

CADMIUM IONS RECOVERY BY CHEMICAL PRECIPITATION METHOD FROM RESIDUAL SOLUTIONS OF GALVANIC PLATING

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Abstract - This study deals with the removal of cadmium (II) from cadmium plating wast water 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- 70⁰ C, 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 limes tone 10%. The final effluent is corresponding to SR ISO 8288, as regards the content of allowed cadmium ion. The optimized conditions and entire 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, which 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- 2000mg/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 adsorption 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 to 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). These stabilizers contain organic salts of cadmium: cadmium laureate and cadmium stearate, cadmium alloys (eg.: 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, electro dialysis, 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 crystallized 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 combining out of cadmium ion was made on the solution of 1000 mg Cd/ L (0,088 M) based upon the cadmium nitrate.

The solution containing was treated with a solution of oxalic acid 0,5 M at a well defined ratio, with a controlled temperature and pH, under mechanic movement, reaction time – 10 minutes.

The obtained cadmium oxalate precipitate is crystal-white, a bit decantable and sedimentable. This was filtered and washed with distilled water. The filtered and washing waters were collected in a 250 mL balloon from which there was made the chemical analysis of roasted cadmium. A well determined quantity from the obtained oxalate was dissolved in hydrochloric acid 18%. The obtained solution was passed in a 100mL balloon. The chemical analysis of cadmium cation used complexometric methods and spectrophotometry of atomic absorption with flame (SAAF).

The oxalate anion was found out by titration in sulphuric acid environment, at 80°C with potassium permanganate 0,1 N.

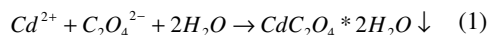
Thermogravimetric and thermogravimetric studies confirm the chemical composition of the obtained cadmium oxalate. These studies used a 1500°C MOM derivatograph Budapest.

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):



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

$$\eta\% = \frac{Cd_{initial}[mg] - Cd_{final}[mg]}{Cd_{initial}} \quad (2)$$

in which:

η = 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, closest 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 was at pH= 5,5 and 60-70°C with increasing doses of oxalic acid, in excess.

Experimental data upon the influence of reagent dose on the efficiency of the degree of the extraction of 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. Rising 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 realized 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.

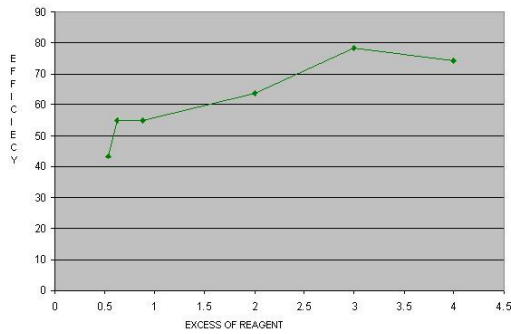


Fig.1 Graphic representation of the reagent dose influence [mL] on the efficiency of cadmium ion extraction

c) The study of the temperature influence on the extraction efficiency

The extraction efficiency was calculated according to relation 1 and the experimental data are presented in fig.3.

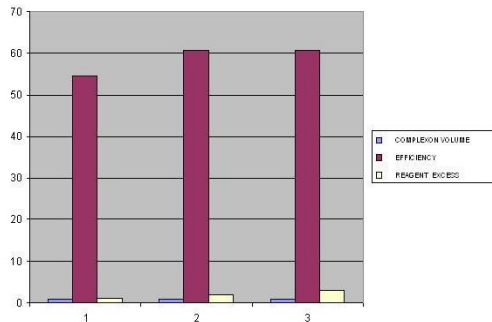


Fig.2 The influence of temperature 20⁰C on the degree of cadmium extraction

We may notice from the graphic representation that the extraction efficiency at a temperature of 20⁰C rises according to the rise of precipitation reagent dose from 54,54 % to 66,66 % and after that it remains the same.

We may notice from the graphic representation of efficiencies at a temperature of 70⁰C, or 20⁰C that the optimum temperature for the cadmium recovery process is that of 70⁰C when a good value of the extraction degree in the shape of cadmium oxalate, crystal – white and hydrated, is obtained (fig.3).

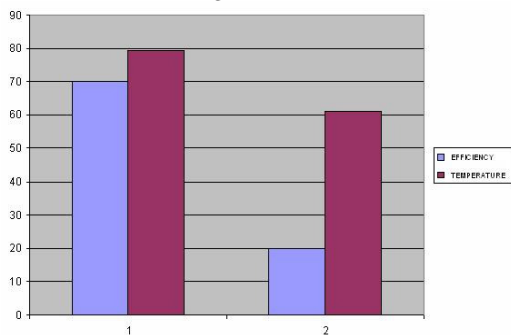


Fig.3 Comparative presentatin of experimental data in different thermic conditions

d) The chemical composition of cadmium oxalate

The cadmium oxalate precipitate obtained at 70⁰C 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 100⁰C 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 dissolved 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 100⁰C is a monohydrate of the CdC₂O₄ · xH₂O type.

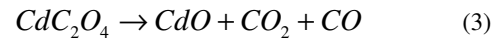
The chemical composition experimentally determined is closet o the theoretic composition:

Experimental composition	Theoretic composition
Cd % = 52,5	Cd % = 52,5
C ₂ O ₄ % = 40,29	C ₂ O ₄ % = 40,29
H ₂ O % = 7,21	H ₂ O % = 7,21

The cadmium oxalate obtained at 20⁰C corresponds to the CdC₂O₄ · xH₂O type, according to thermogravimetric and thermodifferential studies [10-14].

Dehydrated cadmium oxalate is decomposed into cadmium oxyde at low temperature 250- 280⁰C, this representing a great energy saving in the utilization of cadmium oxalate as a by – product.

Between 20-300⁰C the cadmium oxalate loses the crystallization water and between 300-360⁰C it turns into cadmium oxyde according to the reaction equation:



The CO₂ and CO impurity – cleaned obtained oxyde leaves the system.

Carbonates, basic carbonates and cadmium hydroxides calcinate to cadmium oxyde at temperatures of 600-700⁰C. 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.

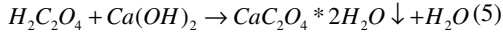
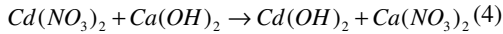
4. TECHNOLOGICAL FLUX

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 percipitation 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:



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 $H_2C_2O_2$ - 0,5 M under continuous movement, 300 rotations / minute for 10 minutes at $60^\circ C$. 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.

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 hydroxydes, 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 oxyde;
- the processing of the initially obtained oxalate in different cadmium salts;
- economically easily accesible 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 oxale can be easily turned into pure oxyde at low temperature (around $350^\circ C$) or it can be used for other applications.

5.CONCLUSIONS

The extraction of cadmium ion with a 80% efficiency in the optimum conditions ensures the

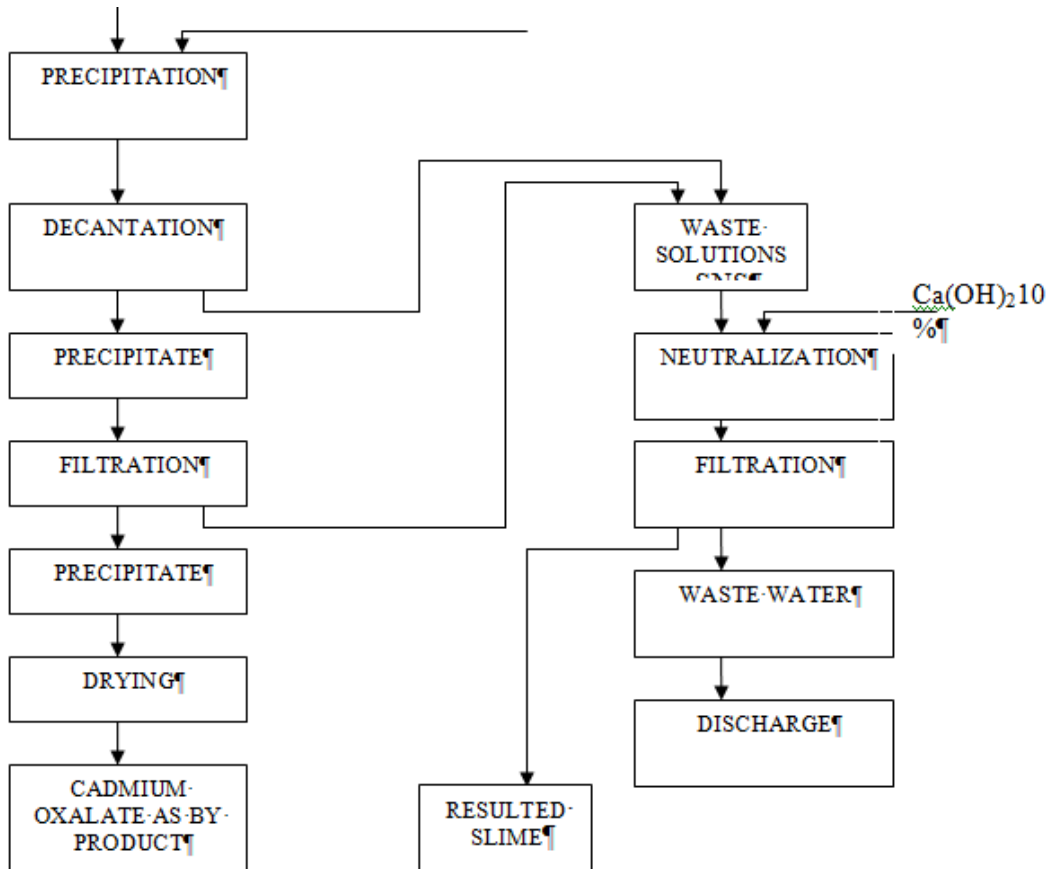


Fig.4 Technological flux of cadmium recovery from waste solutions in the shape of monohydrated cadmium oxalate

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 oxalated anion is falling down a dihydrated calcium oxalate, the remaining cation precipitates as hydroxide, 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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