

CLEANING WASTE WATERS WITH CHROMATES AND OXALIC ACID

Georgeta GAVRIȘ^{1*}, Anda PETREHELE¹, Sanda BOTA¹,
Ioana TOMULESCU¹, Vasilica MERCA¹

¹University of Oradea, Faculty of Science,
Department of Chemistry, Str. Universității, no.1, Romania

* **Correspondence:** Georgeta Gavris, University of Oradea, Faculty of Sciences, University street, no.1 Oradea, Romania, email: georgeta_gavris@yahoo.com
Received: march 2008; Published: may 2008

ABSTRACT. Chromium is used for plating and in chrome steel. The chromates [chromium (VI)] have many industrial uses as pigments, catalysts, fungicides. The waste waters with chromate are usually presented in industries side by oxalic acid produced at aluminum protection surface. This paper proposed a very cheap method for reciprocal treatment due to function as a bidentate ligand of oxalic acid in the form of dianion with many transition metals ions. Preparation of oxalate chromate potassium salt was made in form of $K_3[Cr(C_2O_4)_3]$ anhydrous, using a suitable ratio from oxalic acid, potassium chromate and sulfuric acid. The crystals have been deposited, filtered and washed with ethanol. The product is dried and the yield calculated as a percentage based on chromium is dried.

Keywords: chromate, waste waters, oxalic acid

INTRODUCTION

There are a lot of dates and experimental research about treatment of waste waters containing Cr(VI) which can appears from different sources in a various concentration as diluted solutions or concentrated fluids.

The most investigated sources are electroplating works, tanneries, pigments, where chromate anion concentration begins with 5-50 ppm and may be attends 200-1000 ppm¹⁻³.

The treatment of waste waters with chromium hexavalent shape content are made by chemical reduction method, using reactive agents like $FeSO_4$, Na_2SO_3 , $NaHSO_3$, $Na_2S_2O_5$, SO_2 gaseous, $(Fe + H_2SO_4)$ or electrochemically. All the reduction reactions had taken place in acid range, pH 2-2,5 in the presence of sulfuric acid usually.

By electrochemical reducing it is known a suitable method involving coagulation process assured by $Fe(OH)_3$.

If besides of chromate anions there are an eloxal process (on aluminium) with oxalic acid, then appears also waste waters with oxalic acid.¹ The high concentration of oxalate anion in the presence of sulfuric acid might be a good notification for reciprocal treatment waste waters coming from chromium electroplating and waste waters coming from aluminum protect surface by eloxal process.

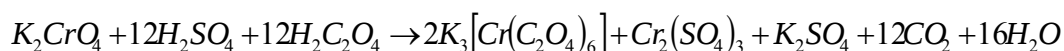
* hexavalent chromium could be reduced by oxalic acid in the presence of sulfuric acid

* it could be obtained a new trivalent chromium compound in the shape of oxalate/chromium complex.

MATERIALS AND METHODS

All the reagent were chemically pure or ultra pure: Merck, Fluka, Reanal in the next order: potassium chromate 0,1M sulfuric acid 1:2 vol, potassium permanganate 0,1N (F=1), oxalic acid 0,5M (F=1), Mohr salt 0,1N (F=1), sodium hydroxide 0,1N (F=1), standard chromium etalon 0,05 mg/mL, deionised water.

The apparatus were: analytical balance Toledo, spectrophotometer UV-VIS, IR-Spectrophotometer KBr cell, magnetic stirrer. The hexavalent chromium content was titrimetrical determined with Mohr salt 0,1N and potassium permanganate 0,1N in sulfuric acid range., pH 2. Oxalate anion was analysed titrimetrically with potassium permanganate on boiling⁴. The traces of hexavalent chromium untransformed in chromium oxalate complex compound was photometrical determined by means of diphenylcarbazide at 573 nm, together with Cr(III), between 1 and 20 mg/l. The cation Cr(III) was eliminated by precipitation with sodium hydroxide at 60°C and pH 9⁵. In the filtrate was determined Cr(VI). The chemical equation to obtain oxalate chromium potassium salt compound is:



It was prepared one saturated potassium chromate solution acidified with sulfuric acid at 70-80°C, under

magnetic stirrer, was added a little quantities from 0,5M oxalic acid as long as solution has a violet color.

After chemical reaction, a violet crystals of $K_3[Cr(C_2O_4)_6]$ have been separated.

STUDY AREA

The influence of the oxalic acid concentration upon extraction degree of a $K_3[Cr(C_2O_4)_6]$ was studied in accordance with Table 1.

Table 1
THE INFLUENCE OF OXALIC ACID EXCESS UPON CHROMIUM OXALATE COMPLEX OBTAINING^{6,7}

K_2CrO_4 0,1M [mL]	H_2SO_4 2N [mL]	H_2SO_4 0,5M [mL]	Excess $H_2C_2O_4$ %
20	2	12	0
20	2	16	33,33
20	2	18	50
20	2	20	66,66
20	2	24	100

Table 2
THE CONVERSION OF HEXAVALENT CHROMIUM TO $K_3[Cr(C_2O_4)_6]$

Oxalic acid excess %	Cr^{+6} filtrate [mL]	Mohr salt 0,1N [mL]	$KMnO_4$ 0,1N [mL]	Reduction $Cr(VI)$ to $Cr(III)$, %	Cr^{+6} residual [mg/L]
0	32	10	8,3	60,26	429,84
33,33	31	10	8,8	71,63	307,09
50	35,3	10	9,3	79,03	226,26
66.66	31	10	9,8	91,81	88,02
100	31	-	-	99,80	2,07

RESULTS AND DISCUSSIONS

The results presented in Table 2, allowed to calculate the formula conversion percentage from $Cr(VI)$ to $Cr(III)$, as follows:

$$C, \% = \frac{N_i - N_f}{N_i} \cdot 100 \quad (2)$$

$$Cr(VI)_{res} [mg/l] = \frac{4}{30} \cdot (10 - F_{KMnO_4} \cdot V_{KMnO_4}) \cdot V_{filtrate} \cdot A_{Cr} \quad (4), \text{ where } A_{Cr} = 52,00$$

$$C, \% = \frac{2 \cdot 10^{-3} - \frac{4}{30} \cdot (10 - F_{KMnO_4}) \cdot V_{filtrate} \cdot 10^{-4}}{2 \cdot 10^{-3}} \cdot 100 \quad (3)$$

where:

N_i = initial mol number of chromium (VI); $2 \cdot 10^{-3}$

N_f = final mol number of chromium (VI)

The residual hexavalent untransformed chromium was calculated from Table 2 and formula (3):

The excess of oxalic acid increase the extraction degree up to 99,80% being a good factor for process efficiency and a cheap complexation reagent.

The chromium oxalate complex was determined by IR spectrophotometer (Germany) and its diagram shows in figure 1 (see below).

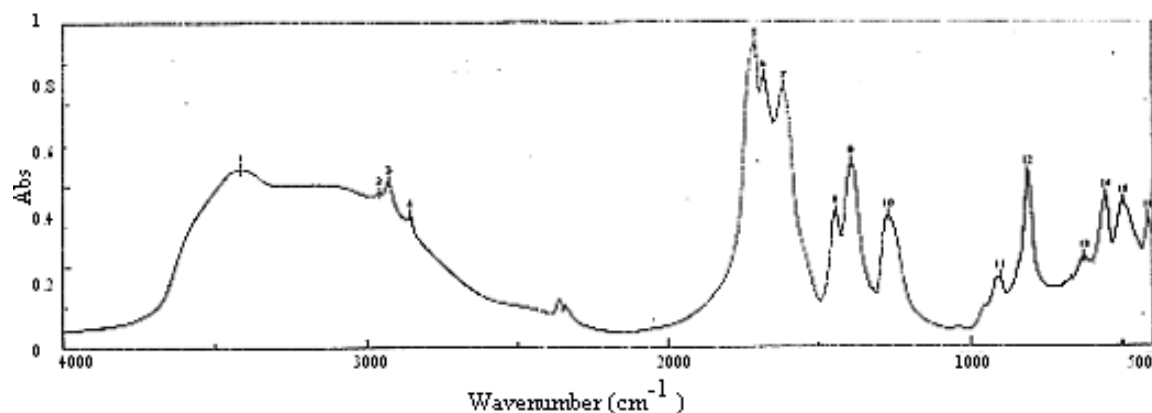


Fig. 1 IR spectrum of oxalic acid (HOOC-COOH)

The IR-spectrum analysis is representative for oxalate anion between wave numbers of our compound. The vibration from 900 cm^{-1} corresponds to C-C bond. The signals between $1650\text{-}1200 \text{ cm}^{-1}$

attribute to vibration band from C=O and C-O bonds. The last vibration band is very large and dues by O-H bond. In spectrum can see deformation bands, δ_{H-O-H}

between 1700-1640 cm^{-1} and $\delta_{\text{O-H}}$ from 1450 to 1210 cm^{-1} .

CONCLUSIONS

The reciprocal treatment of hexavalent chromium and oxalic acid presented in waste waters coming for electroplating surfaces works, might be successfully applied as well as, the both concentration are large.

The optimal excess of oxalic acid are 100%.

The maximum extraction degree was 99% into $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_6]$.

Chemical analysis of chromate untransformed made by photocolometric and titrimetric methods, confirming 99% extraction degree.

The IR spectrum confirmed the structure and composition of chromium oxalate complex.

By reciprocal treatment it was realised a sub-product and the cleaning in the same time waste waters with chromate anion, oxalic acid and sulphuric acid

REFERENCES

- Grunwald, E. and Oniciu., L., Galvanotechnics, Scientific and Encyclopedic Publishing House, Bucharest, 1980
- Dash. P., Srinivasa Rao. K, Sarani. D., and Roy. P., Jnl. of Chem. Techn. and Biotechn., (77), pp 1107-1113, 2002
- Bazan J. K., Bisang J.M., Jnl. Appl. Electrochem., (34). pp 50-54, 2001
- Macarovici C., Inorganic quantitative chemical analysis, Romanian Academic Publishing House, Bucharest, 1979
- Gavriş G., Environment polluted chemistry, Publishing Univ. House, Oradea, 2003
- Olaru R., Suteu D., and Păduraru C., The utilization of celulozic materials for waste water deppolution, Chem. Jrn, (7). pp 123-128, 1998
- Gavriş G., Iovi A., and Sebeşan M., Stady of the cleaning process of the waste water with zinc ions content, Chem.. Bull. Politehnica Univ.Timişoara, 50 (64), pp. 166-168, 2005

