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Technological solution for the treatment of wastewater resulting from metallic coatings using recovered products from metallurgical slag

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ABSTRACT

The presence of metals in the aquatic environment has become a concern of great importance worldwide as they represent a significant risk for human health. The aim of this paper is to propose a treatment solution for wastewater resulting from metallic coating activities. The novelty degree is given by the chemical reagent employed, namely aluminium sulphate recovered from metallurgical slag using a Romanian patented method. The removal of the pollutants should take into account all the aspects of the treatment process, including the aspects regarding the functioning and maintenance of the treatment facility. Experiments were conducted and the mechanical and chemical treatment processes were simulated at laboratory scale. The results showed high efficiencies for the removal of contaminants. Secondary aluminium slag have an important pollution potential for groundwater and soil due to their toxicity; the minimisation and the recycling of such wastes is required for ensuring the protection of environmental factors.

Keywords: *recovered aluminium sulphate, metallic coatings, metallurgical slag, wastewater treatment.*

1. INTRODUCTION

The processes employed for metallic coating provide low volumes of wastewaters with significant concentrations of contaminants. In order to discharge these wastewaters in the sewer, the quality requirements provided by the national legislation harmonised with the European legislation – Water Framework Directive 60/2000/EC need to be met [1].

High concentrations of toxic substances (heavy metals) exceeding the limit values are not accepted as they have an inhibitory effect on the process of biological treatment conducted within the municipal wastewater treatment plant. Also, these substances are found in the final effluent and have a negative impact on the receptor [2-6].

High contents of suspended matter may be problematic with regard to the fouling and narrowing of the municipal sewer.

The removal of specific contaminants from this type of wastewaters is accomplished by means of chemical methods and coagulation-flocculation is such a method [7-9].

On the other hand, aluminium industry has progressed ignificantly in the recent years. However, high volumes of slag result and hinder the economic activity of the industrial manufacturers. The landfilling of such slag is a worldwide acknowledged issue. Leaching of metallic ions may lead to severe contamination of groundwater and soil due to their bioaccumulation bioacumulare [10-13].

In the context of minimising the ecological footprint of mankind, the reduction of existing slag by means of valorificating them in products used for wastewater treatment purposes is preferred and efforts are being made in this sense in order to ensure the sustainable development and environmental quality.

The aim of this study is to use the aluminium sulphate recovered from secondary aluminium slag for the removal of contaminants from wastewaters and proposes a technological solution for the adequate treatment of wastewaters containing high levels of heavy metals. Previous studies proved the properties of recovered aluminium sulphate and the results showed that the product is a useful coagulant and may be used successfully for the removal of pollutants from wastewaters [14,15].

2. EXPERIMENTAL SECTION

The treatment experiments were conducted on wastewaters resulting from a manufactory that performs zinc electroplating in alkaline media and black finishing.

Starting from the data regarding the load of pollutants from wastewaters, various treatment methods were employed at laboratory scale and their efficiencies were the determining factor in the choice of the optimum technological solution for the treatment of the effluent.

The simulation of the mechanical treatment at laboratory scale was accomplished in Imhoff cones. Water resulting from mechanical treatment was further subjected to a chemical coagulation-flocculation process using aluminium sulphate recovered from secondary aluminium slag resulting from small and medium capacity smelters from Romania.

The aluminium-based product employed was prepared using a patented Romanian method that implies the chemical and

hydrometallurgical treatment the slag in acidic media followed by evaporation and cristallisation of the resulting solution [16,17].
The anionic polyelectrolyte Floerger FR 1023 was used as flocculation agent.

Chemical treatment was performed in a laboratory setup that employed the Jar-test method [18]. The working conditions provided the rapid dispersion of the coagulant in the water sample (n = 160 rpm) for 2 minutes, followed by pH adjustment to a optimum value (pH = 8) and slow stirring of the flocculant (n = 40 rpm) for 20 minutes so that the formation of flocs is achieved and a chemically stable sludge results. The treated wastewater was transferred in Imhoff cones; sludge sedimentation process and removal efficiency were investigated.

3. RESULTS SECTION

The main quality characteristics of treated wastewater are compared to the maximum allowed values in Table 1. As one may see, the effluent is alkaline and is significantly contaminated with suspended matter, organic matter (COD-Cr), biogenic elements (nitrogen and phosphorus), sulphates and heavy metals (zinc, chromium, cadmium, nickel and copper).

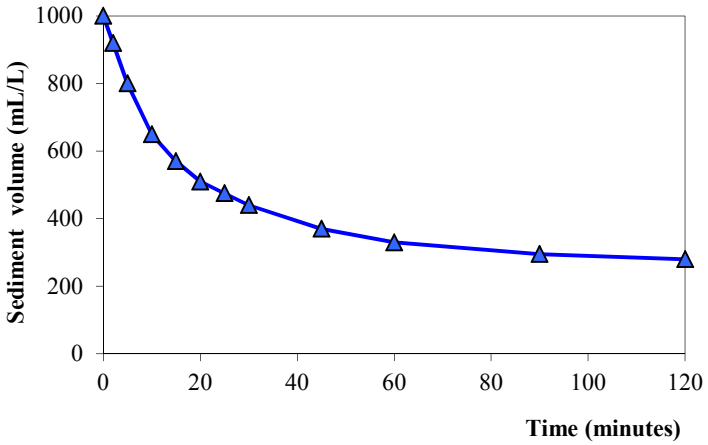

Figure 1. The dynamics of gravitational sedimentation of suspended matter from the wastewater.

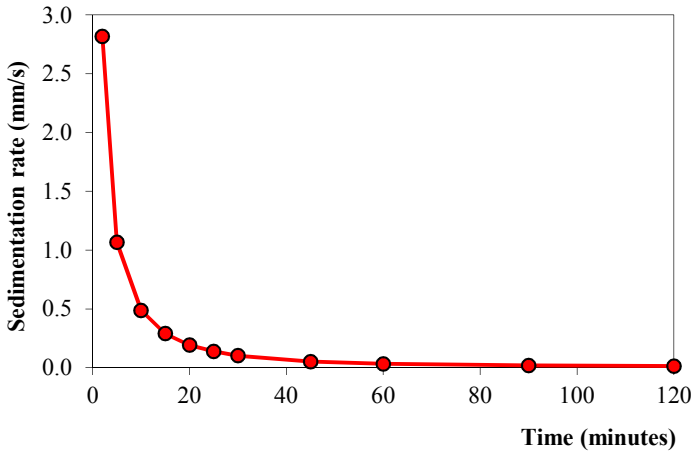

Figure 2. The behaviour of sedimentation rate for suspended matter from wastewater.

The first phase of wastewater treatment included the gravitational sedimentation of suspended matter for 2 h. The evolution of the process is depicted in Figures 1-2. As one may notice from the shape of the curves, the solids were easily deposited after 30 minutes. The volume of sediment collected after 2 h is approximately 28% of the volume of wastewater and has a content of dry matter of 62.2%, of which 99.4% is inorganic (mineral) substance and only 0.6% is organic (volatile) matter. The composition of the sediment is mainly inorganic and the following distribution of heavy metals is found: 14% zinc, 1.2% total iron, 1.2% total chromium, 0.06% lead, 0.02% copper, 0.02% nickel and 0.002% cadmium.

The removal efficiencies were generally higher than 90% (Table 2). Although the mechanical treatment by means of gravitational sedimentation generates wastewater with improved quality, the resulting effluent does not meet the requirements for the discharge in the municipal sewer.

In the second phase of the experimental program, the chemical treatment of the mechanically treatedwastewater was accomplished using aluminium sulphate recovered from metallurgical slag. The chemically treated wastewater was transferred in Imhoff cones. The gravitational sedimentation curve for the sludge was determined and is depicted in Figure 3 which describes a dynamic sedimentation process. The volume of sediment generated after 2 h is approximately 18% of the volume of wastewater. The content of dry matter is 82.4%, of which 99.9% is inorganic substance and only 0.1% is organic matter.

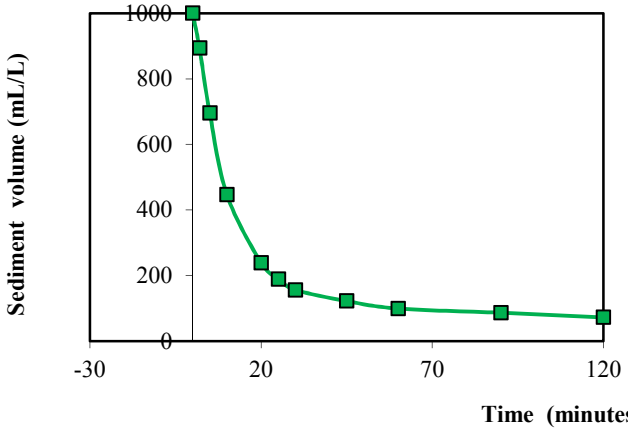

Figure 3. The volumetric sedimentation curve of the chemical sludge generated during the treatment of wastewater with aluminium sulphate recovered from metallurgical slag.

Table 3 shows the results of the physicochemical indicators describing the effluent. The treated wastewater was clear and a significant part of the colour was removed; the wastewater colour changed from brownish to light yellow. As regards the quality of treated wastewaters, all the analysed indicators meet the requirements and the discharge in the receptor is no longer an issue for ensuring the protection of the environment.

Table 1. The quality of wastewaters resulting from zinc plating.

Quality parameter	Measured value	MAC
Colour	brown	-
pH	**9.4**	6,5-8,5
Chemical oxygen demand (COD-Cr, mg O_2/L)	**2266**	500
Total suspended solids (mg/L)	**6604**	350
Anionic surfactants (mg/L)	1.7	25
Total phosphorus (mg/L)	**140**	5
Ammoniacal nitrogen (mg/L)	**49**	30
Sulphates (mg/L)	**1562**	600
Zinc (mg/l)	**930**	1
Total chromium (mg/L)	**67**	1.5
Lead (mg/L)	**5**	0.5
Cadmium (mg/L)	**1.2**	0.3
Nickel (mg/L)	**1.6**	1
Cooper (mg/L)	**1.6**	0.2
Total iron (mg/L)	74	-

Table 2. The efficiencies of contaminants removal achieved for the gravitational sedimentation of the wastewater

Quality parameter	Measured values (mg/L)		Efficiency (%)	MAC
	After sedimentation	Before sedimentation		
pH	**9.3**	**9.3**	-	6.5 – 8.5
Total suspended solids	**6604**	**675**	89.8	350
COD-Cr	**2266**	384	83.1	500
Anionic surfactants	1.7	0.23	86.5	25
Total phosphorus	**140**	**5.5**	96.1	5
Ammoniacal nitrogen	**38**	**38**	0	30
Sulphates	**1562**	**1520**	2.7	600
Zinc	**930**	**9**	99	1
Total chromium	**67**	0.5	99.3	1.5
Lead	**5**	< 0.2	> 96	0.5
Cadmium	**1.2**	**1.16**	3.3	0.3
Nickel	**1.6**	< 0.1	> 93.8	1
Cooper	**1.6**	0.16	86.2	0.2
Total iron	74	6.9	90.7	-

MAC – maximum admisible value

Table 3. The efficiencies of contaminants removal achieved during the chemical treatment of wastewater using recovered aluminium sulphate

Quality parameter	Measured values (mg/L)		Efficiency (%)	MAC
	After chemical treatment	Before chemical treatment		
pH	**9.3**	7.3	-	6.5 – 8.5
Total suspended solids	**675**	155	77.0	350
COD-Cr	384	328	14.6.	500
Anionic surfactants	0.23	0.12	33.3	25
Total phosphorus	**5.5**	0.7	47.8	5
Ammoniacal nitrogen	**38**	25	87.3	30
Sulphates	**1520**	570	34.2	600
Zinc	**9**	0.22	62.5	1
Total chromium	**0.5**	< 0.05	> 90	1.5
Lead	< 0.2	< 0.2	-	0.5
Cadmium	**1.16**	0.16	86.2	0.3
Nickel	< 0.1	< 0.1	-	1
Cooper	0.16	0.09	43.8	0.2
Total iron	6.9	1.82	73.6	-

MAC – maximum admisible value

4. CONCLUSIONS

Wastewaters resulting from metallic coatings activities contain contaminants with high toxicity and their pretreatment needs to be undertaken prior to their discharge in the municipal sewer or natural receptor.

The proposed technological solution takes into consideration installations that are easy to exploit, flexible (batch functioning) and have low investment costs and provide the quality requirements provided by the legislation.

The treatment technology includes two phases, namely mechanical and chemical treatment. The chemical treatment is performed using aluminium sulphate recovered from metallurgical slag; this product is prepared starting from secondary aluminium slag using a Romanian patented method and has good coagulation properties.

Raw wastewater is collected in a storing and homogenisation tank that also acts as a decanter. Following the gravitational sedimentation, the wastewater is pumped in the reaction tank. The primary sludge is removed and subjected to thickening and dehydration before landfilling.

The technological flux of the coagulation-flocculation process is based on chemical reactions and comprises the preparation, the dosage and the mixing of the reagents using appropriate installations and equipment. The chemical treatment is followed by the sedimentation of the sludge and the discharge of treated wastewater in the municipal sewer. The resulting sludge is also collected for further treatment.

The global efficiencies of the treatment of wastewater with high heavy metal content using the proposed technological solution are significant (higher than 90% for specific quality indicators such as suspended matter, heavy metals and phosphorus) and the use of aluminium sulphate recovered from metallurgical slag promotes the product as a viable alternative to chemical coagulants currently used.

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