

COMPARATIVE STUDY ON THE RECOVERY OF ZINC, CADMIUM AND LEAD CATIONS FROM WASTE WATERS USING PRECIPITATION METHOD

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Abstract

This paper contains a comparative study between recovering of zinc, cadmium or lead cations from waste waters from industries. Zn^{2+} , Cd^{2+} and Pb^{2+} cations were precipitated as oxalate salts. In all experiments, concentrations of Zn^{2+} , Cd^{2+} and Pb^{2+} in initial solution were less than 1 g L^{-1} , so these often resulted from waste waters. Optimum conditions (pH, temperature, reagent excess) for recovery of these cations as oxalates were determined, using 1 N oxalic acid as precipitation reagent and $NaHCO_3$ as pH adjuster. Recovery yield of all studied cations were over 95% and finally their concentration in solution were under 5 mg L^{-1} . Crystalline structures of isolated oxalates, $ZnC_2O_4 \cdot 2H_2O$, $CdC_2O_4 \cdot 3H_2O$ and PbC_2O_4 , were proved with FT-IR, thermogravimetry and SEM methods. The presence of crystallisation water and the number of water molecules in the composition of $ZnC_2O_4 \cdot 2H_2O$ and $CdC_2O_4 \cdot 3H_2O$ were recorded in TG-DTA-DTG curves. Decomposition temperatures were typical for these oxalate salts.

Key words: zinc, copper, lead, waste waters, recovery

INTRODUCTION

Waste waters with high concentration of zinc, cadmium and lead cations can result after discharge waters (Ahmed R. et al. 2006) from electronic (McLay W. J. et al, 2000), galvanic (Matlock M.M. et al., 2002), aeronautical industries (Abd El-Moniem et al., 2005), paints and pigments industry based on heavy metals compounds (Hagen T., et al, 2004) and also from the extraction and processing of non irons minerals (Ahmad S. et al, 2002, Burtică, G. et al. 2000, Feng J et al., 2007). Concentrations of these cations in waste waters depend significantly by technological recovering stage (Mahvi A. H. et al., 2005, Poon C. P, 1984).

The recovery of Zn^{2+} , Cd^{2+} and Pb^{2+} using classic methods like chemical neutralisation, coagulation (Marder L. et al., 2003), ionic exchange, adsorption (Srinivasa, K.R. et al, 2002), electrolyse (Huang H. et al., 2009) using just now was difficult to achieve. Gavris et al. (Gavris G. et al., 2005, Gavris G. et al., 2006) published before similar studies for zinc, cadmium and lead cations

with concentrations in range 10–100 mM, and using NaOH solutions as pH regulator (Gavris G. et al., 2008). Unfortunately, waste waters from the most industrial processes contain zinc, cadmium or lead cations in concentration under 1 g L⁻¹. For this reason, we proposed to improve the precipitation with 1 N oxalic acid, using NaHCO₃ as pH adjuster, for solutions of Zn²⁺, Cd²⁺ and Pb²⁺ with concentrations less than 1 g L⁻¹ (~3.0 mM).

Recovery yield (%) of studied cations as oxalate was calculated with next formula (1):

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

α is recovery yield (%)

$C_{i,Me^{2+}}$ is initial concentration of the cation (mg L⁻¹) in solution before the precipitation with oxalic acid

$C_{f,Me^{2+}}$ is final concentration of the cation (mg L⁻¹) after the precipitation and the isolation from solution as oxalate.

MATERIAL AND METHODS

Reagents used in all experiments were high chemical purity and their solutions were prepared only with bidistilled water. In samples, Zn²⁺, Cd²⁺ and Pb²⁺ concentrations were determined with spectrophotometric and AAS methods. The pH monitoring during the experiments was carried out with Multi 720 Inolab series WTW equipment. Cation concentrations were determined with both T-60 UV-VIS model spectrophotometer and AAS Thermo Electron M Series M5 Dual and STAT accessory – atomic capture according to SR ISO 8288 (Cordaş, E. et al, 1998). Thermogravimetric analyses were performed with a derivatograph Paulik Erdely 1500 C MOM Budapest, with at heating speed by 5°C min⁻¹, in the range 20-500°C and with α -Al₂O₃ as reference material in static air stream. The FT-IR spectra were recorded with a JASCO 430 FTIR spectrometer, KBr pellets, in range 400–4000 cm⁻¹.

Three solutions of Zn²⁺, Cd²⁺ and Pb²⁺ by 1 g L⁻¹ concentration were prepared from ZnSO₄·7H₂O, Cd(NO₃)₂·4H₂O and Pb(NO₃)₂ salts. Stoichiometric mixtures between 50 mL (0.165 mmol) 1 g L⁻¹ Zn²⁺ solution and 1.53 mL (0.165 mmol) 1N oxalic acid were prepared to 20°C, under continuous stirring for 10 minutes, to different pH values: 1.0, 2.0, 3.5, 4.0, 4.5, 5.5 and 5.7. The pH values were adjusted with 2%, 5% and 10% NaHCO₃ solutions. Precipitates were filtrated and were brought to 200 mL and then Zn²⁺

concentrations were determined. Experiments were repeated in the same mode for 50 mL Cd^{2+} (0.162 mmol), respectively for 50 mL Pb^{2+} (0.151 mmol) . The recovery yield (%) of Zn^{2+} , Cd^{2+} and Pb^{2+} cations as oxalates from solutions to different pH values were recorded in Fig. 1.

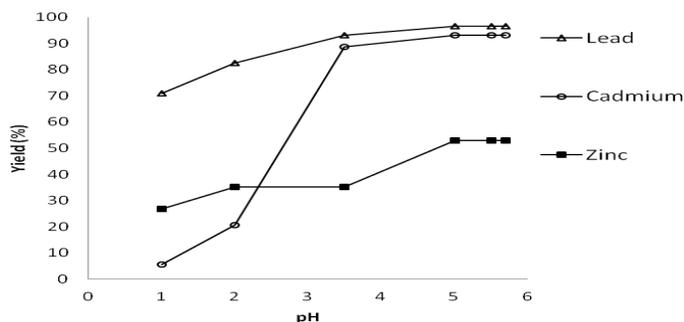


Fig. 1 The variation of recovery yield (%) for Zn^{2+} , Cd^{2+} and Pb^{2+} with pH

In Fig. 1 can see that the highest recovery yield of all studied cations after precipitation with oxalic acid was achieved to pH 5.0-5.7. In this range, the recovery yield was 52.94% for Zn^{2+} , 93.25% for Cd^{2+} and 96.53% for Pb^{2+} .

Further, Mixtures between each studied cation and 1 N oxalic acid added in 10%, 20%, 50%, 80% and 100% excess, kept to 20°C, under permanently mixing, for 10 minutes, at pH 5.5. In Fig. 2 plots of yield variation with oxalic acid excess were shown. Solutions and precipitates resulted after experiments were analysed.

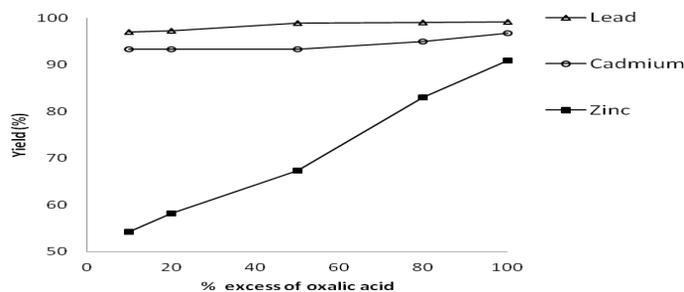


Fig. 2. The variation of recovery yield for Zn^{2+} , Cd^{2+} and Pb^{2+} with excess of oxalic

The excess of oxalic acid influenced slowly the recovery yield of cadmium and lead cations, but an excess more 50% increased the recovery yield of zinc (Fig. 2).

For determination of optimal temperatures for separation of each cation, in reaction mixture, 1N oxalic acid was added in 100% excess. Experiments were performed to pH 5.5, for 10 minutes at the following temperatures: 20°C, 40°C, 60°C and 80°C. Variations of recovery yield (%) with temperature for all studied cations were plotted in Fig. 3. Precipitates were filtrated and were analysed. The concentration of cations in solutions was determined too.

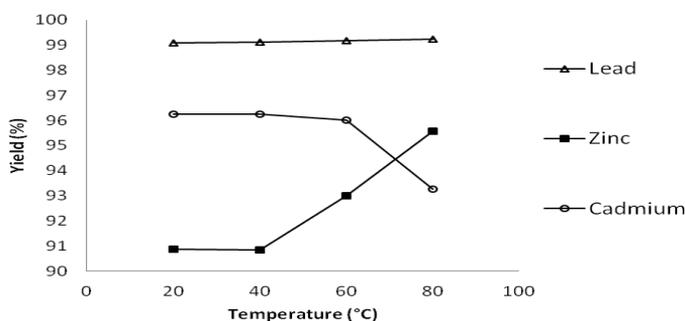


Fig.3 The variation of recovery yield (%) of Zn^{2+} , Cd^{2+} and Pb^{2+} with temperature

The recovery yield of zinc (Fig 3) increased with temperature and became maximal at 80°C (95.56%). In Fig. 3 was shown that the recovery yield of cadmium was very good in range 20–60°C. The slight decrease of yield from 96.8% at 60°C to 93.25% at 80°C was due to increase of the ionic force in solution caused by excess of oxalic acid. Instead, the recover yield of lead cation preserved over 99% in whole temperatures range.

RESULTS AND DISCUSSION

Data from thermogravimetric analysis of precipitates separated from Zn^{2+} , Cd^{2+} and Pb^{2+} solutions were recorded in Table 1. As can be seen in TG curves, the weight lost occurred in two steps for zinc and cadmium salts and in a single step for lead salt. In the first step, under 140°C, were lost crystallisation water molecules from $ZnC_2O_4 \cdot 2H_2O$ and $CdC_2O_4 \cdot 3H_2O$ and appeared as an endothermal process in DTA curves. Exothermal processes around 350°C, for all studied precipitates, were assigned to damage of crystalline structures and

was associated with a second weight lost in TG curve due to decomposition of oxalates to metal oxides, CO and CO₂ (Xiong Y. et al., 2013).

Table 1

Thermogravimetal analysis of ZnC₂O₄·2H₂O, CdC₂O₄·3H₂O and PbC₂O₄

Compounds	DTA		DTG		TG	
	Endothermal (°C)	Exothermal (°C)	(°C)		(% weight)	
ZnC ₂ O ₄ ·2H ₂ O	140	370	140		19	57
CdC ₂ O ₄ ·3H ₂ O	80	320	85	318	21	49.5
PbC ₂ O ₄	-	350	-	350	-	24.4

In FT-IR spectra of ZnC₂O₄·2H₂O (Wladimirsky A et al., 2011), CdC₂O₄·3H₂O and PbC₂O₄ (Mancilla N. et al., 2009) were obtained characteristic vibrational bands for oxalate anion (Deshpande A. S. et al., 2001). Infrared bands of ZnC₂O₄·2H₂O spectra were recorded in Fig. 5 and were assigned to following bands (Parekh B.B. et al., 2008): ν(O-H) to 3377 (b, vs), ν_{as}(C-O) to 1630 (vs), ν_s(C-O) and ν_s(C-C) overlapped to 1363 (s), ν_s(C-O) and δ(O-C-O) overlapped to 1315.5 (s), ν_s(C-C) and δ(O-C-O) overlapped to 824 (s), ρ(H₂O) to 750 (s) and δ_{ring} to 619 (m), 494 and 451 cm⁻¹.

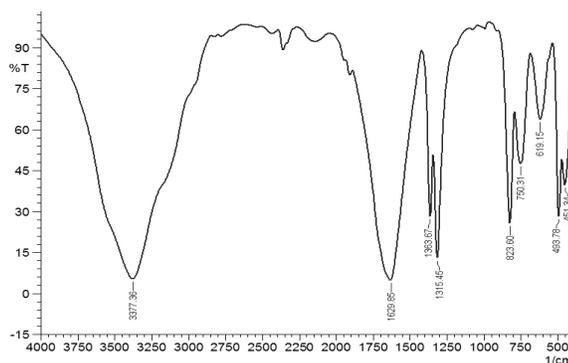


Fig. 4 FT-IR spectra of ZnC₂O₄·2H₂O

In FT-IR spectra of CdC₂O₄·3H₂O recorded in Fig. 6 were occurred next vibrational bands: ν(O-H) to 3559 (b, vs), ν(C-O) to 1607 (vs), ν_s(C-O) and ν_s(C-C) overlapped to 1381 (s), ν_s(C-O) and δ(O-C-O) overlapped to 1313.5, ν_s(C-C) and δ(O-C-O) overlapped to 777 (s), and δ_{ring} to 600 and 523(m) cm⁻¹. Vibrational band of ν_s(C-C) and δ(O-C-O) was shifted to lower energies than in ZnC₂O₄·2H₂O spectra and was overlapped by ρ(H₂O) band

In FT-IR spectra of PbC₂O₄ were noted next vibrational bands: ν_{as}(C-O) to 1608 (vs), ν_s(C-O) and ν_s(C-C) overlapped to 1380 (s), ν_s(C-O) and δ(O-C-

O) overlapped to 1310, $\nu_s(\text{C-C})$ and $\delta(\text{O-C-O})$ overlapped to 780 (s), and δ_{ring} in range 465-480 (m) cm^{-1} .

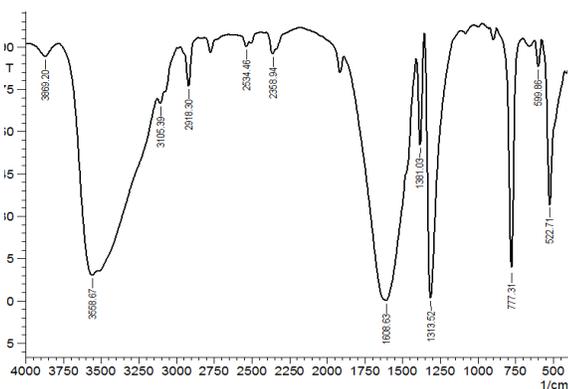


Fig. 5 FT-IR spectra of $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$

Microscopic analysis SEM revealed crystalline structures characteristic for oxalates of zinc, cadmium and lead (Fig. 6). Cadmium oxalate found to have a triclinic structure (Arumugam D. et al, 2013). According to the SEM image, PbC_2O_4 was precipitated as micrometric rhombic plates with thickness of hundreds of nanometers. By thermal decomposition at 500°C of PbC_2O_4 , a porous mass of lead oxide was obtained. Both pores and particles have sizes up to 300 nm. The obtained oxide has lamellar structure, the observed particles being composed from packed plates with thickness smaller than 50 nm.

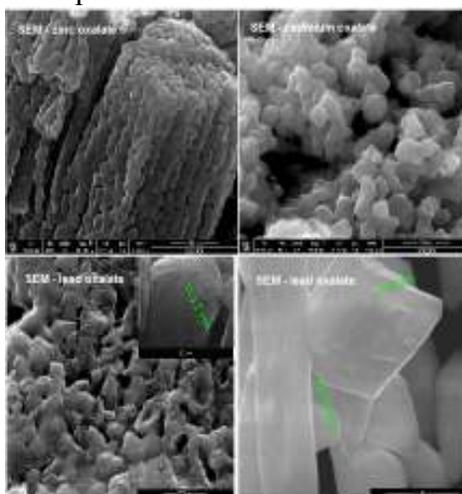


Fig. 6 Microscopic analysis SEM of $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ and PbC_2O_4

CONCLUSION

The recovery of zinc, cadmium and lead cations as oxalate were the best achieved to pH 5-5.7. Increasing of oxalic acid excess favoured the recovery of zinc cation and had minimal influence in recovery of cadmium and lead cations. While the recovery yield of Cd^{2+} and Pb^{2+} varied insignificantly with temperature, Zn^{2+} recovery increased with temperature and was maximal at 80°C . The recovery yields of all studied cations from solutions by concentrations under 1 g L^{-1} ($\sim 3.0\text{ mM}$) were very good, over 95%. The recovery yield in the same conditions increased in order $\text{Zn}^{2+} < \text{Cd}^{2+} < \text{Pb}^{2+}$. Using of NaHCO_3 as compared with NaOH reached the recovery yield of cations, even smaller concentrations than other studied before. Using of cheap reagents, obtaining high recovery yield independent of temperature and amount of reactants, especially for cadmium and lead cations are advantages of this method.

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