

Influence of Different Electroplating Sludge Types on the Iron Ions Recovery Yield

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Electroplating sludge resulting from wastewater (washing wastewater and technological solutions) treatment is considered to be a hazardous waste, being a mixture of hydroxides of many heavy metals such as: iron, chromium, copper, nickel, cadmium or zinc. The metal compounds from electroplating sludge have a great economic value, thus, a number of techniques have been investigated in order to recover them. This paper presents the results of the research activity in the laboratory in order to recover Fe (II, III, VI) from two types of electroplating sludge: a fresh sludge from wastewaters treatment and an old sludge, stabilized by disposal for many years. Iron recovery was performed by the solubilization of the sludge in several stages, to yield hydroxides or metal salts of chromium, iron, or zinc. The iron recovery has been performed from the cake obtained after the chromium recovery. In this cake, the iron is present in the form of divalent, trivalent and hexavalent iron. The iron recovery yield was 98.50% from fresh sludge (recovery in one stage) and 96.80% from old sludge (recovery in two stages).

Keywords: electroplating sludge, iron, recovery yield

Treatment and coating processes of metal surfaces require the use of some hazardous substances which are further discharged as washing wastewater and process waste solutions. The process waste solutions that are discharged derived from metal surfaces preparing operations (degreasing, pickling passivating, polishing, etc.) and from the discharge of active washing wastewater (copper, nickel, chrome, zinc or cadmium plating) [1]. The treatment of electroplating wastewater leads to the generation of a sludge that require disposal and is considered a hazardous waste due to the high content of heavy metals in its composition [2]. Among the most hazardous inorganic pollutants for the environment, heavy metals from antropogenic sources play a special role [3]. The pollution with heavy metals represents an important global issue ever since the early 1970s because of their extremely toxic effect even at low concentrations [4]. One of the highest environmental risk is the omnipresence of heavy metals due to their toxicity, persistence and lack of biodegradation [5]. The presence of heavy metals in environment causes toxicity problems. Because of this, even today, these persistent pollutants represent an important issue in Europe [6,7]. However, it can be considered that this type of sludge contain valuable elements, in particular different metals [8]. The electroplating sludge could be reused as material for the extraction of most metals, such as iron, chromium, zinc, etc in order to use them as raw materials [9]. An alternative to use these materials from a hazardous waste is the separation and obtaining of metal salts or metal oxides from sludge in order to recycle them [10]. An iron reach sludge can be found in electroplating industry, where iron comes from pickling and polishing operations of steel and cast iron. The iron extraction in the form of iron oxide allow its use as a potential raw material (pigment) in many industries (ceramics, construction, chemical).

This paper presents a study at laboratory scale, by performing a procedure for iron recovery from electroplating sludge. Our interest was focused on the

recovery of valuable iron from different types of electroplating sludge, in order to achieve a recovery yield of metal ions as high as possible. The investigations were carried out in order to specify the correlation between metal ions recovery yield from the electroplating sludge and the age of sludge.

Experimental part

Two types of electroplating sludge have been investigated in order to recover the iron ions:

A *fresh sludge* (FS) sampled from a detoxification and neutralization plant (LANCY type) of water and waste solutions from chemical and electrochemical coatings installations. Lancy procedure is a direct method of detoxification and consists of immersing the parts removed from the electrolyte containing toxic substances directly into a neutralizing solution that serves, at the same time, as washing bath [11].

An *old sludge* (OS) sampled from the decanter of a decommissioned wastewater treatment plant. This sludge is the result of physico-chemical mixed wastewaters treatment derived from various treatment and metal finishing processes (zinc plating, copper plating, cadmium plating, etc.). The sludge is older than 20 years and stabilized by freeze-thaw phenomena and solar activity [12].

The content in metals has been analyzed by atomic absorption spectrometry (AAA), with air-acetylene flame and graphite furnace.

The results are showed in table 1.

It has been observed a variation of the metal ions content for the two types of investigated sludge. The fresh sludge (FS) derived from wastewater treatment by Lancy procedure, therefore much of the metal ions content was recycled in the treatment process.

The process for recovering heavy metals has been consisted in extraction of chromium, iron and zinc by the sludge solubilization in several stages in order to yield hydroxides or metal salts with economic value. Recovered

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Sludge sample	Metals content (%)								
	Fe	Cr	Zn	Ni	Cu	Cd	Pb	Mn	Ca, Mg, Na
FS	9.10	0.27	18.10	0.05	0.009	0.004	BDL*	BDL*	BDL*
OS	21.30	8.00	2.44	0.22	0.930	0.710	0.130	0.240	BDL*

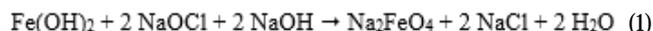
Table 1
CHEMICAL
COMPOSITION
OF THE TWO
SLUDGE SAMPLES

*below detection limit

metal oxides can be used as pigment/dye in ceramic materials, building materials or chemicals, harmless cake with traces of metals remaining after recovery from waste can be eliminated as non-hazardous landfills. The first step consisted in the chromium recovery. Both types of sludge have been dried at 105°C in drying oven Binder type for 24 h (water content of the sludge= 67wt.%) and milled in a porcelain jar to obtain particles with average diameters < 90 µm.

The chromium recovery has been performed by the oxidation of the sludge samples in the strong alkaline medium at a pH= 12.0–12.5 with sodium hypochlorite (NaOCl) 12% and sodium hydroxide (NaOH) 20%, followed by steps of filtration, washing, precipitation or reduction and precipitation of chromium (trivalent or hexavalent) from the obtained chromate solution. The precipitates have filtered, washed and dried, in order to obtain pigments based on chromium (chromium hydroxide, lead chromate). Technological parameters - reaction temperature, reaction time and oxidizing agent concentration have been varied. The results showed that the highest chromium (VI) extraction yield was 84.2% for FS at a reaction temperature of 80 °C and a reaction time of 30 min, using 200% excess of oxidizing agent. The highest chromium (VI) extraction yield was 52.33 % for OS at a reaction temperature of 90 °C and a reaction time of 30 minutes, using 300% excess of oxidizing agent. For OS sludge, second stage of chromium extraction from the first stage cake was carried out under the same experimental conditions. Destabilizing the sludge structure in the first extraction stage allowed to increase the chromium extraction yield in the second extraction stage. The total chromium (VI) extraction yield was 93.19% in two stages [12].

Iron is present in the cake obtained after the chromium recovery in the divalent, trivalent and hexavalent form. Fe (VI) was obtained in the first phase of chromium recovery by partial oxidation of Fe (II) to Fe (VI) in the form of sodium ferrate (Na₂FeO₄). The chemical reaction is (eq1):



The sludge cakes have been dried at 105°C for 24 h (water content of the sludge 65 wt.%) and milled in order to obtain particles with average diameters <90 µm and to increase the reaction area of the sludge.

The iron recovery flowchart is presented in the figure 1.

The solubilization of wet cake containing iron and zinc has been performed with sulfuric acid (H₂SO₄) 20% at pH= 1.0–1.5.

The solubilization reactions are the following:

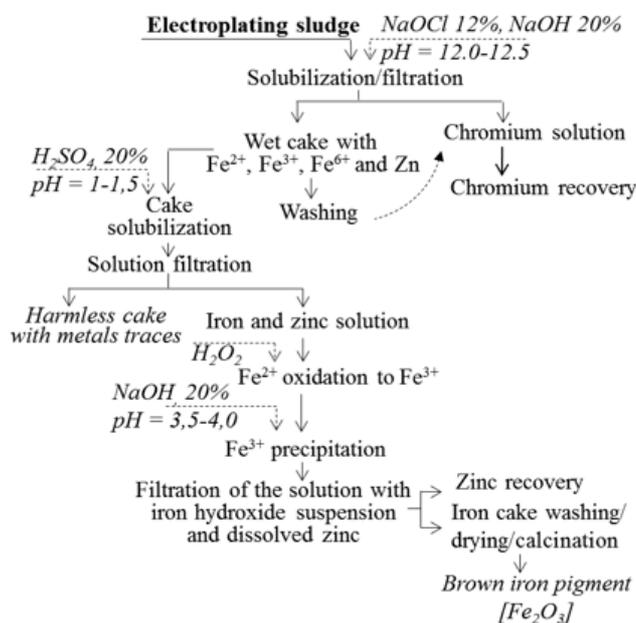
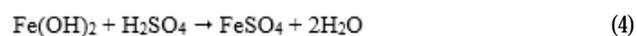
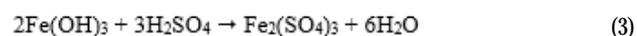
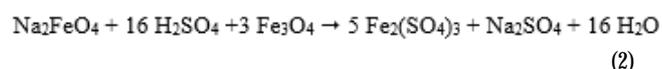


Fig. 1. Iron recovery flowchart from electroplating sludge

The solution has been filtered with a vacuum pump, thus obtaining a solution containing Fe (II), Fe (III) and Zn (II) and a wet harmless cake with metals traces. The wet cake resulting from filtration was multi-stage washed for full recovery of adsorbed iron by the cake.

The oxidation reaction of divalent iron to trivalent iron has been performed in two stages: in the first stage of chromium recovery - the oxidation with NaOCl 12% and NaOH 20% and in the second stage - oxidation with H₂O₂.

Technological parameters - reaction temperature and time have been varied. The experiments have been carried out in cylindrical 1000 ml glass beakers on thermostatic water bath. The samples were stirred throughout the reaction time. The L/S ratio was kept constant in all experiments.

Results and discussions

A iron recovery at a yield as high as possible was aimed. Two parameters have been varied, namely temperature and time of reaction.

Since the chromium recovery from the old sludge (OS) has been performed in two stages, the divalent iron has been completely oxidized and it was not required further oxidation with hydrogen peroxide.

The results obtained for both type of sludge are presented in table 2.

Recovery yield of iron are presented in figure 2.

The results showed that the highest iron recovery yield is 98.5% for FS at 80 °C/30 min and 62.34% for OS at 70 °C/30 min. It is notice that the iron solubility depends on the sludge age and composition. The difference between the iron recovery yields from the two types of sludge can be explained by the fact that, during the solubilization, the structure of the OS sludge was much more stable than the FS sludge structure, due to long-term storage.

Sample	Parameters	FS sludge		OS sludge	
		$Q_{i\text{ FS}} = 13.65\text{ g}$		$Q_{i\text{ OS}} = 10.65\text{ g}$	
		$Q_{r\text{ FS}}\text{ (g)}$	$\eta_{\text{Fe}}\text{ (\%)}$	$Q_{r\text{ OS}}\text{ (g)}$	$\eta_{\text{Fe}}\text{ (\%)}$
F1	70°C/15 min	10.8758	79.68	6.4568	60.63
F2	70°C/30 min	11.5225	84.41	6.6392	62.34
F3	70°C/60 min	12.6542	92.70	5.8510	54.94
F4	80°C/15 min	12.8995	94.50	5.0627	47.54
F5	80°C/30 min	13.4450	98.50	4.8443	45.49
F6	80°C/60 min	13.2564	97.12	4.3051	40.42
F7	90°C/15 min	13.1154	96.08	4.0112	37.66
F8	90°C/30 min	13.0065	95.29	3.8450	36.10
F9	90°C/60 min	12.6587	92.74	3.8254	35.92

Table 2
THE RECOVERY YIELD OF IRON

where: $Q_{i\text{ FS}}$, $Q_{i\text{ OS}}$ = initial content of iron in sludge,
 $Q_{r\text{ FS}}$, $Q_{r\text{ OS}}$ = content in iron recovered from sludge,
 η_{Fe} = iron recovery yield

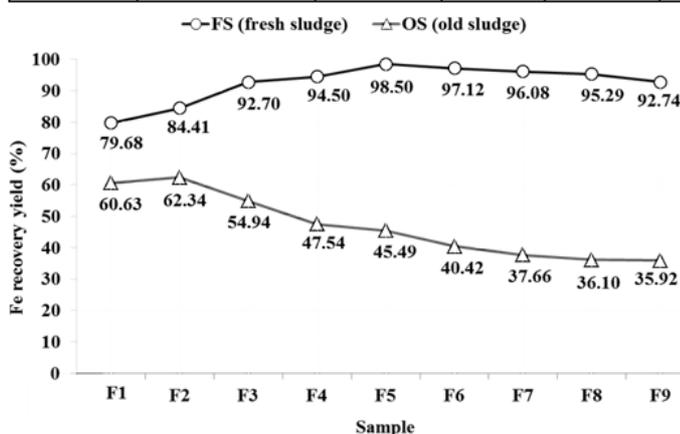


Fig. 2. Recovery yield of iron

In order to increase the iron recovery yield from the stabilized sludge (OS), a second stage of iron extraction has been carried out under the same experimental conditions: S/L ratio=1/1, reaction temperature 70°C, reaction time 30 min, stirring throughout the reaction time. Iron recovery yield was 32.87%, with a total iron recovery yield of 96.80%, in two stages. Iron recovery yields are considered quite satisfactory: 98.5% from FS in one extraction stage and 96.80% from OS in two extraction stages.

Experiments conducted in the laboratory led to obtaining brown iron pigment (Fe_2O_3). The pigment has been obtained by the complete precipitation of Fe(III) from the iron and zinc solution, with NaOH 20%, at pH= 3.0-3.5 ambient temperature reaction, 15 min reaction time, continue stirring throughout the reaction time. The precipitate has been filtered with a vacuum pump, the cake was washed stepwise in order to remove all soluble salts adsorbed on the cake, dried and grinded to obtain a brown pigment iron oxide.

Conclusions

In this research study, a procedure for iron recovery from two different galvanic industrial sludge (old and fresh) has been carried out in different experimental conditions. In terms of varied technological parameters (reaction temperature and reaction time), the highest iron recovery

yield was 98.5% for FS at 80°C/30 min (in one extraction stage) and 96.80% for OS at 70°C/30 min (in two extraction stages).

The investigations carried out have highlighted that there is a correlation between iron recovery yield and the age of sludge. The low yield of the iron recovery has been obtained from the old sludge. The structure of the OS sludge has been more stable due to long-term storage, which led to a slower solubilization of iron, requiring two-stage extraction in order to achieve a high recovery yield.

Further work is in progress in order to establish the possibility to recover the obtained pigment into decorative ceramic products.

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