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Treatment of electroplating wastewaters by electro coagulation

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Abstract: A pilot plant study of the treatment of electroplating wastewaters using electroreduction with iron electrode plates, electrocoagulation/ozonation using aluminium electrode set followed by ozonation was presented. The initial effluent was highly enriched in heavy metals and elevated levels of organic contaminants. The concentrations of Cr\textsuperscript{6+}, Fe, Ni, Cu, Zn, Pb, TOC, and COD exceeded the upper permissible limits of 63, 220.2, 1.1, 7, 131.3, 1.7, 12.3 and 11.4 times, respectively. The heavy metal removal was forced either by the coagulation/flocculation using Fe\textsuperscript{2+}, Fe\textsuperscript{3+}, and Al\textsuperscript{3+} ions released into the treated solution by electrochemical corrosion of the sacrificial iron and aluminium electrodes, precipitation of the metal hydroxides as well as co-precipitation with iron and aluminium hydroxides. The principle mechanisms of the organic matter destruction were oxidation by ozone and the indirect oxidation with chlorine/hypochlorite formed by the anodic oxidation of chloride already present in the wastewater. Following the combined treatment, the removal efficiencies of the parameters Cr\textsuperscript{6+}, Fe, Ni, Cu, Zn, Pb, TOC, and COD were 99.94%, 100.00%, 95.86%, 98.66%, 99.97%, 96.81%, 93.24%, 93.43%, and 77.78%, respectively. All the parameters in the final effluent were in agreement with regulated values.

Keywords: Waste Water, Electrolysis, Meta, Electrode

1. Introduction

Highly acidic heavy metal laden effluents, originating from electroplating industry, are of major concern and increasingly subdued to stringent regulations in a way that they must be treated prior to their discharge into the environment. In electroplating units water is used for various processes, thus eventually forming electroplating wastewaters (EWW) highly enriched in acid contents and heavy metals (Zn, Fe, Cr\textsuperscript{6+}, Ni, Cd, Au, Cu) which render them severely corrosive and polluting in nature. Their adverse effect to the environment could be neutralised by the application of the purification methods. Various techniques have been employed so far, including adsorption, physico-chemical treatment, membrane filtration, ion exchange, and electrochemical treatment [1].

The conventional treatment [1] uses three steps: 1) the chromate reduction with sodium hydrogen sulfite (NaH\textsubscript{2}SO\textsubscript{3}), 2) the water neutralization to pH 8 with sodium base, and 3) the heavy metal removal by the coagulation/flocculation process using poly-acrylic acid as a coagulant. Upon the purification procedure, the remaining galvanic waste mud is filtered, pressed and stored. Hereby, no separate treatment is required in terms of collection and disposal of such waste material, which itself is a source of valuable metals, such as Zn, Cr, Cu, Ni, Au, and Ag.

Electrochemical methods have approved so far as a good alternative to the standard physico-chemical methods of the EWW treatment [2-6]. Adhoun et al. [2] presented the process of electrocoagulation by aluminium electrode set which resulted in the copper and zinc decrease down to the permissible limits within the duration of five minutes, while it took 20 minutes for the sufficient Cr\textsuperscript{6+} reduction. The authors found that the removal efficiency increased with increasing current density and pH, and that the maximum COD removal was 64%. Using the electrodialysis membrane at low pH (2.2) Chen et al. [3] managed to concentrate Cr\textsuperscript{6+} up to 191% compared to the initial waste effluent. In another study [4] the 5 hour-electrolysis resulted in 99.9% of copper recovery from EWW containing initial copper concentration of 26 g/L. Up to 100% removal efficiency of Cr\textsuperscript{6+} from the synthetic EWW was accomplished by the electroreduction/electrocoagulation with steel electrode plates [5]. The Cr\textsuperscript{6+} decrease from 500 mg/L down to 0.5 mg/L was carried out by the Fe rotating...
the environmental rules and regulations. Moreover, it should be highlighted that the method is characterised by the technical simplicity, cost-efficiency and requirements for less space compared to the classical methodology. Recently, Elez et al. [8] employed alkaline solid residue, a by-product of the alkaline extraction of zinc and lead from by-products, Fe2+ sulphate and wood fly ash, where the authors combined two waste disposal into the environment, where the removal levels complied with the regulated values as regards the technical simplicity, cost-efficiency and requirements for less space compared to the classical methodology. Recently, Elez et al. [8] employed alkaline solid residue, a by-product of the alkaline extraction of zinc and lead from the electric arc furnace dust, for the purpose of the EWW neutralization/purification. Upon the treatment, all variable levels complied with the regulated values as regards the disposal into the environment, where the removal efficiencies of Pb, Cr6+, Cr(III), Fe, Ni, Cu, and Zn were as follows: 94.92%, 97.58%, 99.59%, 99.48%, 97.25%, and 99.97%, respectively.

The objective of this study was to investigate the removal efficiency of the chromates, heavy metals and organic contaminants by means of a pilot plant unit composed of the electrochemical methods and the ozonation.

2. Materials and Methods

2.1. Wastewater Sampling and Operational Procedure

The EWW sampling was arranged in the Galoks Ltd. electroplating facility, Vrbovec, Croatia. For that purpose the 300 L polyethylene containers were used, while in the laboratory the water was homogenised by mixing for 10 minutes (600 r.p.m) in a single tank prior the analysis. The treatment procedure was performed on 90 L aliquots of wastewater which was pumped into 120 L cylindrical reaction vessel. Electrocoagulation was carried out with iron electrode plates for 15 minute (total surface area = 0.6552 m2; distance between plates = 10 mm; U = 12 V; I = 70 A). Thereafter, electrocoagulation with Al electrode set (total surface area = 0.5688 m2; distance between plates = 10 mm; U = 12 V; I = 65 A) was carried out together with ozonation for additional 15 minutes (constant flow rate of 2.5 mL per minute), while the last 30 minutes of the process was reserved for the slow mixing with ozone in order to complete the coagulation/flocculation process. The treatment procedure was run in triplicate and the measured parameters in the effluent were expressed as mean values.

2.2. Preparation and Analysis of Samples by EDXRF

The samples were prepared for the analysis as follows: 0.5 mL of the untreated wastewater was diluted to 100 mL with double distilled water, while for purified effluent or 100 mL of the sample was taken, adjusted to pH 3 by the addition of hydrochloric acid (Kemika) and ammonium hydroxide (Kemika) and preconcentrated with 2 mL of 1% (w/v) ammonium-pyrolidinedithiocarbamate (APDC) (Merck, Schuchardt, Germany) [9]. Following the complexation which lasted for 20 minutes, the suspension was filtered through a Millipore HAWP filter (pore size - 0.45 µm; diameter - 25 mm) using a Millipore microfiltration system. The prepared thin targets were air-dried, protected by thin mylar foil (2 µm) and analysed with energy dispersive X-ray spectrometry (EDXRF). The samples were irradiated by X-rays generated from X-ray tube ("Oxford instruments") with Mo anode (high voltage: 40 kV; current: 900µA; cooling medium: Air) [9]. The detection of the characteristic X-ray radiation from the sample was conducted with Si drift detector - model SXD15C-150-500 (Canberra, Meriden, USA) (surface: 15mm2; FWHM for 5.9 keV 55Fe: 145 eV; Window: 13 µm Be; cooling: thermo-electrical (peltier)). The incident and emerging angles were 45°. For signal processing DSA 2000 (Canberra) was used. Spectral data were collected by Genie-2000 software (Canberra) while for spectrum deconvolution and quantitative analysis WinAxil software package (Canberra) was used. In order to obtain a good counting statistic, collecting time was 10000 s. The calibration model for the qualitative and quantitative analyses was created on the basis of the measurements of the standard solutions (Merck) having the concentration range from 10 to 200 µg/L, prepared and measured in the same way as unknown samples.

2.3. Measurements of Selected Parameters

The pH value, electrical conductivity (EC) and total dissolved solids (TDS) were measured by PHT-027 - water quality multiparameter monitor (Kellilong Electron). The colour was determined according to the 8025 APHA platinum-cobalt standard method (adopted from Standard Methods for the Examination of Water and Wastewater) using the HACH DR890 colorimeter (Hach Company, Loveland, Colorado, USA). For the accuracy and performance check, a 500 platinum-cobalt unit’s color standard solution (Cole-Parmer, USA) was used. The
turbidity was determined by 8237 absorbptometric method using the HACH DR890 colorimeter. For the accuracy and performance check, the 4000 NTU Formazin stock solution (Cole-Parmer) was used. The chemical oxygen demand (COD) and total organic carbon (TOC) were determined by the reactor digestion method using the HACH DR890 colorimeter. For the sample digestion the DRB 200 reactor (Hach Company) was used.

### 3. Results and Discussion

#### 3.1. The Initial EWW Characteristics

The physico-chemical parameters values measured in EWW prior/following the each treatment phase, together with their upper permissible limits (UPL) [10] are presented in Table 1. It was found that all heavy metals in the initial EWW exceeded UPL as regards the disposal into a natural recipient. The highest increases were found for Fe (220.2 times), Zn (131.3 times), and Cr6+ (63.0 times). TOC and COD, equaling the organic content, were increased 12.3 and 11.4 times, respectively, compared to their UPL.

It is well known that nearly 10 times lower heavy metal concentrations, compared to the values presented in this study, could have adverse cytotoxic, mutagenic and genotoxic effects on the bacterial [11], plant [12], and human test systems [11, 13]. Therefore, this study confirms that the EWW must be treated prior to its disposal in the environment.

Table 1. Physicochemical parameters of electroplating wastewater and treated water with the upper permissible limit [10] for the wastewater

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Initial EWW</th>
<th>Treated EWW</th>
<th>UPL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr6+ (mg/L)</td>
<td>6.3</td>
<td>0.016</td>
<td>0.004</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>440.4</td>
<td>0.072</td>
<td>0.012</td>
</tr>
<tr>
<td>Ni (mg/L)</td>
<td>0.532</td>
<td>0.043</td>
<td>0.022</td>
</tr>
<tr>
<td>Cu (mg/L)</td>
<td>3.5</td>
<td>0.127</td>
<td>0.047</td>
</tr>
<tr>
<td>Zn (mg/L)</td>
<td>262.5</td>
<td>0.407</td>
<td>0.071</td>
</tr>
<tr>
<td>Pb (mg/L)</td>
<td>0.847</td>
<td>0.101</td>
<td>0.027</td>
</tr>
<tr>
<td>pH</td>
<td>6.94</td>
<td>7.46</td>
<td>7.81</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>1180</td>
<td>1180</td>
<td>1180</td>
</tr>
<tr>
<td>EC (mS/cm)</td>
<td>1.69</td>
<td>1.69</td>
<td>1.69</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>370</td>
<td>298</td>
<td>140</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>1430</td>
<td>937</td>
<td>270</td>
</tr>
<tr>
<td>Cl- (mg/L)</td>
<td>184.5</td>
<td>183.7</td>
<td>182.7</td>
</tr>
</tbody>
</table>

#### 3.2. Efficacy of the EWW Treatment

The presence of increased levels of heavy metals and organic contaminants required the three step treatment procedure. Electro reduction by iron electrode plates in the absence of external aeration/ozonation was carried out to reduce Cr6+ levels. The Cr6+ removal mechanism, i.e. reduction of Cr6+ to Cr3+ by means of Fe2+ ions, was accomplished by introduction of ferrous ions into solution by the electrochemical corrosion of the sacrificial Fe anode plates. When converted to Cr3+, it can either precipitate as a poorly soluble Cr(OH)3 or co-precipitate with Fe hydroxides [9, 13] according to the following reactions:

Anode:

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (1)
\]

\[
\text{Cr}^{6+} + 3\text{Fe}^{2+} \rightarrow \text{Cr}^{3+} + 3\text{Fe}^{3+} \quad (2)
\]

Cathode:

\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad (3)
\]

Co-precipitation:

\[
\text{Cr}^{3+} + 3\text{OH}^- \rightarrow \text{Cr(OH)}_3 \quad (4)
\]

\[
\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3 \quad (5)
\]

\[
\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 \quad (6)
\]

Upon the end of electroreduction (the first treatment step), the pH value slightly increased from 6.94 to 7.46, whereas a significant heavy metal decrease was determined, the concentrations of which were reduced below the respective UPL. The Cr6+ removal efficiency, following the electroreduction/electrocoagulation by Fe electrodes set, was found to be as high as 99.75%, similarly to other studies [6, 9]. The removal efficiencies of Fe, Ni, Cu, Zn, and Pb, following the first treatment step, were 99.94%, 91.92%, 96.37%, 99.84%, and 88.08%, respectively (Fig. 1). The highest efficiencies were determined for Fe, Zn, and Cr6+, the elements presented in the greatest amounts in the initial EWW.

![Figure 1. Removal efficiencies of the analysed parameters in the electroplating wastewater samples following the three treatment steps (Fe, Al+++O3, and O3).](image-url)

Quite expectedly, appreciably lower removal efficiencies were determined for the organic contaminants (19.46% for TOC, and 34.48% for COD) following the first treatment step, according to their removal in strongly oxidizing conditions. Their destruction during the first step was achieved by indirect anodic oxidation with...
chlorine/hypochlorite. The latter was formed by anodic oxidation of chloride already present in the EWW, and that was confirmed by the presence of free and total chlorine from the first minute of the reaction. Indirect anodic oxidation of Cl- [9] can be described by following reactions:

**Anode**

\[
2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \\
6\text{HOCl} + 3\text{H}_2\text{O} \rightarrow 2\text{ClO}_3^- + 4\text{Cl}^- + 1.5\text{O}_2 + 6\text{e}^- \\
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \tag{9}
\]

**Summary reactions:**

\[
\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^- \tag{10}
\]

\[
\text{HOCl} \rightarrow \text{H}^+ + \text{OCl}^- \tag{11}
\]

**Cathode**

\[
2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2 \tag{12}
\]

\[
\text{OCl}^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{Cl}^- + 2\text{OH}^- \tag{13}
\]

During the second treatment step, i.e. electrocoagulation with the Al electrode set, the coagulant formed as a result of the electrochemical corrosion of the sacrificial Al anode plates according to the following reactions:

**Anode**

\[
\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^- \tag{14}
\]

**Cathode**

\[
3\text{H}_2\text{O} + 3\text{e}^- \rightarrow 3/2\text{H}_2 + 3\text{OH}^- \tag{15}
\]

Al3+ ions resulted from the electrochemical oxidation of the sacrificial anode, while OH− ions were produced by the reduction of the water at the cathode surfaces; the both formed aluminum hydroxide flocs according to the following reaction:

\[
\text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3 \tag{16}
\]

Hereby, Al(OH)3 adsorbed/coprecipitated the pollutants found in the EWW. Moreover, the hydrogen bubbles, resluting from the water reduction on the cathode, aided the mixing of the solution while on their way to the surface. Simultaneously with the Al based electrocoagulation, the ozone oxidation was carried out to oxidise the organic contaminants and the rest of the Fe2+ into more stable and less soluble Fe3+.

Still in the second step, the additional heavy metal removal, up to 8% compared to the first step, was accomplished by the three processes: 1/ coagulation/flocculation with Fe2+, Fe3+, and Al3+ ions released in the solution by electrochemical corrosion of the sacrificial Fe- and Al-electrodes, 2/ metal hydroxide precipitation, and 3/ co-precipitation with Fe- and Al-hydroxides. The removal efficiencies of Cr6+, Fe, Ni, Cu, Zn, and Pb, following the second treatment step, were found to be as high as 99.94%, 100.00%, 95.86%, 98.66%, 99.97%, and 96.81%, respectively (Fig. 1). These values were closely similar or even better compared to our previous results, also achieved by a pilot plant unit based on electrocoagulation/ozonation of the EWW having increased heavy metal levels [9].

The simultaneous ozone treatment considerably decreased the organic contaminants compared to the initial EWW. The removal efficiencies of TOC and COD were 62.16% and 81.15%, respectively. The COD removal efficiency was app. 17% better compared to the results of Adhoum et al. [2] who used Al-electrocoagulation, presumably due to the presence of ozone in the second step, which is a strong oxidizing agent. Hereby, appreciable removal efficiencies of the two parameters were obtained. However, the values of TOC and COD in the EWW were still elevated, 4.7 and 2.2 times, respectively, as compared with their UPL.

Since the TOC and COD levels were required to be lowered to the regulated values, the third treatment step was employed, involving 30 minutes of the ozone oxidation. The both parameters were reduced below their UPL, thus corresponding to the final removal efficiencies of 93.24% and 93.43%, respectively. At the same time, there was no increase in the heavy metal removal.

Notably, the pH changes during the electrochemical treatment and ozonation were quite low. Thereby, over the treatment procedure there is no need for the solution’s pH measurement and adjustment, thus simplifying the plant unit and lowering its costs.

By comparison with the chemical coagulation method, which includes the addition of Fe- and Al-coagulants in the form of easily soluble salts (chlorides, sulfates), the electrochemical treatment is preferable since solely cations are required for the coagulation/flocculation process. Hereby, there is no increase in EC and TDS values in the treated EWW (Table 1), what is crucial in the case of its reuse.

4. Conclusion

The pilot plant study revealed that the application of the electrochemical methods using iron and aluminum electrode plates combined with ozonation represents a suitable treatment approach for the removal of inorganic as well as organic contaminants from the electroplating wastewaters down to the regulated values. At the optimum treatment conditions the removal efficiencies of Cr6+, Fe, Ni, Cu, Zn, Pb, TOC, and COD were 99.94%, 100.00%, 95.86%, 98.66%, 99.97%, 96.81%, 93.24%, and 93.43%, respectively. All the parameters in the final effluent were significantly lower compared to regulated values.

References


[10] Regulations on limit values of the emission of wastewaters (OG No. 87/10).

