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SELECTIVE RECOVERY BY SOLUBILIZATION OF METALS IONS OF CHROMIUM, IRON AND ZINC FROM ELECTROPLATING SLUDGE TO DEVELOP PIGMENTS FOR CERAMICS INDUSTRY

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ABSTRACT

Electroplating industries discharge large amounts of heavy metals, including chromium (Cr), iron (Fe) and zinc (Zn) ions, in the wastewater resulted from technological processes, as well as in the sludge from wastewater treatment.

In this paper are reported the results of the scientific activity developed in laboratory to recover Cr(VI,III), Fe(III), and Zn(II) from the galvanic sludge by selective solubilization and to obtain metal salts which can afterwards be used as pigments in ceramics industry.

Chromium recovery from the sludge was performed by alkaline sludge oxidation to obtain salts of Cr(VI). We aimed at obtaining two types of pigments based on chromium: chromium yellow pigments by precipitation of Cr(VI) in the form of lead chromate ($PbCrO_4$) and chromium green pigments by reducing Cr(VI) and its precipitation in the form of Cr(III).

Red pigment based on Fe(III) was obtained by solubilizing the resulting sludge after the recovery of chromium and iron precipitation at a pH corresponding to the complete precipitation.

From the remaining solution by recovering Cr and Fe, Zn was recovered as zinc hydroxide [$Zn(OH)_2$] that can be used as raw material in the ceramics industry.

In the experiments performed at laboratory scale, optimal technological parameters were set for the selective recovery of the tested sludge metal ions.

KEYWORDS: electroplating sludge, chromium, iron, zinc, selective recovery

1. Introduction

Treatment and metal surfaces coating processes require the use of hazardous chemical substances which are further discharged as process waste solutions and washing wastewater. The process waste solutions which are regularly discharged come from the metal surfaces preparing operations (degreasing, pickling, passivating, polishing, etching) and from the discharge of active washing wastewater (copper plating, nickel plating, chrome plating, zinc plating, cadmium plating). The technological solutions are discharged when they cannot fit in the technological work parameters through corrections or when the work technology is changed [1].

Given the high concentrations of metallic ions, the main source of wastewater with such content is represented by the process waste solutions which actually have a share of 90-95 % from the amount of discharged salts together with wastewaters from metal plating workshops.

Waters and concentrated solutions from chemical and electrochemical processing operations of metal surfaces are treated through two technologies [2]:

- treatment technologies to result sludge (metal ions precipitation / solid ion exchange prehension / recycled chemical washing, etc.).
- recovery treatment technologies in order to avoid sludge formation and to recover useful compounds.

Collecting and treating waste water (washing water and wastewater concentrates) with heavy metals content (copper, trivalent chromium, cadmium, nickel, zinc, iron, etc.), cyanide and hexavalent chromium are jointly performed, resulting in a precipitation sludge with complex chemical composition, classified as a hazardous waste / eco-toxic waste. Removing it by landfilling implies environmental risks, because of the risk of rainwater leaching (pH = 5.0 – 5.5) of heavy metals content, which leads to soil and surface pollution and to ground water pollution. These treatment processes were originally designed only for retaining toxic substances from water, but they were later adapted to the possibility to recover metal compounds.

The recovery of industrial waste is one of the main national and international research themes concerning the reuse technologies in various industries, correlated with the environmental impact. The reuse potential represents the essential criterion in the waste management approach. From this point of view, the equivalence between the concept of waste and the concept of secondary raw material is increasing [3, 4].

In the following part is presented a process for the selective recovery of metal ions such as chromium (Cr), iron (Fe), zinc (Zn) from the solid sludge resulted from wastewater treatment from a company with activities in the chemical and electrochemical treatment of metal surfaces, namely: galvanizing of metal surfaces.

2. Experimental results

The scientific experiments at laboratory scale have been performed in order to recover Cr(VI,III), Fe(III), and Zn(II) ions from the galvanic sludge by selective solubilization and to obtain metal salts. The galvanic sludge employed in this research was collected from a local plant, after the waste solutions and washing wastewater treatment. The sludge to be tested was milled in a porcelain jar to obtain particles <1 μm in order to increase the reaction surface and was dried at 105 ºC for 24 h (the water content of the sludge was 68 wt.%). The waste was characterized by atomic absorption spectrometry in order to estimate the chromium, iron and zinc content.

The physico-chemical analyses performed on the galvanic sludge revealed the following chemical composition towards dry substance, expressed in percentage (%). This composition is presented in Table 1:

Table 1. *Physico-chemical composition of the analyzed galvanic sludge*

Ions	% towards dry substance	The total amount of the metals in 150 g of sample (g)
Cr	0.27	0.4050
Fe	9.10	13.6500
Zn	18.10	27.1500
Ni	0.05	0.0750
Cu	0.009	0.0135
Cd	0.004	0.0060

2.1. Chromium recovery

The experiments conducted in the laboratory led to the establishment of a procedure for recovering chromium from the galvanic sludge resulting from the galvanic wastewater treatment. The technology of wastewater neutralization is based on the detoxification of waste by reducing chromium (VI) to chromium (III) and then using a hydroxide to precipitate insoluble chromium (III) hydroxide. Other metal hydroxides are also precipitated in the resulting sludge [5, 6].

The chromium recovery procedure includes the alkaline oxidation of Cr(III) to Cr(VI) and Cr(VI) recovery by precipitation.

The phases of chromium recovery procedure are presented in Fig. 1.

PHASE 1: Solubilization of Cr(III) through alkaline oxidation

Solubilization of Cr(III) has been performed from 150 g of the galvanic sludge sample through alkaline oxidation at pH = 12.0-12.5, with sodium hypochlorite (NaOCl) 12% and sodium hydroxide (NaOH) 30%; reaction temperature = 80 ºC, reaction time = 30 minutes; stirring throughout the reaction time.

$$2Cr(OH)_3 + 3NaOCl + 4NaOH = 2Na_2CrO_4 + 3NaCl + 5H_2O \quad (1)$$

Simultaneously with chromium oxidation, a partial oxidation reaction of Fe(II) to Fe(VI) also occurred, in the form of sodium perferrate (Na_2FeO_4), insoluble compound at this stage which will remain in the sludge cake after solution filtering:

$$Fe(OH)_2 + 2\ NaOCl + 2\ NaOH = Na_2FeO_4 + 2\ NaCl + 2\ H_2O \quad (2)$$

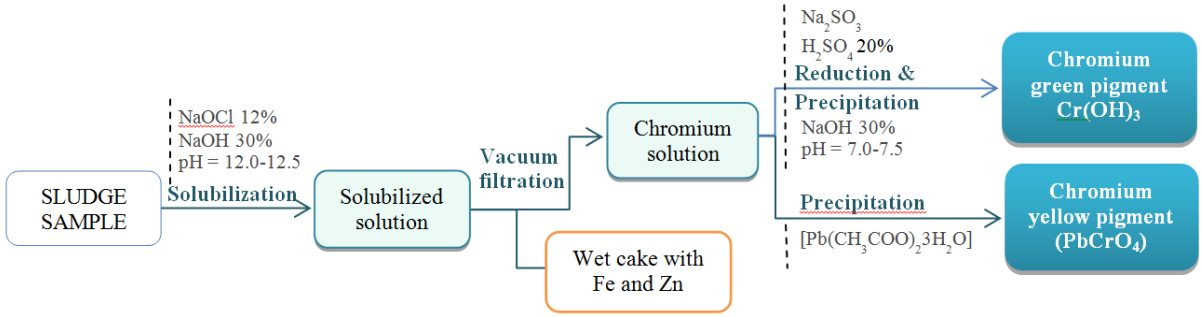

Fig. 1. *The scheme of chromium recovery procedure from galvanic sludge*

PHASE 2: Filtering the chromium solution

Filtering the chromium solution was performed using a vacuum pump, yielding a wet cake containing mainly zinc and iron and a solution of sodium chromate (Na_2CrO_4) which will be subject to processing in order to obtain chrome pigments.

PHASE 3: Washing wet cake from filtration

Washing the wet cake resulting from filtration with vacuum pump was performed for the full recovery of chromium absorbed by the cake.

In the experiments we attempted to obtain two different types of pigments based on chromium:

- chromium yellow pigment by precipitation of hexavalent chromium in the form of lead chromate;
- chromium green pigment by reduction of hexavalent chromium to trivalent chromium and its precipitation in the form of chromium hydroxide.

PHASE 4: Precipitation Cr(VI) with lead acetate [$Pb(CH_3COO)_2 3H_2O$] in the form of lead chromate ($PbCrO4$) – resulting chromium yellow pigment (Fig. 2).

$$Na_2CrO_4 + Pb(CH_3COO)_2 = PbCrO_4 + 2NaCH_3COO \quad (3)$$

Fig. 2. *Chromium yellow pigment ($PbCrO_4$)*

PHASE 5: Reducing Cr(VI) to Cr(III), in acid medium (H_2SO_4 20%) with sodium sulfite (Na_2HSO_3) and its precipitation with sodium hydroxide (NaOH)30% in the form of chromium hydroxide [$Cr(OH)_3$] - chromium green pigment (Fig. 3).

$$2\ Na_2CrO_4 + 3\ Na_2SO_3 + 5\ H_2O = 2\ Cr(OH)_3 + 3\ Na_2SO4 + 4\ NaOH \quad (4)$$

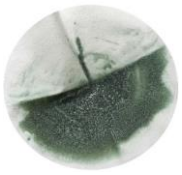

Fig. 3. *Chromium green pigment $Cr(OH)_3$*

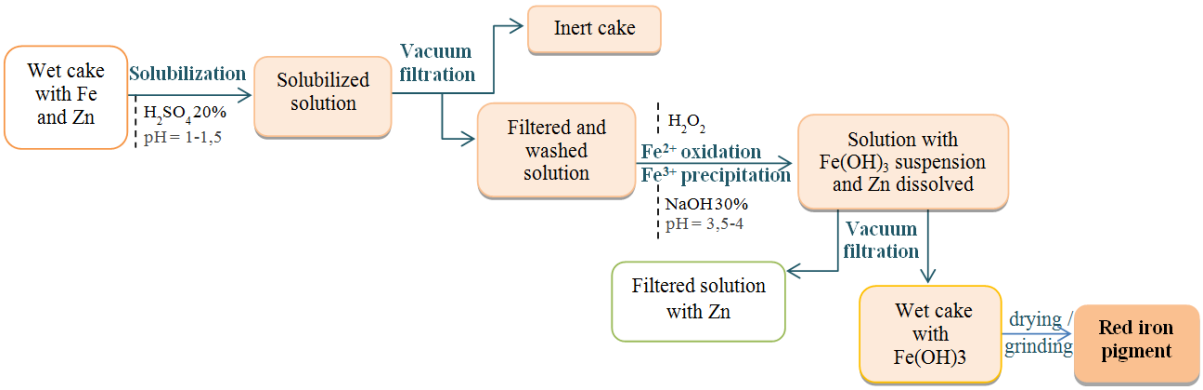

Fig. 4. *The scheme of iron recovery procedure*

2.2. Iron recovery

Iron is present in the cake obtained after chromium recovery, in the form of compound of Fe(II), Fe(III) and Fe(VI). Fe (VI) was obtained in the first phase of a chrome recovery process by partial oxidation of Fe(II) to Fe(VI) in the form of sodium perferrate (Na_2FeO_4).

The phases of iron recovery procedure are presented in Fig. 4.

PHASE 1: Solubilization of the sludge cake remaining after chromium recovery

The solubilization of the sludge cake was performed with sulfuric acid (H_2SO_4) 20% at pH = 1.0–1.5; reaction temperature = 90 ºC; reaction time = 30 minutes; stirring throughout the reaction time.

The iron compounds solubilizing reactions are the following:

$$Na_2FeO_4 + 16\ H_2SO_4 + 3Fe_3O_4 = 5Fe_2(SO_4)_3 + Na_2SO_4 + 16H_2O \quad (5)$$

$$2Fe(OH)_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 6H_2O \quad (6)$$

$$Fe(OH)_2 + H_2SO_4 = FeSO_4 + 2H_2O \quad (7)$$

Simultaneously with iron solubilization, the solubilization of Zn(II) also occurred, according to the following chemical reaction:

$$Zn(OH)_2 + H_2SO_4 = ZnSO_4 + 2H_2O \quad (8)$$

PHASE 2: Filtering the solution

After the solubilization of the sludge cake, the resulting solution was filtered with a vacuum pump, resulting a solution containing Fe(II), Fe(III) and Zn(II) and the wet cake with small traces of metal ions.

PHASE 3: *Oxidation of Fe(II) to Fe(III)*

The oxidation reaction was performed in two stages: in the first stage with sodium hypochlorite (NaOCl) and sodium hydroxide (NaOH) along with Cr(III) (as mentioned above) and the second oxidation step with hydrogen peroxide (H_2O_2), reaction temperature = 90 ºC, reaction time = 30 minutes; stirring throughout the reaction time.

The chemical reaction was:

$$2FeSO_4 + H_2SO_4 + H_2O_2 = Fe_2(SO_4)_3 + 2H_2O \quad (9)$$

PHASE 4: Complete precipitation of Fe(III)

The ferric sulphate [$Fe_2(SO_4)_3$] formed in the previous steps was precipitated at pH = 3.5- 4 with sodium hydroxide (NaOH) 30%; temperature reaction - ambient, reaction time = 15 minutes, stirring throughout the reaction time, to obtain a suspension of iron hydroxide. The chemical reaction was:

$$Fe_2(SO4)_3 + 6\ NaOH = 3\ Na_2SO_4 + 2\ Fe(OH)_3 \quad (10)$$

PHASE 5: *Filtering the suspension obtained after precipitation of Fe (III) with a vacuum pump and washing the wet cake from filtration for full recovery of red iron pigment (Fig. 5).*

The zinc recovery was performed from the remaining solution after iron recovery.

The phases of zinc recovery procedure are presented in Fig. 6.

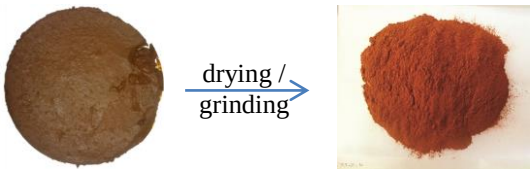

Fig. 5. *Wet cake of iron* *Red iron pigment $Fe(OH)_3$*

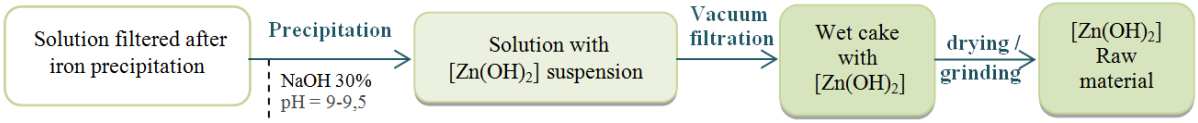

Fig. 6. *Scheme of zinc recovery procedure*

PHASE 1: Precipitation of Zn

The precipitation was performed with sodium hydroxide (NaOH) 30% by raising the pH of 4 to 9-9.5; reaction temperature - ambient, reaction time = 15 minutes.

The pH was raised from 4 to 9-9.5 to ensure the complete precipitation of zinc.

$$ZnSO_4 + 2NaOH = Zn(OH)_2 + Na_2SO_4 \quad (11)$$

PHASE 2: Filtering the solution with a vacuum pump and washing the wet cake from filtration for full recovery of zinc as zinc hydroxide $[Zn(OH)_2]$ (Fig. 7).

Fig. 7. *Zinc hydroxide $[Zn(OH)_2]$*

This scientific activity at laboratory scale led to selective recovery efficiency for the studied metal ions of: 84.20 % for chromium; 99.93 % for iron; 85.74 % for zinc (Table 2).

Table 2. *Metal ions recovery efficiency*

Ions	The initial amount of metals in the sludge sample (g)	The total recovered amount of metals in solution (g)	Recovery efficiency (%)
Cr	0.4050	0.3410	84.20
Fe	13.6500	13.6410	99.93
Zn	27.1500	23.2771	85.74

4. Conclusions

The main conclusions of this experimental research are:

The recovery efficiency for the 3 metals ions is considered quite satisfactory but future research will continue to improve it by establishing optimal technical parameters and to obtain an inert sludge cake behaving as an inert material in terms of recovery of useful compounds which are the topic of this research.

The experiments conducted in the laboratory led to the obtaining of: Chromium yellow pigment ($PbCrO_4$), Chromium green pigment $Cr(OH)_3$, Red iron pigment $Fe(OH)_3$; zinc hydroxide $[Zn(OH)_2]$ as raw material.

Future research will focus on analyzing the possibilities for capitalization of metal ions recovered as pigments in glazes for ceramic products industry.

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