Comparative Study on Lead(II) and Cadmium(II) Recovery from Solutions by Chemical Precipitation

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Abstract: The paper presents a study regarding a possible way for the removal and the recovery of lead (II) and cadmium (II) ions from wastewaters with relatively high concentrations. The proposed method is based on the precipitation of the metal ions as oxalates with low solubility in water. A systematic study to establish the optimum conditions for a high degree of metal recovery as lead oxalate and cadmium oxalate is presented. The studied parameters were: the pH, the excess of reactant reagents, the initial concentration of ions and the temperature. The crystalline products obtained correspond to: anhydrous lead (II) oxalate (PbC_2O_4) and trihydrate cadmium oxalate ($CdC_2O_4*3H_2O$). The extraction degree of metals was around 99% for lead (II) and lower, around 70% for cadmium (II). A possible technological flux for the removal of the studied ions from wastewaters as crystalline oxalates is proposed.

Keywords: lead, cadmium, oxalate, recovery, precipitation

1. Introduction

Toxic metals are often discharged by a number of industrial processes and this can lead in turn to the contamination of freshwater and marine environment. The release of industrial wastewater containing cadmium to the environment is strictly controlled due to the toxic nature of soluble cadmium and lead cations [1]. Heavy metals are major pollutants in marine, ground, industrial and even treated wastewaters [2]. Industrial waste constitutes the major source of various kinds of metal pollution in natural waters [3].

To reduce the environmental impacts it is necessary to remove these substances from wastewaters before being discharged in the environment. Lead is a cumulative toxin in the body, like bones marrow. Lead is a powerful neurotoxin, but kidney damage also occurs as a result of exposure to Pb. In spite of these inconveniences, lead is an important element with many industrial uses; however, in its ionic form in industrial wastewater is extremely toxic and strict environmental laws impose its removal from wastewater, or waste water streams. Particularly, the electronic and galvanic industries generate waste water streams with Pb^{2+}, diluted nitric acid and nitrates, coming from lead deposition on steel surface. Lead concentration values are in a wide range, between 40 and 1000 mg Pb^{2+}/L [2-5]. Industry (nickel – cadmium batteries, cadmium pigments, ceramics with cadmium etc) is also the main source of pollution with cadmium.

There are different possibilities for the treatment of waste waters with heavy metals like nickel, cobalt, cadmium, copper, lead, iron and other cations from metal plating industries, electronic industries, metal processing . Waste waters streams contain besides Ni(II), Cu(II), Cd(II) Co(II), Cr(VI), Zn(II) and Pb(II), various salt specifically like chlorides, sulfates, nitrates, fluorides and also chelating agents, surfactants, sulphuric acid, boric acid. If the process goes in alkaline pH, then, residual solutions contain carbonates, phosphates, sodium hydroxide. [6,7]

The methods used in practice, according to the literature, for metal ions removal, depending on their concentration in the waste water streams are: ionic exchange, adsorption on zeolites, chemical precipitation, electrolysis, chemical reduction, biosorption. [8-12]

Chemical precipitation represents however an efficient way of heavy metal removal from waste water stream, with a high level of concentration. Pb^{2+} was chemically precipitated with starch xantate, sodium hydroxide, 1,3-benzenediamidoethanethiol dianion ($BDET^{2-}$), sodium di-(n-octyl) phosphinate [7], ammonium zirconyl oxalate, $(NH_4)_2ZrO(C_2O_4)_2$, respectively [13-18]. The cations precipitation with sodium hydroxide, carbonates, phosphates or lime stone gives amorphous compounds of Ni, Co, Cu, Cd, Cr, Pb or Zn which are difficult to separate, wash, filtered, guard and store in a stable composition because of their instability to air, humidity, CO2.

In this work we present a comparative study regarding lead (II) and cadmium(II) recovery from solutions by chemical precipitation as lead oxalate and cadmium oxalate, using oxalic acid as the precipitation reagent. The dependence between the precipitation process parameters (initial pH, temperature, excess of precipitation reagent) and the recovery degree of the metal ions ($\alpha\%$) was studied in order to establish the optimum precipitation conditions.

2. Experimental

2.1. Materials and methods

All the used reagents were chemical pure (Merk, Fluka, Amex): $Pb(NO_3)_2$, $Cd(NO_3)_2$, $H_2C_2O_4.2H_2O$ volumetric solution of titriplex III, 0,05M, 1N HNO_3 solution, 0,1N $KMnO_4$ solution, Eriochrome Black T, ammonium buffer solution (pH=10).

The working synthetic solutions containing 1g Pb^{2+}/L and 1g Cd^{2+}/L have been treated with a 0,5M $H_2C_2O_4$ solution, at defined parametrs: $H_2C_2O_4$: M^{2+} ratio, temperature and pH values, under continuous stirring. The pH was adjusted to the desired value by adding NaOH 10% solution or HNO_3 10% solution. The residual concentration of Pb^{2+} in solutions was determined by both FAAS and complexonometric titrations.

The lead oxalate precipitate has been filtrated, washed and the dried powder has been characterised. For this purpose a well known quantity of oxalate was dissolved in HNO_3 solution (1:2 vol). The cation analysis was performed through complexonometric and FAAS methods. The oxalate anion was determinate by permanganometric titration in the presence of sulphuric acid, at 80^0C [20].

2.2 Experimental techniques

Pb^{2+} and Cd^{2+} content in the working solutions was determined by both complexonometric titration and by flame atomic absorption spectrometry (FAAS), using a spectrophotometer ThermoElectron M Serie M5 Dual, according to SR ISO 8288 [20,21]. The thermal analysis of the precipitated oxalates was performed on a derivatograph 1500 MOM Budapest, for a sample mass of 100 mg, a heating rate of 5°C/min, under static air atmosphere, up to 500°C. The FTIR spectra were registered with a JASCO 430 FTIR spectrometer, in KBr pellets, in the range 400–4000 cm^{-1}.
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3. Results and Discussion

Our previous studies regarding the recovery of Ni^{2+} and Co^{2+} cations from waste waters have shown that the precipitation of these ions as crystalline oxalates represent is efficient, especially at high level of concentrations of these ions. This paper represent an extension of our studies on applying the precipitation as crystalline oxalates on the removal of other divalent ions (Pb^{2+} and Cd^{2+}) from wastewaters with high M^{2+} content.

The recovery efficiency of each cation was calculated using the relation:

$$\alpha,\% = \frac{C_{i,Me^{2+}} - C_{f,Me^{2+}}}{C_{f,Me^{2+}}} \cdot 100 \qquad (1)$$

where:
α represent the degree of recovery, % (mass percent)
$C_{i,Me^{2+}}$ – the initial concentration of the metal cations, [mg/L];
$C_{f,Me^{2+}}$ – the residual concentration of the cation, after the precipitation, [mg/L].

The influence of various parameter such as: precipitation temperature, reaction mass pH, excess of precipitation reagent upon the α% parameter was studied in order to establish the optimal precipitation conditions.

3.1. Influence of the initial pH

The influence of the reaction mass pH on the recovery efficiency α% of Pb(II) and Cd(II) as oxalates from aqueous solutions with [1g M^{2+}/L] was studied at 20°C, using 10% excess of oxalic acid, for a time of reaction of 10 minutes, under mechanical stirring at 300 rot/min. ph values of the reaction mass were modified in the pH range 1.0 – 6.5.
The residual cadmium and lead content in the remaining solutions after chemical precipitation was determined by atomic absorption spectrometry and confirmed also by complexonometric titrations.

The obtained experimental data are shown in Table 1.

TABLE 1. Values of recovery degree and reaction mass pH

No.	pH	$C_f(Pb^{+2})$ [mg/L]	$\alpha_{Pb(II)}$ (%)	$C_f(Cd^{+2})$ [mg/L]	$\alpha_{Cd(II)}$ (%)
1	6,5	1,09	98,9	56,7	43,3
2	5,5	1,09	98,9	56,7	43,3
3	4,5	1,09	98,9	56,7	43,3
4	3,5	1,77	98,2	56,7	43,3
5	2,5	1,77	98,2	56,7	43,3
6	1	1,79	98,2	56,7	43,3

The results presented in table 1 shows that the increasing of the initial pH value from 1 to 6.5 does not influence the value of the recovery degree. It results also that in the used conditions the recovery degree for Cd ions is very low, compared to the one obtained for Pb^{2+}. According to these results we choose as optimum pH value for the precipitation of both lead and cadmium ions a pH of 4.5.

3.2. Influence of the temperature

The experimental data regarding the influence of temperature over the recovery degree, at optimum pH, optimum reagent excess at 20°C, respectively at 75°C, are shown in Table 2.

TABLE 2. Values of recovery degree at different temperatures

T°C	$\alpha\%(Pb^{2+})$	$\alpha\%(Cd^{2+})$
20	98,9	61,0
75	99,2	79,5

From the data shows in Table 2 results that while for Pb^{2+} the influence of temperature on the recovery degree in form of lead oxalate is insignificant, in case of Cd^{2+}

precipitation the degree of recovery significantly increases from 60% to 79.5%. Thus, we have established for the precipitation of Pb^{2+} and Cd^{2+} as oxalates different optimum temperatures: room temperature and 75°C, respectively.

3.3. Influence of the excess of oxalic acid

The experimental data obtained for the chemical precipitation of a 1g Pb^{2+}/L solution at pH = 4.5, for the optimum temperature (room temperature for Pb^{2+} and 75°C for Cd^{2+}), for a reaction time of 10 min, under mechanically stirring 300 rot/min, with different excesses of oxalic acid (compared to the stoechiometric necessity) are shown in Fig. 1.
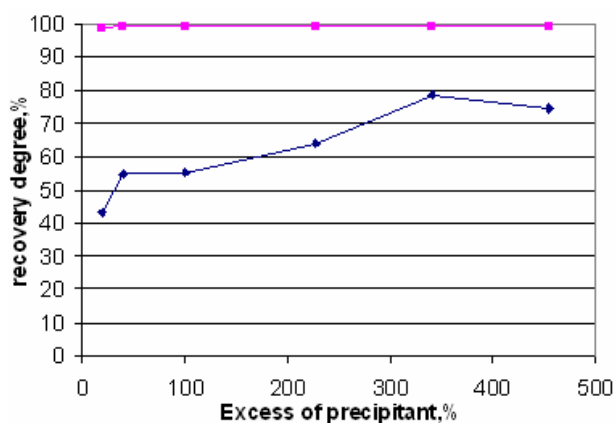

Figure 1. Dependence of the recovery degree of M(II) ions on oxalic acid excess ($\blacksquare$ Pb^{2+} ; $\blacktriangle$ Cd^{2+})

From the evolution of the curve presented in Figure 1, it results that the lead recovery degree α% slightly increases with the excess of precipitation reagent. For a reagent excess of 100%, the lead recovery degree increases only with 0,26% and the final value was 99,2%. The value of 0,26% may be considered not significant for the process. A reagent excess of oxalic acid higher than 22% is not necessary. In case of Cd^{2+} precipitation, the excess of the precipitation reagent significantly increases the recovery degree. The maximum of the recovery degree is 78.5% for a very large excess of 340%. In this case, the removal of Cd ions as oxalate must be associated to another step of Cd removal. In case of Pb^{2+} the optimum reagent excess for lead is between 10-22% of 0,5M oxalic acid solution, with a recovery degree about 99,2%.

3.4. Thermal analysis and FT-IR study of the precipitated Cd(II) and Pb(II) oxalates

The crystalline precipitates obtained for Pb^{2+} and Cd^{2+} have been studied by thermal analysis and FT-IR spectrometry. Fig.2 presents the derivatograms obtained for the dried precipitates of lead oxalates (a) and cadmium oxalate (b).

From the shape of TG and DTA thermal curves it results that the two precipitated oxalates have different thermal behaviour. Thus lead oxalate decomposes in a single step at ~350°C, with an exothermic effect. There is no mass loss up to 300°C due to the lack of crystallization water, so the precipitated lead oxalate is anhydrous. The thermal decomposition of lead oxalate in a single step takes place according to the equation (2):

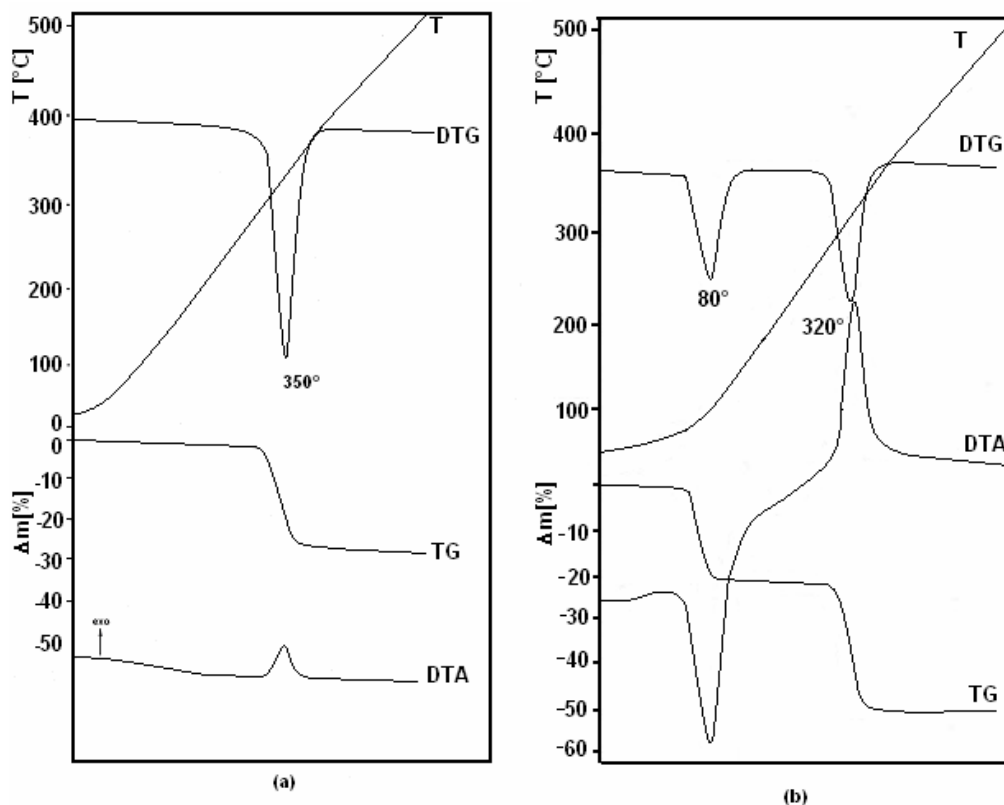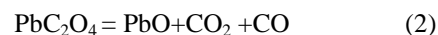$$PbC_2O_4 = PbO + CO_2 + CO \qquad (2)$$

Figure 2. Derivatogram of the dried precipitate of lead oxalate (a) and cadmium oxalate (b)

The experimental mass loss of 25% is much closed to the theoretical one (24.4%).

In case of cadmium oxalate, the thermal decomposition takes place in two steps: an endothermic step in the range 70 – 100°C with a mass loss of 21% and an exothermic step, in the range 280- 350°C, with a mass loss of 27%. The first step represents the loss of the crystallization water, while the second step corresponds to the decomposition of anhydrous cadmium oxalate to cadmium oxide, as represented in the equations (3) and (4):

$$CdC_2O_4 \cdot xH_2O \rightarrow CdC_2O_4 + xH_2O \qquad (3)$$
$$CdC_2O_4 \rightarrow CdO + CO_2 + CO \qquad (4)$$
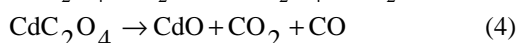
The loss of 21% water correspond to a number of three moles of crystallization water, thus the formula of the precipitated cadmium oxalate is $CdC_2O_4.3H_2O$.

The content of Pb and Cd in the obtained oxalates was confirmed by atomic absorption spectrometry, while the content of oxalate ions was determined by permanganometric titrations. The results of chemical analysis were much closed to the theoretical ones.

The isolated compounds were also characterised by FT-IR spectrometry. The obtained FT-IR spectra are typical for M(II) oxalates. Thus, in the range 1550-1600 an intense band appear in both spectra, assigned to the OCO asymmetric stretching vibrations, while the band from ~1300 cm^{-1} correspond to the OCO symmetric stretching vibrations $\nu_s(OCO)$ [22]. The weak bands or shoulders that appear around 1050 cm^{-1} are assigned in literature to the C-C stretching vibrations [23]. The sharp band that appears at 772 cm^{-1} is attributed to the OCO group bending vibrations $\delta(OCO)$. Figure 3 presents the FT-IR spectrum obtained for lead oxalate.
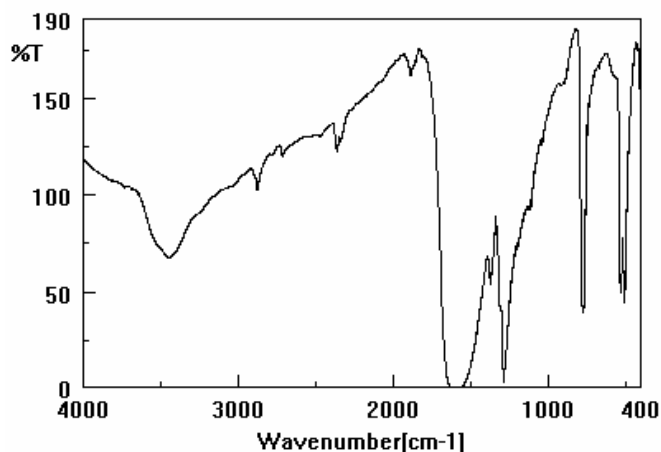

Figure 3. The FT-IR spectrum of lead oxalate

3.5. Technological flux of Pb(II) and Cd(II) removal from wastewater

In order to eliminate and recovery the lead and cadmium ions from waste waters, in form of crystalline oxalates, two steps are necessary: the precipitation of lead and cadmium ions as oxalates (equations (5) and (6)), using an excess of oxalic acid and the removal of oxalate anions and the residual M(II) ions by precipitation with 10% milk of lime, when the composition of the wastewater becomes acceptable for discharging in the environment [24, 25]. The reactions corresponding to the precipitation of Pb^{2+} and Cd^{2+} ions together with the $C_2O_4^{2-}$ with Ca (OH)$_2$ are described by the equation (7), (8) and (9).
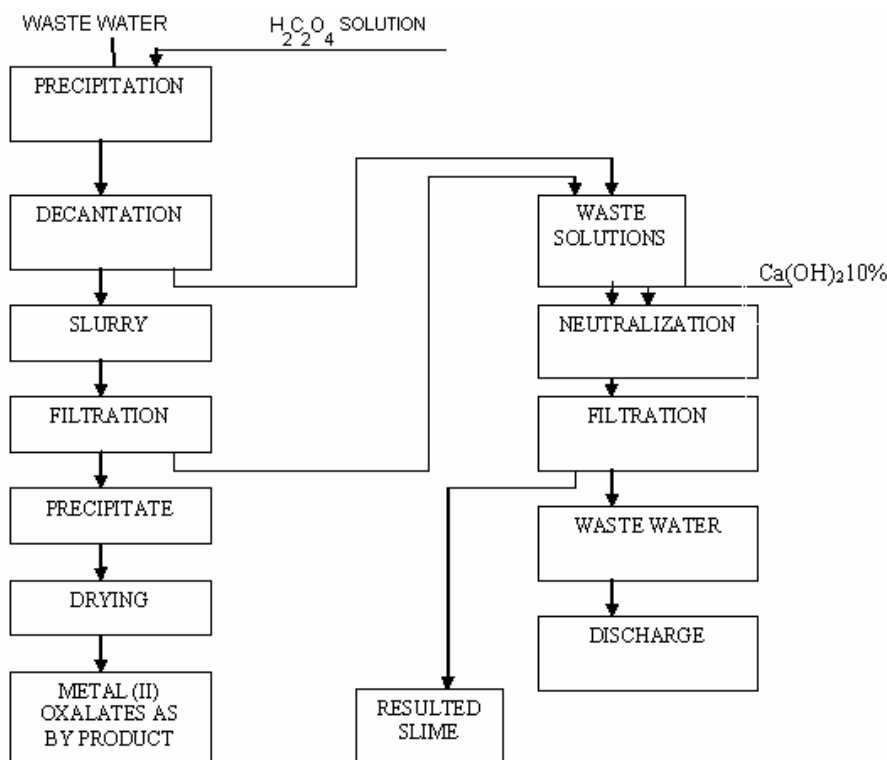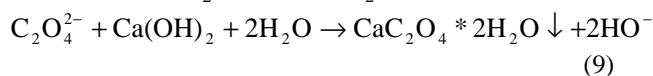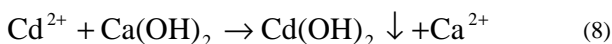

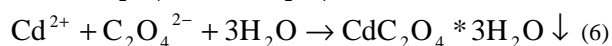Figure 4. Technological flux proposed for the removal of the studied M(II) ions from wastewater

$$Pb^{2+} + C_2O_4^{2-} \rightarrow PbC_2O_4 \downarrow \qquad (5)$$

$$Cd^{2+} + C_2O_4^{2-} + 3H_2O \rightarrow CdC_2O_4 * 3H_2O \downarrow \quad (6)$$

$$Pb^{2+} + Ca(OH)_2 \rightarrow Pb(OH)_2 \downarrow + Ca^{2+} \qquad (7)$$

$$Cd^{2+} + Ca(OH)_2 \rightarrow Cd(OH)_2 \downarrow + Ca^{2+} \qquad (8)$$

$$C_2O_4^{2-} + Ca(OH)_2 + 2H_2O \rightarrow CaC_2O_4 * 2H_2O \downarrow + 2HO^-$$
$$(9)$$

A possible technological flux for the removal of the studied M(II) ions from wastewater with their recovery as crystalline oxalates is presented in fig. 4.

4. Conclusion

The precipitation of Pb^{2+} and Cd^{2+} solutions as crystalline oxalates represent an easy way to recover the metal ions from waste waters. The recovery of metal ion as crystalline oxalates, from waste waters has the following advantages: the speed of cleaning, filtering, washing which is superior compared with the case of amorphous precipitates, the compact volume of the precipitate and the accessibility of the precipitation reagent. Another important advantage is that the crystalline oxalates can be easily transformed in pure oxides, at low temperature, about 350^0C. The recovery of heavy metals as oxalates resolves both the environmental problems and the problem of transitional metals recovery.

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