичені іоніти можуть бути регенеровані і використані повторно.

Процес видалення зважених часток з рідини за допомогою бульбашок, що утворюються під час електролізу, називається електрофлотацією. При електрофлотації бульбашки газу, що утворюються в результаті електролізу і знаходяться в зваженому стані в рідині, взаємодіють з частинками забрудненика, в результаті чого частинки і бульбашки газу прилипають одна до одної через низьку поверхневу енергію на межі поділу фаз рідина-газ. Утворений флокулянт має меншу щільність, ніж вода, що полегшує його транспортування до поверхні рідини, де накопичується зважений осад, який періодично видаляється з обладнання.

Очищення стічних вод методом електродіалізу полягає у видаленні розчинених мінеральних солей, кислот, лугів і радіоактивних речовин у багатокамерному пристрої (електродіалізаторі) під впливом постійного струму. Цей метод також широко використовується для опріснення розсолів. Застосовується для очищення стічних вод від сполук фтору і хрому зі ступенем знесолення 75–80 %.

Домішки можуть бути видалені зі стічних вод шляхом розташування декількох мембран, через які по черзі проходять позитивно або негативно заряджені іони. Ці мембрани утворюють камеру концентрації та камеру опріснення. В одній камері іони концентруються, а в іншій – видаляються.

Ультрафільтрація – це процес мембранного розділення, призначений для очищення води від домішок розміром до 0,01–0,1 мікрона. Середній робочий тиск для цієї технології є 2–3 МПа. Середній розмір пор ультрафільтраційної мембрани становить 0,01–0,03 мкм. Рушійною силою ультрафільтрації є різниця тиску між двома сторонами мембрани (робочий тиск і атмосферний тиск). *Ключові слова:* іонообмінна обробка, гальванопластика, електрофлотація, електродіалізатор, ультрафільтрація.

Introduction. Electroplating is one of the most hazardous industries. Since the enterprises are characterized by a wide variety of technological processes, the composition of solutions and electrolytes, and a wide range of processed parts, the resulting wastewater is quite diverse in terms of both its qualitative and quantitative composition. The workshops and sites operating in the country are built using the same technology and solve only the tasks of either coating or metal surface treatment, with little or no regard for the processes of removing heavy metal ions from wastewater, recycling galvanic waste, and protecting the environment [1].

Many enterprises still use old and no longer effective treatment processes, and sometimes do not have any treatment facilities at all, which leads to untreated and insufficiently treated wastewater entering surface water bodies. A fundamental solution to the problem of water pollution is to develop and implement closed water recycling cycles and resource-saving technological processes that allow valuable components to be returned to production, eliminating the discharge of polluted wastewater into water bodies, and are economically viable and environmentally friendly. The existing technological scheme for the treatment of wastewater from electroplating shops of coal mining enterprises has been improved based on its post-treatment by ion exchange. The use of ion exchange filters at the final stage of wastewater treatment is proposed. The implementation of the proposed improved technological scheme of wastewater treatment significantly reduces the content of pollutants, such as heavy metal compounds, to water quality standards and, thus, the production system of closed water circulation, i.e., returning up to 95 % of the purified water to its own production needs (preparation of solutions and electrolytes, washing operations, etc.) [1].

Ion-exchange method. Ion exchange purification is a process used to remove heavy metals, salts of alkaline and alkaline earth metals, free mineral acids, alkalis, and some organic substances from the wastewater of electroplating operations.

This method of purification is widely used to make valuable solutions from the electroplating process suitable for reuse, as well as to produce clean process water that can be used in cleaning processes.

Ionite is an organic and inorganic polymeric material. It can absorb positively or negatively charged ions from electrolyte solutions and exchange them in equal amounts with other ions of the same charge sign. Depending on the charge sign, the exchanged ions are cations and anions. There are also amphoteric ionite and amphoteric solvents that can exchange cations and anions simultaneously [2–4].

Ion exchange is reversible and the saturated ionite can be regenerated and reused.

Ion exchange resins are synthesized as microparticles consisting of a branched polymer matrix and functional groups. Polymer matrices are classified by the type of polymer that acts as a linear backbone and crosslinker. Divinylbenzene (DVB) and styrene-divinylbenzene (SDB) are the most used.

Depending on the value of the dissociation constant of the functional group, strongly acidic salts of cationic acids (such as H^+ or Na^+), strongly basic salts of anionic acids (such as OH^- or salts), and mixed ionite are distinguished (Fig. 1) [5].

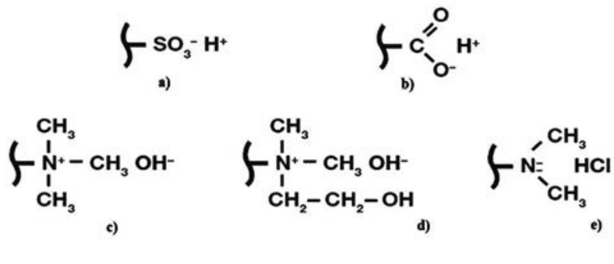

Fig. 1. Functional groups of polymeric organic compounds: a) – strongly acidic; b) – weakly acidic; c), d) – strongly basic; e) – weakly basic

Strongly acidic cationic acid salts containing SO_3^- are used to treat wastewater from electroplating operations.

Table 1 shows the main characteristics of certain anionites and cationite [6].

Table 1

Properties of cationic and anionic acid salts used for electroplating wastewater treatment [6]

Notation	Characteristic			
	Active group	Granulometric composition, mm	General exchan-geability, mg-eq./g	working ability to exchange, g-eq./L
Cationite				
KPS	SO_3H	0.4–1.3	4.7	1.4
KS 10	SO_3H	0.4–1.3	4.6	1.1
Anionite				
SBT	$N(CH_3)OH$	0.7–2.1	3.1	0.4
AK 40	$NH_2 \cdot NHR$	0.4–1.3	5.6	1.4

Ionic loading of filters of various designs. Typically, wastewater is treated by passing it through an ion exchange medium with cations (H^+) and anions (OH) in sequence. When strong and weak acidic anions are present in the water, ion exchange occurs in two stages: first with a weakly basic anionite to remove strong acidic anions, and then with a strongly basic anionite to remove weak acidic anions. In the process of wastewater treatment, the ionite is saturated with cations and anions through the following reactions (1, 2):

$$nR - H + Me^{n+} = R_n - Me + nH^+ , \quad (1)$$

$$nR - OH + An^{n-} = R_n - An + nOH^- . \quad (2)$$

Prior to loosening, the saturated ionite is regenerated with clean water at an intensity of 3–5 $dm^3/(sec \cdot m^2)$. Cationic acids are regenerated in 2–8 % solutions of mineral acids, while anionic acids are regenerated in 2–6 % solutions of caustic alkalis. These processes can be represented by the following reactions (3, 4):

$$R_n - Me + nH^+ = nR - H + Me^{n+} , \quad (3)$$

$$R_n - An + nOH^- = nR - OH + An^{n-} . \quad (4)$$

After regeneration, the ionite is washed. The solution produced during the ion exchange process is further processed to recover and neutralize valuable chemicals.

The advantages of ion exchange are high quality wastewater treatment, ease of operation and maintenance, low energy consumption and the ability to reuse up to 95 % of the treated water. However, this method also has disadvantages, such as the high cost of reagents required for ion exchange, a large area and high salt concentration in wastewater. The salts accumulated because of the exchange cannot be discharged directly into the sewerage system. They must also be brought to MPC standards or sent for disposal [7].

Electroflotation method. The process of removing suspended particles from a liquid using bubbles generated during electrolysis is called electroflotation. During electroflotation, gas bubbles generated by electrolysis and suspended in the liquid interact with contaminant particles, causing the particles and gas bubbles to adhere to each other due to the low surface energy at the liquid-gas interface. The resulting flocculant has a lower density than water, which facilitates its transport to the surface of the liquid, where a suspended sediment accumulates and is periodically removed from the equipment [8].

The electroflotation method involves the physical and chemical processes of bubble formation during electrolysis, the adhesion of bubbles and contaminant particles, and the transfer of the formed flocculant to the surface of the treated liquid.

The efficiency of the flotation method can be improved by increasing the surface area of the bubbles and the area of contact with the particles. Smaller bubbles increase the overall surface area and reduce the distance between the particles and bubbles, increasing the likelihood of collision between them. In electroflotation, the bubbles are 100 microns or smaller, resulting in a higher degree of purification compared to conventional flotation [9].

The main actor in electroflotation is the hydrogen bubbles released at the cathode. The size and density of hydrogen bubbles depend on the composition and temperature of the process solution, the surface tension of the electrode-solution interface, the material, shape and roughness of the electrode, and the current density. By changing these parameters, it is possible to adjust the size and density of gas bubbles during electrolysis, i.e., the technological process of water purification in accordance with the nature of the contamination [10].

The negative charge of hydrogen bubbles creates an excess of OH^- ions in the cathode cavity, which helps to repel bubbles from the electrode surface. The higher the electric field strength and the magnitude of the electrode charge, the greater the force that repels the bubbles from the electrode, and the smaller the bubbles. The greater the surface roughness of the electrode, the greater the electric field roughness. The electric field strength is higher at protrusions, corners and small radius wires and rapid growth and separation of small bubbles can be expected due to the increase in current density.

The saturation of liquid hydrogen bubbles is directly proportional to the cathodic current density and inversely proportional to the density and radius of the hydrogen bubbles (i.e., their growth rate).

The optimum current density depends on the physical and chemical properties of the system and should generally not exceed 3 A/dm^2 when treating wastewater from insoluble impurities [11].

Electrochemical modules for deep post-treatment are designed to remove small ions from wastewater in the presence of various anions, in the ratio of any component. The module is based on the electroflotation removal of insoluble compounds of heavy non-ferrous metals, mainly in the form of phosphates, by flotation with hydrogen and oxygen bubbles separately or in a mixture at pH 7–10. The use of titanium anodes with an insoluble oxide coating ensures high quality treatment without secondary water pollution. Floating sediment is removed from the electroflotation cell using a filament collector [12].

The advantages of the electroflotation method include treatment in accordance with the MPC requirements, low reagent consumption, ease of operation, small equipment footprint and removal of grease, oil products and suspended solids. The disadvantages of this method are the following: insufficiently high performance of the electroflotation unit, emissions of H_2 bubbles, electrode and maintenance costs, and significant sedimentation [13].

Electrodialysis method

Wastewater treatment by electrodialysis involves the removal of dissolved mineral salts, acids, alkalis, and radioactive substances in a multi-chamber device (electrodialyzer) under the influence of direct current. This method is also widely used for brine desalination. It is used to treat wastewater from fluorine and chromium compounds with a desalination rate of 75–80 %.

Impurities can be removed from wastewater by arranging several membranes through which positively or negatively charged ions alternately pass. These membranes form a concentration chamber and a desalination chamber. Ions are concentrated in one chamber and removed in the other (Fig. 2). [14].

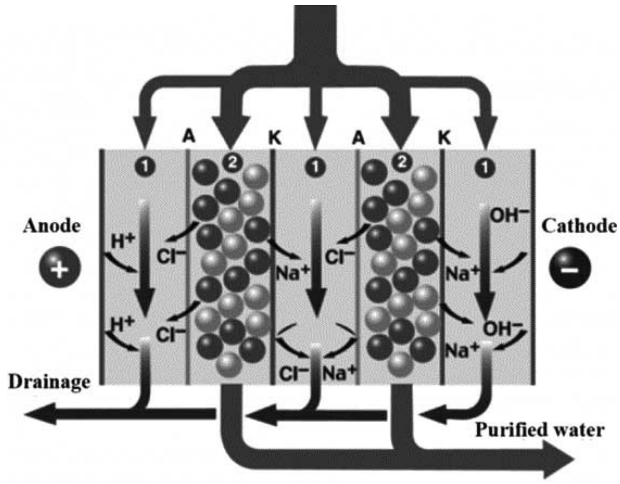

Fig. 2. The process of electrodialysis.
K – cationic membrane; A – anionic membrane;
(-) – cathode; (+) – anode

The electrodialysis cathode is made of stainless steel or titanium, and the anode is made of coated titanium or graphite. The service life of the membrane depends on the degree of pollution of the wastewater with suspended solids and ranges from 2 to 5 years [15].

The electrodialysis complex is periodically cleaned with sulphuric acid. This ensures that the electro-dialysis plant remains operational and prevents excessive electrical resistance due to the formation of a salt film on the membrane.

Fig. 3. Type of filtration through an ultrafiltration membrane

The advantages of the electrodialysis method are purification to the MPC level, return of up to 60 % of the purified water to the recycling cycle and recycling of valuable components [16–18].

The disadvantages of this method are the need for pre-treatment of wastewater from oils, surfactants, solvents, organic matter and hardness salts, high energy consumption, high cost of membranes, complexity of operation and sensitivity of membranes to changes in wastewater parameters [19].

Ultrafiltration

Ultrafiltration is a membrane separation process designed to purify water from impurities up to 0.01–0.1 microns in size. The average operating pressure for this technology is 2–3 MPa. The average pore size of an ultrafiltration membrane is 0.01–0.03 microns. The driving force behind ultrafiltration is the pressure difference between the two sides of the membrane (operating pressure and atmospheric pressure) [20].

Ultrafiltration membranes are used to retain colloidal and high molecular weight substances, bacteria, and viruses. However, since any salts dissolved in the water pass through them, this process is often used as a pretreatment step before reverse osmosis or ion exchange [21].

Organic and inorganic polymeric materials are used to make membranes. Ceramics and cermet are common inorganic materials. Polyester sulphone (PES), polystyrene (PS), polyacrylonitrile (PAN) and polyvinylidene fluoride (PVDF) are the best organic polymers. They have good permeability, are easily modified, hydrophilic, and have high mechanical strength. The problem with such membranes is their low thermal stability [22].

The main types of membrane elements are hollow-fiber, tubular, flat frame and roll membranes. Hollow-fiber and tubular membranes are characterized by the highest specific capacity and compactness. They are also designed to ensure efficient membrane surface regeneration [23].

There are two types of filtering configurations: «from the outside in» and «from the inside out» (Fig. 3). The main advantage of the first type is that the surface of the fibers can be cleaned with air, which reduces the consumption of reagents for membrane cleaning. Pressurized air blowing loosens contaminants on the membrane surface and facilitates their removal [24].

Mechanical and colloidal contaminants are removed by backwashing the membrane, biological contaminants by oxidant backwashing, inorganic contaminants by acid cleaning and organic contaminants by alkaline cleaning.

The advantages of water purification by ultrafiltration are the automation of the process, the ability to remove many contaminants (colloids, polymeric substances, bacteria, and viruses) simultaneously, low reagent consumption, small equipment area and relatively low electricity consumption. The disadvantage is that it does not remove dissolved inorganic substances [25].

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