

RECOVERING OF MANGANESE CATIONS FROM INDUSTRIAL WASTEWATER USING OXALATE PRECIPITATION

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Abstract

The recovering of manganese from waste waters was realized using oxalate anions under pH control. The main advantages of the method was the pH range of precipitation with oxalate takes place to lower value than in other methods and with smaller energetic consume. The optimal conditions for the isolation of manganese from water solution like manganese oxalate were established. The precipitation of manganese was made at pH around 5.5 and the solution can be recycling in industrial process with minimum cost. Temperature variation affected insignificantly manganese separation from solution, the yield increased little from 20 °C to 80 °C. A 15% excess of oxalate acid to manganese precipitation streamlined its synthesis. In conclusion, the best yield of manganese cations separation from waste waters after precipitation with oxalic acid under pH control with bicarbonate potassium solution was 92.5%. The manganese concentration was reduced from 50 mg to 12,1 mg. The composition of solid produce resulted from this method was analyzed quantitatively with atomic absorption. The structure of $Mn(C_2O_4) \cdot 2H_2O$ was supported with thermogravimetry and FT-IR techniques.

Key words: manganese, oxalate, waste waters, FT-IR

INTRODUCTION

In this paper we exposed a new method for manganese recovering from wastewater resulting from phosphatating operation of the metal surface in galvanic bath (Burtica et al., 2009), machine building industry, pharmaceutical industry and others (Zhang et al., 2017). Just now, manganese recovering from waste solution was carried over pH 9 using ionic exchange method with cationic resin, chemical precipitation with classic agents like NaOH, $Ca(OH)_2$, sodium phosphate or sodium carbonate or electrochemical method with a high energetic consume (Oniciu, 1980). Manganese recovering was studied for average concentrations of these cations in wastewaters, from 25 to 500 $mg \cdot L^{-1}$.

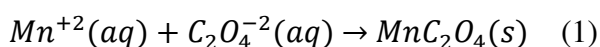
MATERIAL AND METHOD

1 $g \cdot L^{-1}$ solution was prepared from $MnSO_4 \cdot 4H_2O$. Manganese cations were precipitated to oxalate salts with 1N $H_2C_2O_4$ solution. pH was kept under control with $NaHCO_3$ solutions. Manganese was determined with complexometric method using 0,05M EDTA in pH 10 buffer solution in

the presence of eriochrome black T as indicator. All reagents used in these experiments were high chemical purity. The experiments were effectuated under a strict pH control using a multimeter Multi 720 Inolab series WTW equipment. Manganese concentration was determined with both volumetric method using EDTA solution and AAS Thermo Electron M Series M5 Dual and STAT accessory – atomic capture (Lajunen et al., 2009). Thermogravimetric curves were plotted with a derivatograph Paulik Erdely 1500 C MOM Budapest, with a heating speed by $5^{\circ}\text{C min}^{-1}$, in the range 20-500°C in the presence of $\alpha\text{-Al}_2\text{O}_3$ as reference material into a static air stream. The vibrational spectrum of manganese precipitate was effectuated with JASCO 430 FTIR spectrometer, working in the range 400–4000 cm^{-1} , in KBr pellets.

The precipitation of manganese was effectuated with oxalic acid in optimal condition and carefully because we proposed to obtain only pure manganese oxalate, $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, free from other manganese compounds. The influence of pH, temperature and oxalic acid quantity on the yield of manganese recovery from solution was determined. The produce obtained after precipitation was analyzed with quantitative, FT-IT and thermogravimetric methods.

Equations of the manganese precipitation is writing below (1):



The recovery yield (%) of manganese from wastewater using oxalate precipitation was calculated using mathematical formula (2) noted below:

$$\alpha(\%) = \frac{C_i - C_f}{C_f} \cdot 100 \quad (2)$$

where C_i is the concentration of manganese cation (mg L^{-1}) into the initial solution and C_f is the concentration of manganese cation (mg L^{-1}) into the final solution after precipitation with oxalic acid.

RESULTS AND DISCUSSION

Study of pH influence

50 mL manganese solution (0.91 mmol, 50 mg Mn) were precipitated with stoichiometric quantity of 1N oxalic acid (1.82 mL, 0.91 mmol). At room temperature, under vigorously stirring (300 rot min^{-1}), adding NaHCO_3 solution for pH control monitoring with a pH-meter. Reaction time for all experiments was 60 minutes. The precipitate was separated and manganese concentration into the filtrate was found with one of the quantitative methods. Results were recorded in Fig. 1. In Fig. 1 could see an increase significantly of yield (%) after pH 5, with the best values between 5.5 and 6.0. A higher pH value was not recommended because increase

significantly the chance to obtain other salts, for example MnCO_3 . In this situation, we decided to continue our experiment to pH 5.5, under a rigorous control.

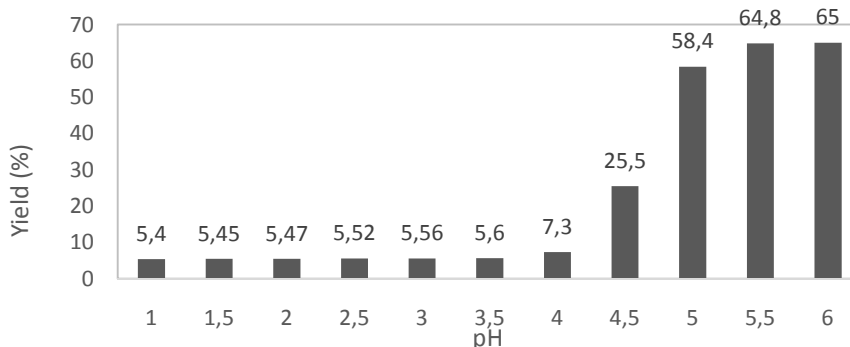


Fig. 1. Recovering yield of manganese with oxalic acid at different pH values

Determination of oxalic acid necessary

In this study, in each baker containing 50 ml manganese solution was added 1N oxalic acid in excess variable from 10% to 100%. In each baker the reaction mixture was adjusted to pH 5.5 with NaHCO_3 solutions. After a reaction time by 60 minutes at the room temperature, the precipitate was removed from solution by filtration and the residual manganese was determined from filtrate.

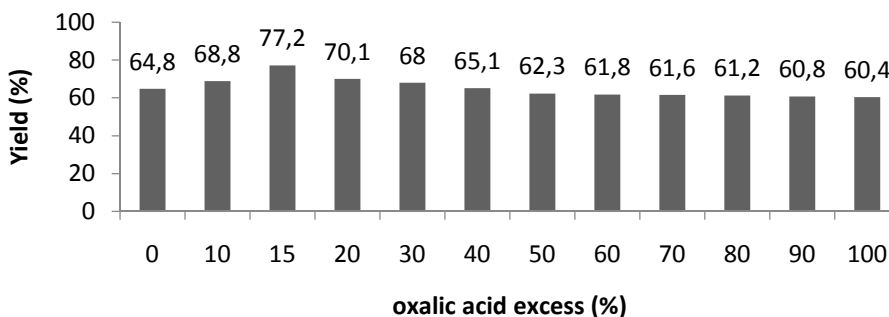


Fig. 2. The yield obtained for different acid oxalic quantity using in manganese synthesis

The variation of yield for different excess of oxalic acid was recorded in Fig. 2. In conformity with results using of oxalic acid with a 15% excess was recommended to use for a good separation of manganese from solution.

Study of the temperature influence

Four mixtures between 50 mL manganese solution 1g/L (0.91 mmol) and 2.17 mL 1N oxalic acid (1.09 mmol) were prepared. pH was adjusted at 5.5 with 10% NaHCO_3 solutions under vigorously stirring. One baker was

kept at room temperature and other were placed in the water bath at 40 °C, 60 °C, respectively 80 °C for 60 minutes. The samples were filtrated, and manganese from filtrate was quantitatively determined with analytical methods. The recovering yield was calculated with formula (2). Results from these experiments were recorded in Table 1. It was showed in Table 1, the recovering yield of manganese like oxalate started to increase at 60 °C (84.5 %) to 92,5% at 80 °C.

Table 1

Influence of temperature in the manganese recovering from wastewater

Temperature (°C)	Mn from filtrate (mg)	Yield (%)
20	11,4	77,2
40	11,4	77,2
60	7,29	84,3
80	3,75	92,5

FT-IR spectra of the solid produce from oxalate precipitating

In Fig.3 FT-IR spectra of the product obtained from the precipitation process, dried at 60°C was plotted. The broad absorption band around 3380 cm^{-1} corresponds to the $\nu\text{O-H}$ stretching vibrations (Fatemeh et al., 2009). This observation provides evidence for the presence of chemically bound H_2O in the manganese oxalate. The double absorption peaks appeared at 1653 and 1624 cm^{-1} caused by the symmetrical and asymmetrical vibrations of the carbonyl group, which are related to the existence of the $[\text{Mn}(\text{C}_2\text{O}_4)\cdot 2\text{H}_2\text{O}]$ compound. According to the literature, the uncoordinated COO group, characterized by a single stretching absorption band at 1750–1700 cm^{-1} , shifts towards the lower frequency and splits into two bands (as observed above) when it combines with metal ions as oxalate (Liu et al., 2009). The deformational mode of water usually seen around 1600 cm^{-1} is, however, masked by the doublet. The sharp absorption peaks at 1363 and 1310 cm^{-1} are assigned to both modes, symmetric stretching vibration $\nu_s(\text{C-O})$ and deformation vibration $\delta(\text{OCO})$. The peak at 815 cm^{-1} can be attributed to bending mode of OCO group, while the sharp band at 494 cm^{-1} is characteristic for the M – O bond vibrations (Ahmad et al., 2010). Thus, FT-IR absorption confirms the formation of $[\text{Mn}(\text{C}_2\text{O}_4)\cdot 2\text{H}_2\text{O}]$.

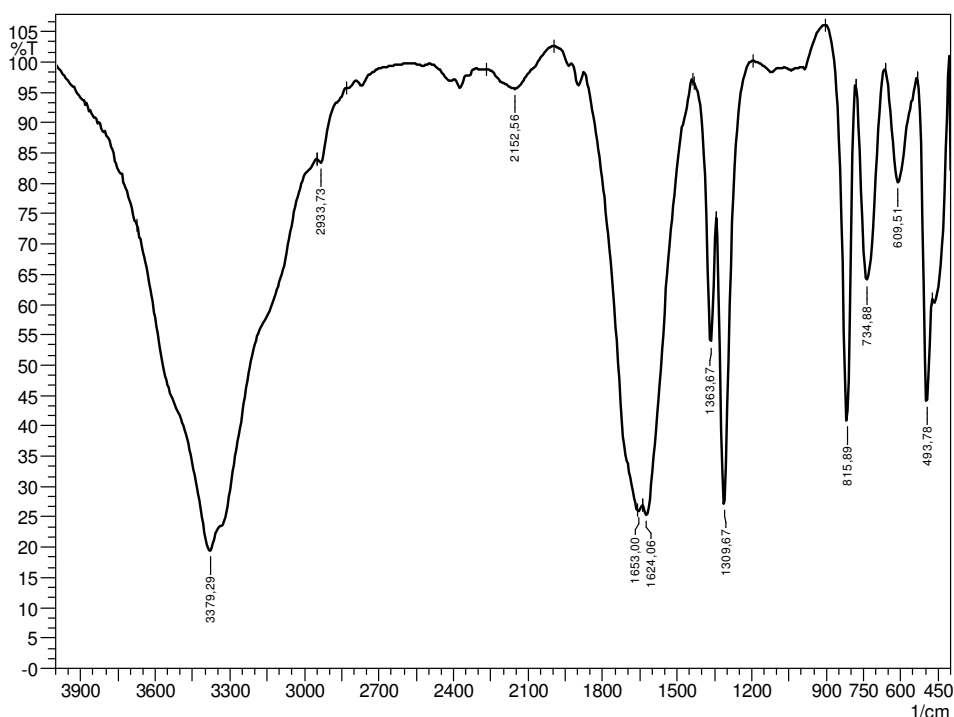


Fig. 3. FT-IR spectra of solid residue from oxalate precipitation

Thermogravimetric analyses of solid produce from oxalate precipitation

Thermal decomposition of $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ proceeded in two stages (Fig. 4). In the first, substantial weight loss of ~20% occurs in the temperature range of 171–230 °C (peak position at 184 °C) and it is attributed to removal of crystalline water of $\text{Mn}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ (water content being 20.1 wt%). The resulting anhydrous oxalate exhibits good thermal stability in the temperature range of 210–295 °C, in accord with the data reported in literature (Todor, 1972). The second stage corresponding to decomposition of anhydrous oxalate which began at 523 °C. Different ambients (viz., O_2 , air, N_2 or Ar) have been employed for decomposition of manganese oxalate dihydrate to study the formation of various manganese oxides (Thota et al., 2010). Thus, decomposition of solid produce MnC_2O_4 in helium atmosphere took place just to MnO, while in oxygen atmosphere, the decomposition produce was Mn_2O_3 . Regarding the decomposition in air, the formation of both Mn_2O_3 and MnO_2 oxides have been reported (Malecka et al., 2003).

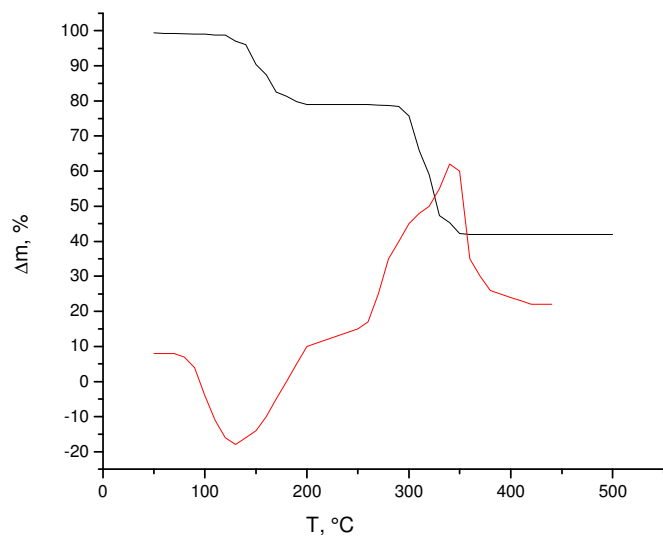


Fig.4. TG and DTA curves of the precipitated produce dried at 60°C

The nature of the decomposition product in our condition (thermal decomposition in static air atmosphere, with 5deg/min) was analyzed by FT-IR techniques. Figure 3 presents the FT-IR spectra of the decomposition product.

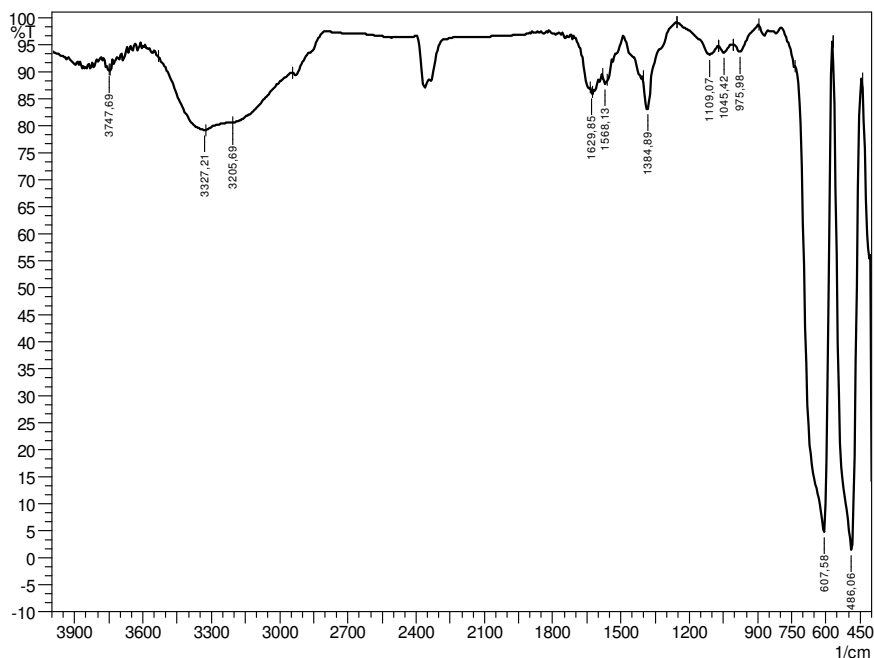
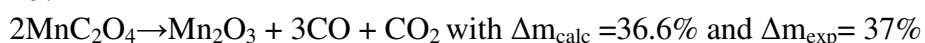
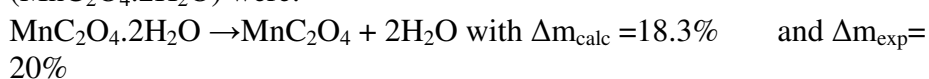


Fig. 5. FT-IR spectrum of decomposition produce of $Mn(C_2O_4)$ in oxygen atmosphere

The FT-IR spectrum of decomposition product of manganese oxalate in oxygen atmosphere (Fig. 5) exhibited some bands of adsorbed water and the organic parts. According to the literature, the peaks 612 and 529 cm^{-1} were assigned to the asymmetric and symmetric Mn–O–Mn stretching vibrations, respectively (Salavati-Niasari et al., 2009). The peak position at 400 cm^{-1} is assigned to the Mn–O–Mn bending vibration mode. FT-IR spectrum confirmed the formation of Mn_2O_3 oxide at 500°C after the thermal decomposition of the precipitated product. In conclusion, the reactions that describe the thermal behavior of the precipitation product ($\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) were:



Values of the practical mass variation for both decomposition reactions were very closely with data resulting from theoretical mass variation.

CONCLUSIONS

The highest yield of separation of manganese from the wastewaters was 92.5% and it was reached at 80 °C, at pH 5.5 and working with 15% excess of oxalate anions. A 15% oxalate in excess was recommended, because at higher quantities of oxalate the transformation of precipitate $\text{MnC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ in soluble complex anion $[\text{Mn}(\text{C}_2\text{O}_4)_2]^{-2}$ became very probably. FT-IR and thermogravimetric analysis confirmed that $\text{MnC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ was the structure and the composition of solid product resulting from wastewater. More, FT-IR spectra of decomposition product resulting after the thermal analysis showed the transformation of $\text{MnC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ after losing of water molecules in Mn_2O_3 at 523 °C, characteristic transformation for this compound in oxygen atmosphere.

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