

OPTIMIZATION TECHNIQUES FOR THE NEUTRALIZATION OF THE POLLUTED WATERS FROM METAL PLATING

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ABSTRACT

The problems related to the protection of the environment are regarded especially as a result of the local pollution by the industry and agriculture or by the overcrowded areas, which have led to the disturbance of some ecosystems and to worse living conditions of people. The extensive use of chemical substances in the technological processes demands special measures concerning the protection of the environment. A major problem is the purification of industrial waste water.

KEYWORDS: metal plating, polluted water, purification

1. Introduction

In this paper, we will present a solution for the treatment of the cyanides water from galvanic industry.

The removal of the residual pollutants existing in the effluents from the mechanical - biological purification stations of waste waters implies the use of the electrolysis processes effects in order to resolve the issues of the related domain. A series of conditions, locally established in Romania, through the Technical Rules of Waters Protection (NTPA001 and NTPA002), and on the European plan for the member states through the CCEE Directives no. 271/91 and no. 676/91 are designed to fit within the specify limits the acceptable level of the pollutants in the effluents.

NTPA - 001 refers to the waste waters of any kind, namely to waste water, industrial waste, agro-zootechnical, of mine or deposits water, evacuated through arranged fire systems coming from own technological processes, as well as from the mixed used water, which were or not cleaned. The values shown in these norms are maximum admissible values.

NTPA - 002 refers to the quality of waste water, from both social and economic activities, which are to be evacuated in the sewerage networks of the towns and, directly, in the treatment plants. The establishment of technological process, the origin and the quality characteristics of the waste water requires the knowledge of the industrial process for a judicious design of the purification stations.

Therefore, it is necessary to know the origin of the main flows and their main characteristics to define the method of purification. The reduction of waste water requires the use of new technologies. The main harmful substances of industrial waste water are the organic substances, the substances in the suspension, the toxic substances and the heavy metals, the synthetic detergents, etc. The recovery of the valuable substances from the waste waters is aimed at their reduction of the discharged harmful substances [1].

As a result of these chemical analysis we have chosen to preserve the existing neutralization process and following it, to apply an electrolytic oxidation followed by a process of adsorption on activated charcoal and a final filtration in a granular filter with sand.

2. Waste water neutralization

For the waste water in A basin (with cyanides):

- it is adjusted the pH of the solution between $7 \div 8$: if the $\text{pH} < 7$, NaOH is added; if the $\text{pH} > 8$, HCl is added;
- 4 l sol. CaCl_2 / 4 t sol. tank is added (5 kg $\text{CaCl}_2/100$ l H_2O);
- stirred 15 minutes;
- 3 l $\text{FeCl}_3/1000$ l sol. tank is added;
- stirred for 15 minutes;
- add 2.5 l polyelectrolyte/1000 l sol. from the tank;
- mix $3 \div 5$ minutes;
- after agitation $2 \div 3$ hours are expected for sludge decantation.

For the waste water in B basin (with metallic ions):

- add the H₂SO₄ to pH = 0 ÷ 2;
- add sodium metabisulfite for reducing chromium hexavalent from +6 to +3 up to the point of change of color from red to blue-green;

- add, all the time, sodium metabisulfite (the solution is obtained by dissolving 10 kg quantity of sodium in 100 l hot water);
- after a primary settling, the water of the tanks 5 and 6 are entered in the tanks 7 where takes place the final decantation and, then, filtering.

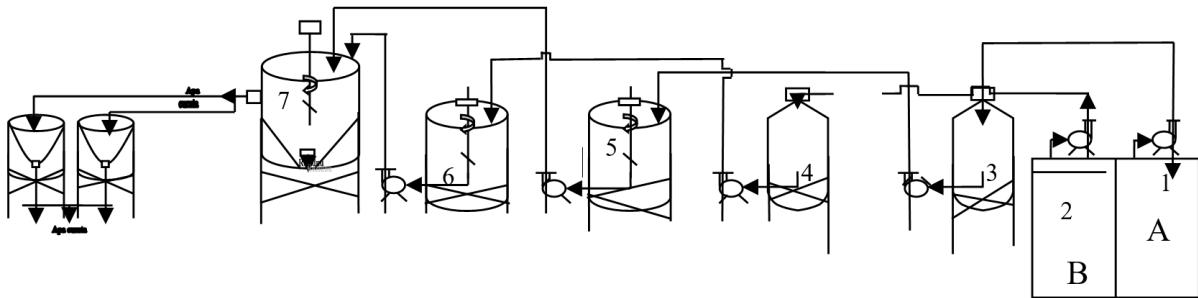


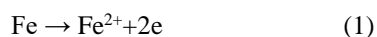
Fig. 1. Electro chemical purification of waste water to metal plating

In the mechanical engineering industry, there is the electro-metallurgy branch in aqueous galvanic-technical medium. The waste waters resulting from the washing of the galvanic covered pieces or electrochemical treated contain toxic impurities, often, non-biodegradables Cr⁶⁺, CN⁻ etc. which require their cleaning before discharging in the natural circuit. The removal of the hexavalent chromium combinations will be carried out by chemical reduction or electrochemical ions at Cr³⁺, less toxic and whose combinations are mostly insoluble [2].

The chemical methods have the disadvantage of being effective in a pH-acid limited area and require reactants for carrying out the reduction reaction. The electrochemical methods eliminate these disadvantages and, in addition with the removal of ions containing Cr⁶⁺, other harmful impurities can be removed. The electrochemical treatment consists in subjecting the contaminated water to an electrolyze process with water-soluble anode made of alloyed aluminum with 0.01-1 % indium or gallium as well as of iron or ferrous material [3].

In the case of using iron anodes, as a result of the electrolysis process, the following processes take place:

- on cathode: a) the reduction of chloride H⁺ ions and, therefore, the alkalizing of the cathode space; b) the reduction of Cr⁶⁺ at Cr³⁺ chloride ions, which together with the OH⁻ ions make forming an insoluble precipitate, Cr(OH)₂;
- on anode: the iron ionization in accordance with the reaction:



The Fe²⁺ ions precipitate in the form of ferrous hydroxide, rough, which, in the presence of dissolved oxygen, passes, partly, in the ferric hydroxide. The total reaction product is an insoluble hydroxides complex that incorporates impurificator ions in the form of Cr(OH)₃.

The presence of iron complex determines that the chromium hydroxide, which normally require a specific pH domain for a full precipitation, should no longer be sensitive to pH, this can vary within broad limits (pH = 4-11).

The studies have been carried out on synthetic waters, containing 200 ppm Cr⁶⁺ and 20 g/L sodium sulphate necessary to increase the conductivity [4]. The original solution and the filtrate after the electrolysis process of have been subjected to the analysis for the Cr⁶⁺ and Cr³⁺ ions determination after the "iodometric" manganometrical method.

Is was used a parallelepiped shaped cell made of plexiglass, having a useful 0.3 l capacity. The anodes and cathodes have the dimensions 50 x 30 x 1 mm (the grilling surface - 30 cm²) and they were made of the same carbon steel material [4].

The electrodes have been fitted in parallel and in series at a distance of 0.8 cm. In the case of fitting in parallel, the electrode number was variable, while in the case of fitting in series, we worked with a constant number of nine electrodes, which corresponds to eight electrochemical cells.

3. Experimental results

The experiments have pursued the effectiveness of the polluted waters purification and the specific consumption of energy, depending on the density of

the anode (number of anode manufacture) and the time of the electrolysis.

There have been made tests with a number of four anodes at smaller density and time electrolysis. It was found that, both anode current density decreases less than 0.2 A/dm², as well as of the electrolysis time reduction below 30 minutes have adverse effects on the treatment efficiency (Table 1); also, the efficiency of the purification at the parameters of the electrolysis of links the point A (anode surface 1.2 dm²) is presented.

Table 1. The efficiency of the purification

The density of the anode current	Time for electrolysis	Treatment efficiency	Obs.
[A/dm ²]	[min]	[%]	
0.2	30	100	Point A
0.18	30	92.3	
0.15	30	83.9	
0.2	25	83.0	
0.2	20	64.2	

The dependence of the specific energy consumption on the current density for the variable anode areas is: 1-0.3 dm²; 2-0.6 dm²; 3-0.9 dm²; 4-1.2 dm². In accordance with the fitting of the electrodes in parallel, a surface anode of 1.2 dm² (four anode manufacture) provides an effective way of 100% at a current density of 0.2 A/dm² and a treatment duration of 30 minutes, the energy consumption being 0.45 kWh/m³.

The precipitate which was formed, includes the impurificator in the form of chromium hydroxide, and it has the appearance of powder and is easily filtered. The only disadvantage of this procedure consists in the relatively high treatment duration which does not allow the achievement of a continuous process.

The fitting in series of the electrodes allows the increase of the current anode density for a relatively low volumetric density, whereas total intensity in the circuit is equal to the intensity of a single electrochemical cell. Based on these grounds we aimed to reduce the time for electrolysis processes by increasing the density of the current on an electrode. Admitting that maintaining water during ten minutes in the electrolyzer leads to performing a continuous flux treatment we tried to find the optimum current density which will ensure a high efficiency and minimal power consumption for this time.

It is found that the efficiency of the treatment increases from 37 to 96.7% when the density of current increases from 0.2 to 1 A/dm², after which,

the increase of current density two and three times, raises the efficiency only with few percent.

The energy consumption also has a high increase at the current densities by 2 and 3 of/dm², caused by the increase of the voltage at the terminals, a result of strong polarization of electrodes. Therefore, under the conditions of fitting of the electrodes in series a 10-minute treatment can be made, at a current density of 1A/dm², thus ensuring a efficiency over 95% with a power consumption of approximately 1 kW/m³.

The optimal conditions were obtained in the conditions of an electrochemical treatment with steel carbon anodes fitted in series.

The use of higher concentrations of Cr⁶⁺ ions led to the drop in the efficiency of the method because of electrode passivation. If the case of parallel fitting electrodes, an anode surface of 1.2 dm²/0.3 l solution at a current density of 0.2 A/dm² for 30 minutes allows to perform a treatment with an efficiency of 100% and a consumption of 0.45 kWh/m³.

The fitting of an equal number of electrodes allowed the reducing of the electrolysis time to 10 minutes, the efficiency of the treatment being 96.7 % at the density of 1 A/dm², with a power consumption of 1.1 kWh/m³. The water treatment containing Cr⁶⁺ ions in a cell with pads fitted in parallel is twice more economical than in the case of their fitting in series, but it shows the disadvantage of a higher duration and of the process discontinuity [5].

The option for a system or the other will depend on the quality of the waters which are to be purified, the need for a continuous process being imposed in the case of chroming installations with a higher production.

3.1. Electrolytic purification of industrial waste water

The development of the industry and in particular of the chemical industry imposes special measures concerning the protection of the environment; in this context, a major problem is the purification of industrial waste water.

The development and implementation of sewage technologies at a technical contemporary level require a modern process to ensure a more advanced impurificator removal at a low cost.

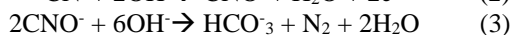
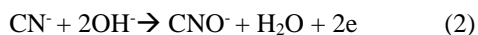
Among the processes applied at present for purification waste water, a special place is occupied by the electrochemical methods, because of the possibilities they can offer:

- a wide area of appliance;
- the advanced destruction of the biodegradable impurificators;
- the recovery or the regeneration of valuable products.

Depending on the way the removal of the impurificators is made, the electrochemical methods can be classified into three main processes: electrolysis, electrodialysis, electroflotation.

3.1.1. Electro-chemical treatment of waste waters containing different inorganic impurificators

The oxidation of electro-chemical cyanide from waste waters (destruction of free and complex cyanide), the destruction of CN⁻ ions, after the electrolysis, is the result of conduct of the following processes:



In order to intensify the process of oxidation, small quantities of chlorides are frequently added in the polluted waters. The chlorine released on anode exercises an oxidizing action on CN⁻, according to the reaction:



One of the methods of purification of the solutions containing the ferrous and potassium ferricyanide propose their treatment in an electrolyzer with graphite anode and steel cathode at a current density of by 0.8-30 A/dm².

In order to intensify the process, 3-6 g/l of CaCl₂ for 1 g ferrous and ferri-cyanide are introduced in solutions.

Thus, 500 ml of solution, containing 1 g/l Fe(CN)₆³⁻ to which 3 g CaCl₂ were added, were subjected to the electrolysis process at a current anode density of 7-8 A/dm², under a voltage of 5 V, at a temperature of 90 °C and pH = 3.

After 30 minutes of electrolyze time, the solution was pure, free of CN⁻ or Fe²⁺ and Fe³⁺ (ions which have been precipitated as hydroxides).

3.1.2 Removal of chloride As³⁺

Removal of chloride As³⁺ from the leaks waters in the sulfuric acid industry can be achieved through electrolysis in a cell with two separate compartments through an orifice (cationic membranes a MK-40 type).

Water, containing As³⁺ (535 mg/l, pH = 1.5-3.5) is passed through the anodic space and through the cathodic space a conductive solution pass (3-5% NaCl or Na₂SO₄). In this process, the iron soluble anode it used. During the electrolysis process, the anode dissolution with Fe²⁺ ions formation and the

oxidation of As³⁺ ions at As⁵⁺ ions take place, which, together with ferrous hydroxide, form an insoluble complex [4].

The degree of purification depends to a great extent on the density of the current. The optimum density is 1.9 A/dm², to which the degree of purification is 99.7 % (the arsenic concentration of decreases from 534 mg/l to 1.6 mg/l, after 30 minutes of electrolysis).

3.3. The recovery of iodine from the metal iodides contained in the waste waters

The residual solutions from the deposited titanium containing TiI₄ (5 g/l), to which 5% HNO₃ has added were subjected to the electrolysis with platinum pads at a current density of 3.5 A/dm², at 25 °C. The iodine formed on anode was precipitated and filtered [5].

The electro-chemical recovery of FeSO₄ and FeSO₄ resulting as sub-products in the manufacture of TiO₂, is done by the electrolysis in a cell with two separate compartments through a membrane able to avoid the passing of NH₄⁺ cations from anodic compartment to the cathodic one and also to allow the passing of SO₄²⁻ ions from the cathodic compartment to the anodic one. After the electrolysis, the iron is deposited on the cathode on the anode (NH₄)₂S₂O₈ is formed.

4. Conclusions

Waste waters from metal plating contain between 1000 and 3000 mg/l metallic ions from various anions, complexion agents or shine agents, showing a high degree of toxicity.

The electrolysis of such waters, under certain conditions, allows their denoxiousness and metals recovery. The toxic metallic ions can be removed by reduction in the process of cathodic process, when their recovery is achieved by their embedding in hydroxides precipitations, resulting from the electrolysis with the water-soluble anode (usually of iron). At the same time, with the metallic ions removal, and the oxidation of some harmful anion is carried out, such as CN⁻ or some organic compounds present in the water.

Such toxic metals (Cr, Pb, Hg, Zn, Mn, Cd) and CN⁻ have been removed from waste water through electrolysis process, in the presence of the sodium chloride, using the soluble anode made of iron and cathodes made of an insoluble material.

The metals toxic ions have been precipitated as ferrites and removed by filtration, and CN⁻ has been oxidized to CO₂ and N₂.

For the recovery of metals from the diluted solutions, the electrolysis with a cathode made of current particles enclosed in a rotating perforated cylinder is carried out.

Waste water (the electrolyte) is circulated among the cathode particles using a pump.

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