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Study of the Cleaning Process with Cadmium Ions from Residual Waters

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Abstract: these studies propose an original method of cleaning the residual waters using Cadmium ions in form of Cadmium oxalate in optimal conditions of extracting and establish the suitable technological flux.

Keywords: cadmium, ions, waste water

1. Introduction

From building machine industry, electronics, electro technique and organic synthesis industry results waste waters solutions with cadmium ions, in acid or alkaline medium in form of ordinary salts like: $CdSO_4$, $CdCl_2$, $Cd(NO_3)_2$, CdO, accompanies of chlorhydric acid, sulphuric acid, chlorides, etc.

Extracting cadmium by chemical precipitation in form of cadmium oxalate resolves the environment protection problem, recovering the transition material with cheap reactive and easy process of cadmium oxalate.

The solubility product of CdC_2O_4 is $1,5 \cdot 10^{-8}$, [1], this permits the quantitative separation, with efficiency of 99%. The oxalate acid excess and the rest of cadmium it's removed with $Ca(OH)_2$ solution 10%.

In the specific literature are known methods and processes of cleaning waste waters with cadmium, by chemical precipitation in form of hydroxide, carbonate, ionic exchange process, electrolytic etc.[2,3]

2. Experimental

Taking into consideration the fact that residual waters solutions proceeded from the acid cadmium process [4] have an medium content of 5-6g Cd^{2+}/dm^3, studies have been made on a Cd^{2+} solution (0,001÷0,1M). As reactant of precipitation it was used oxalic acid 0,5M.

The cadmium content has been determined by complexonometry (by titration with complexon III-0,05M in the presence of black eryochromium T indicator, at pH=10, [5] ammoniac buffer and by atomic absorption using the atomic absorbing spectrophotometer type AAS – 30 Karl Zeiss Jena.

The cadmium solution was treat with an oxalic acid solution 0,5M under continuous stirring, on well determined pH, with well defined report cadmium/oxalic acid at temperature and concentration well determined.

The obtained precipitate, was washed, dried, and than analyzed, after followed the chemical and termic analysis using an derivatograph type Paulik Erdely.

3. Results and discussion

The researches have followed the influence of the different parameters during the process (pH of the reaction mass, optimal dose of reactive, cadmium concentration and the temperature) on the cadmium extraction degree.

The process is based on reaction:

$$Cd^{2+} + C_2O_4^{2-} + 3H_2O = ZnC_2O_4 \cdot 3\ H_2O\downarrow$$

a) pH of the reaction mass

The pH of reaction mass influence on cadmium extraction degree is given in the table 1 and figure 1.

TABLE 1. The extraction degree dependence on pH of the reaction mass at an excess of oxalic acid of 10%, at t=20°C, reaction time 10 minutes.

Nr. crt	pH	α,%
1	1	23
2	1,5	26
3	2	31
4	2,5	35
5	3	40
6	3,5	41
7	4,5	43
8	5	43
9	5,5	43

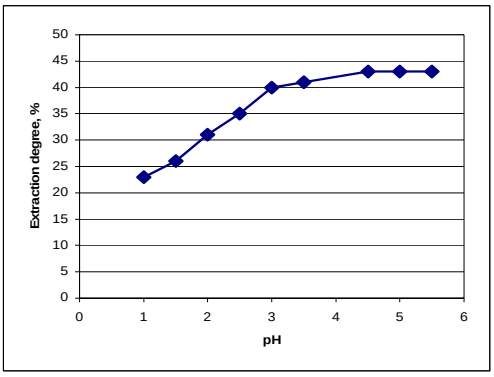

Figure 1. Extraction degree dependence on the reaction mass pH.

From these data results that the extraction degree increases the same with increasing of pH with 43%, than it stays constant. So, it can be considered that the optimum pH of the process is pH ≥ 4.

b) Oxalic acid dose

The experimental data regarding the optimal dose of oxalic acid excess are given in table 2 and figure 2.

TABLE 2. The extraction degree dependence on oxalic acid excess, at temperature of 20°C, reaction time 10 minutes, pH 5,5.

Nr.crt.	Exces%	α,%
1	10	43
2	20	50
3	30	54
4	40	58
5	50	68
6	70	84
7	100	98,86
8	150	98,86

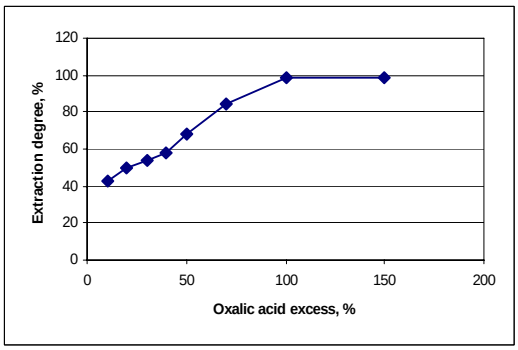

Figure 2. Extraction degree dependence on oxalic acid excess

The experimental data shows that the extraction degree increases a lot with increases the oxalic acid excess and tends to a constant value at an excess of over 100%, when reaches the value 98,86.

c) Cadmium concentration

The experimental data regarding the cadmium concentration influence from the residual solution, on separation degree are given in table 3 and figure 3.

TABLE 3. The cadmium extraction degree dependence on concentration in solution, at 20°C, reactive excess 100%, reaction time 10 minutes and pH=5,5

Nr. crt.	C[M]	α,%
1	0,001	87,25
2	0,01	92,40
3	0,016	95,33
4	0,025	96,07
5	0,033	97,25
6	0,05	98,86
7	0,1M	98,86

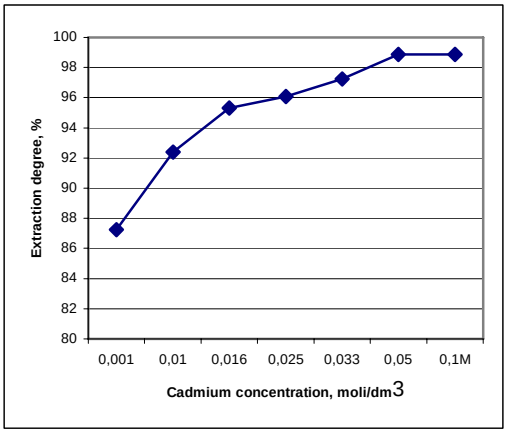

Figure 3. Extraction degree dependence on cadmium concentration

From the presented data results that the cadmium extraction degree diminish on lower concentrations than 0,016M.

Therefore, residual solutions with 3÷11 g Cd^{2+}/dm^3 content permits cadmium separation in form of oxalate, at normally temperature, according to the parameters determined on points a) and b).

d) Chemical composition of cadmium oxalate

The obtained Cadmium oxalate, washed, dried in a exactly quantity, was dissolved in HCl 18 % concentration, c.p. The cadmium was determined complexonometric at pH=10 with black eryochromium T indicator, using complexon III 0,05M, and gravimetric with $(NH_4)_2HPO_4$, solution 10%, in form of cadmium pyrophosphate [8],and the oxalate, by titration with KMnO, 0,1N [8].

TABLE 4. Chemical composition of cadmium oxalate

Nr.crt.	Cd, %	C_2O_4, %	H_2O Cr, %
1	44,21	34,61	21,18
2	44,15	34,52	21,33
3	44,10	34,58	21,32
MEDIA	44,15	34,57	21,27

4. Conclusions

The cleaning process of residual waters with Cd ions devolves with a maximum efficiency of extraction at pH optimum of ≥4 and optimal dose of reactive 100% excess.

The precipitate is crystalline, white, perfectly settling down. Different from the amorphous cadmium precipitates which have slow speed of sedimentary, filtration and wash difficultly , chemical instability under air action, the crystalline form of oxalate have superiors advantages, the crystalline precipitate is settling down momentary, in big acicular crystals, well storage on the bottom of the brightener, with small considerable volume of precipitate, face the amorphous forms.

These results can be applied for cadmium ions concentration domain between 3÷11 g Cd^{2+}/dm^3, with 99% efficiency.

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