Abstract - This study deals with the removal of cadmium (II) from cadmium plating wastewater by chemical precipitation in shape of white crystalline precipitate, using oxalic acid 0,5M as chemical reagent. It was studied the influence of pH, dose of reagent, temperature and also the influence of initial concentration of cadmium cation. The efficiency of process was expressed in percentage for all the experiments. The removal of cadmium (II) from wastewater stream and discharged was made to optimum pH, optimum dose of precipitation agent, temperature 60-70⁰C, for an initial concentration of 0,0088 M Cd²⁺/L. The extraction degree attained 80% profitability (removal of cadmium ion). The quantity of cadmium unextractable like cadmium oxalate shape was removed by precipitation with limestone 10%. The final effluent is corresponding to SR ISO 8288, as regards the content of allowed cadmium ion. The optimized conditions and entered process cadmium recovery are presented in a technological flux.

Keywords: wastewater, cadmium, recovery, precipitation

1. INTRODUCTION

The release of industrial wastewater containing cadmium to the environment is strictly controlled due to the toxic nature of soluble cadmium cation. To reduce the environmental impacts it is necessary to remove this substance from wastewater before its discharged in the environment. One of the largest cadmium sources, with contributes largely to water pollution, are the electroplating industries that use cadmium acid baths. The main problems associated to this process, from the environmental point of view, are the deposition baths and rinsewaters discharges [1-5].

Wastewater could contain a various amount of cadmium cation between 20-2000 mg/L. The known methods for cadmium removal in scientific literature are: ionic exchange coagulation and precipitation, adsorption on residual Fe(OH)₃, Cr (OH)₃, activated carbon absorption process, adsorption on zeolitic mass, directly osmosis.

It has been estimated that more than 45% of all cadmium is used in wastewater streams. Although precipitation is the method most commonly used, this study is based on idea that a crystalline precipitation is very important and could eliminate the main disadvantage: the separation of chemical precipitations (due the amorphous shape of extracted substances) [6-9].

The polluting potential of industry is considered to be the main source of spoiling the environment with cadmium in liquid or solid form as cadmium compounds coming from manufacturing, using and obtaining products containing cadmium or from its presence as a natural, but unfunctional impurity. From the first category we mention: nickel – cadmium batteries, cadmium pigments, ceramics with cadmium etc. The last are used to ensure a better protection against corrosion, especially in salty and alkaline environments, to obtain a good lubrication or a small friction value, cadmium based stabilizers (this delay the degradation process of PVC caused by exposure to heat or ultraviolet light). This stabilizers contain organic salts of cadmium: cadmium laureate and cadmium stearate, cadmium alloys (e.g.: copper – cadmium alloys in which the cadmium doubles the mechanic resistance of pure copper), electronic compounds with cadmium.

There are information according to which the cremation of products containing cadmium increases the cadmium emissions and the risk of being taken ill to people and environment. In solid offals are also, other sources of cadmium emissions: iron, steel, gypsum, cement and other remainings of non-ferrous metals (Zn, Pb, Cu), alloys, metals, fossil fuels and natural substances like grass, plants and food which may contain cadmium, too. Recent studies have proved that these pollute with 1% from all cadmium sources of polluting. Cadmium infested waste waters may result from non-ferrous metalurgic industry, electronic industry, electrochemic coverings with cadmium base don cadmium nitrate in acid environment. The refused concentration of cadmium varies between large limits: between 20-2000 mg Cd/L. The technologies in use for releasing the waste waters with a content of cadmium appeal to Ionic exchange techniques, absorption on different absorbent materials, electrodialysis, reversed osmosis, coagulation and precipitation.

Extracting the cadmium ion by precipitation with oxalic acid in the shape of precipitated crystal white hydrated oxalate of cadmium applied for used solutions with a major content of cadmium may solve the problem of environment and ensures the extraction of the cadmium ion with a cheap reagent easy to work with.
2. EXPERIMENTAL

For chemical analyses we have used Merck, Fluka, Amex reagents and the following devices: spectrophotometer of atomic absorption with flame, AAS Thermo Electron M Series M5 Dual and STAT accessory – atomic capture according to SR ISO 8288, derivatograph Paulik and Erdely 1500 C MOM Budapest, Toledo analytical balance, a device of bidistillation of water, highly precision glassware A+, electrical thermostat drying stove, Merck cadmium standard 1000 mg Cd/ L. The solutions used for the volumetric analysis had the factor F = 1,0000.

The extraction of cadmium ion in the cristalized shape of hydrated cadmium oxalate has many advantages compared to amorphous forms of cadmium compounds, carbonated hydroxide, or basic cadmium carbonate obtained by precipitation with hydroxides, carbonates or alkaline phosphates.

The study of recuperative combing out of cadmium oxalate. These studies used a 1500°C MOM derivatograph Budapest.

The studies and researches concerning the treatment of wastewater containing cadmium with the recovery of the cadmium ion have taken into consideration the influence of the following parameters:
- the pH of the reaction mass;
- the best quantity of precipitation agent;
- the best temperature for the process;
- the technological flux.

3. RESULTS AND DEBATES

The process is based upon the following reaction equation (precipitation):

$$Cd^{2+} + C_2O_4^{2-} + 2H_2O \rightarrow CdC_2O_4 \cdot 2H_2O \downarrow$$  \hspace{1cm} (1)

The degree of extraction (efficiency) of cadmium ion is calculated using the following relation:

$$\eta\% = \frac{Cd_{\text{initial}}[mg] - Cd_{\text{final}}[mg]}{Cd_{\text{initial}}}$$  \hspace{1cm} (2)

in which:
\(\eta\) = the degree of extraction (efficiency) of cadmium cation in percentage;

\(C_i\) = the concentration of cation expressed in [mg/ L] before the precipitation with oxalic acid;

\(C_f\) = the concentration of cation expressed in [mg/ L] after the precipitation with oxalic acid;

a) The study of influence of the pH of the reaction mass

The study of influence of the pH of the reaction mass on the efficiency of the degree of the cadmium ion extraction was made upon a well determined quantity of solution (25 mL of solution of 1000 mg Cd/ L) to a well determined ratio of precipitation reagent according to the reaction equation under mechanic movement, at the temperature of 60–65°C.

Experimental data concerning the influence of the pH of the extraction in the form of cadmium oxalate are presented in fig.1. We may notice that on the values tested for the pH, one will obtain the same value for the remaining cadmium:56, 733 mg Cd/ L for an extraction efficiency of 43,28%.

In a graphic presentation of obtained data we can notice that in the interval of the studied pH : 1–5,5, the pH does not influence the degree of extraction, the maximum efficiency being of 43,28%.

We may therefore consider the best value for pH – 5,5, closer to the neutral value of 7, as being the best for extracting cadmium.

b) The study of the best dose of precipitating reagent

This study were at pH = 5,5 and 60–70°C with increases doses oxalic acid, in excess.

Experimental data upon the influence of reagent doses on the efficiency of the degree of the extraction the cadmium ion are presented in fig.1.

From the graphic representation one can notice that the excess of reagent favors the efficiency of the cadmium ion extraction. This is influenced in a positive manner by rising of oxalic acid dose. The degree of extraction is rising according to the rising of oxalic acid dose of 43% (excess of reagent of 10%) till the maximum value obtained – 79% - corresponding to a large excess of reagent. Raising the dose of precipitation reagent over this value has a bad influence on the value of the best extraction degree that was obtained, this drops 4% when the use of oxalic acid is raised by 1 mL.

We may therefore consider that the optimum dose of oxalic acid is 0,5 M, 3 mL for an optimum pH of 5,5 and a process temperature of 60–70°C.

The experimental data upon the influence of temperature on the value of the degree of cadmium ion extraction are represented in fig.2. The study was realised at a pH of 5,5 and temperature of 20°C in the same conditions of movement, decantation and filtration.

The filtered and washing waters were brought to a 250mL balloon. The waste cadmium analysis was made...
using the complexonometric and SAAF methods, the results being approximately the same.

d) The chemical composition of cadmium oxalate

The cadmium oxalate precipitate obtained at 70°C was chemically analysed to establish the chemical formula and the hydration water contained. The analysis methods are these presented in the experimental part: complexon III titration 0.05 M (factor =1) and SAAF, according to SR ISO 8288. The dried precipitate at 100°C to a constant weight was weight using the Toledo balance. The mass of dried precipitate which was analysed was m= 0,1381 grams of cadmium oxalate.

The precipitate was dissolve in azotic acid 1:2 vol. The results of complexonometric analysis was closet to that obtained by using the SAAF method. 72.50 mg of cadmium were found a percentage experimental content of 52.5% Cd.

The oxalate anion was analysed by using the permanganometric method, the value obtained being 3.18%.

From the cadmium value obtained it results that the cadmium oxalate dried at 100°C is a monohydrate of the CdC$_2$O$_4$·H$_2$O type.

The chemical composition experimentally determined is closet o the theoretic composition:

<table>
<thead>
<tr>
<th>Experimental composition</th>
<th>Theoretic composition</th>
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<tbody>
<tr>
<td>Cd % = 52.5 Cd % = 52.5</td>
<td></td>
</tr>
<tr>
<td>C$_2$O$_4$ % = 40.29 C$_2$O$_4$ % = 40.29</td>
<td></td>
</tr>
<tr>
<td>H$_2$O % =7,21 H$_2$O % =7,21</td>
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</table>

The cadmium oxalate obtained at 20°C corresponds to the CdC$_2$O$_4$·H$_2$O type, according to thermogravimetric and thermodifferential studies [10-14].

Dehidrated cadmium oxalate is decomposed into cadmium oxyde at low temperature 250- 280°C, this representing a great energy saving in the utilization of cadmium oxalate as a by – product.

Between 20-300°C the cadmium oxalate loses the crystallization water and between 300-360°C it turns into cadmium oxyde according to the reaction equation:

$$CdC_2O_4 \rightarrow CdO + CO_2 + CO$$ (3)

The CO$_2$ and CO impurity – cleaned obtained oxyde leaves the system.

Carbonates, basic carbonates and cadmium hydroxides calcinate to cadmium oxyde at temperatures of 600-700°C. From these data one may infer that the process undergoes with a reduced electrical energy consuming, and the by- product CdO may be used in the pigment industry, cadmium compounds etc.

4.TECHNOLOGICAL FLUX

According to experimental data and the study of improving the recovery of cadmium ion we offer the following technological flux to get cadmium oxalate.

The fully eliminate the cadmium after the 80% recovery of innitial cadmium we made a precipitation of 10% milk of lime at a pH of 10. The oxalic acid that
remained falls down as calcium hydrated oxalate and cadmium hydroxyde.

The reactions resulting by precipitating the Cd$^{2+}$ ion Ca (OH)$_2$ and by neutralizing the excess of oxalic acid are:

\[
\text{Cd(NO$_3$)$_2$ + Ca(OH)$_2$ $\rightarrow$ Cd(OH)$_2$ + Ca(NO$_3$)$_2$} \quad (4)
\]
\[
\text{H$_2$C$_2$O$_4$ + Ca(OH)$_2$ $\rightarrow$ CaC$_2$O$_4$ + 2H$_2$O} \quad (5)
\]

The slime resulted contains Cd (OH)$_2$ and Ca (OH)$_2$ and the waste discharged solution is according to the standards SR ISO 8288 concerning the accepted quantity of cadmium (under 1 mg Cd/L) see in fig. 4.

The discharges solution containing cadmium ions is treated with H$_2$C$_2$O$_4$- 0.5 M under continuous movement, 300 rotations / minute for 10 minutes at 60°C. The crystal – white precipitate which is obtained is left to fall down then it is filtered and washed. The washing waters are collected into a reaction bowl and neutralized with Ca (OH)$_2$ 10% till a pH of 8.5-9 [15].

The slime resulted is retained, the waste waters are discharged according to the standards of quality SR ISO8288.

5. CONCLUSIONS

The extraction of cadmium ions with a 80% efficiency in the optimum conditions ensures the obtaining of crystalized insoluble precipitates of monohydrated cadmium oxalate. The crystalized form is stable in air, carbon dioxide and light as compared to amorphous forms known for hydroxides, carbonates, basic cadmium carbonates. The process of recovery discharging as metal oxalate for the cadmium ion from different discharged products presents the following advantages:

- the speed for falling down, filtration, washing is obviously superior than that for the amorphous shapes;
- reduced and compact volume for the precipitate;
- low consume of energy for the many usage by-products when being processed: eg. cadmium oxide;
- the processing of the initially obtained oxalate in different cadmium salts;
- economically easily accessible precipitation reagent (synthesis, price, transport, chemical stability);
- it is easy to obtain the optimum value for pH by using certain substances, as well as the right dose of oxalic acid and temperature, if necessary;
- the crystall cadmium oxalate can be easily turned into pure oxide at low temperature (around 350°C) or it can be used for other applications.

Fig. 4 Technological flux of cadmium recovery from waste solutions in the shape of monohydrated cadmium oxalate
The excess of oxalic acid and the cation that remained can be eliminated by treating the filtered and washing waters with milk of lime 10%. In this way, the oxaled anion is falling down a dihydrated cacium oxale, the remaining cation precipitates as hydroxyde, the metal content being under 0,1 mg/L, the pH of the solution becomes right and the effluent can be discharged according to the approved legislation concerning the quality of environment and waters- SR ISO 8288.

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