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Original paper

Research on the efficiency of wastewater treatment facility in heavy metal removal from leachate

Treatment efficiency in heavy metal removal

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Abstract The research carried out followed the concentrations of heavy metals in the leachate before and after the introduction of the aeration lagoon in the leachate treatment system from the Glina waste dump, Ilfov county.

The method used for measuring the heavy metals content in the leachate was the flame atomic absorption spectrometry, according to the current standards.

The reduction of the concentration varied between 42% and 61% in chromium and exceeded 60% in copper. The efficiency of the purification system was 56-73% for iron removal. Manganese removal from the leachate by lagoon biological purification registered large differences, i.e. between 46% and 74%. The reduction of lead concentration was achieved in approximately 40%-78%, compared to the initial concentration. The removal of the zinc concentration from the system had a efficiency, i.e. more than 75%. The results were satisfactory for the effluent discharge into the sewerage network.

Keywords Leachate, heavy metals, wastewater treatment efficiency.

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Introduction

Heavy metals are elements with a double role in plant life and in ecosystems. They can be microelements absolutely necessary for the growth and development of plants but also heavy metals when their concentration exceeds certain limits affecting the ecosystem in general.

The impurification of soil, surface and groundwater with heavy metals as a result of pollution has disastrous effects for a long period of time (DURENKAMP M. & al [7]). Therefore, it is absolutely necessary to determine with great precision the concentration of heavy metals from the city's landfills and from leachate, respectively.

Heavy metals are known for not being mobile elements. Therefore, once they are present in an eco-system, they are extremely hard to remove and usually they move to another system (Table 1).

Economic development and demographic explosion generate huge quantities of waste with different chemical composition and variable content of harmful heavy metals. Improper management of these residues results in environmental pollution and degradation.

The main contamination way of the environment with heavy metals from the landfills is the improperly treated leachate and the release of the permeate in the environment with heavy metals content (CSUTAK O. & al [6]).

The potential sources of heavy metals from landfills and their effects are summarized in Table 1.

Tabel 1.

No.	Metal	Heavy metal source	Remarks	Origin in waste
1	Chromium	Hexavalent chromium used in leather industry.	Toxic to aquatic species and microorganisms.	Household waste and leather workshops
2	Copper	Metal waste attacked by soft or acidic waters and copper salts.	Does not bioaccumulate.	Installation waste or WEEE accidentally reaching into the storage
3	Zinc	Zinc tubes and parts; materials containing zinc.	Commonly found in leachate. In low concentrations it reduces the harmful effect of cadmium.	Construction and demolition waste (e.g. galvanized sheet)
4	Cadmium	Batteries and other parts, waste moisture.	Highly toxic to microorganisms.	WEEE accidentally reaching into the storage.
5	Manganese	Found in small quantities; accompanies iron.	In the presence of organic substances it is a favorable medium for the development of microorganisms.	Street waste, workshop waste, household waste
6	Lead	Tubes and fittings from installations of old buildings.	Lead settles in leachate without causing bioaccumulation issues	Demolition and installation waste
7	Iron	Iron waste, ash, soil.	Favors the development of Ferro bacteria.	Street waste, workshop waste, household waste

The main objective of the research is to increase the efficiency of the leachate treatment system from the Glina urban waste dump.

The specific aim of this paper is to determine the efficiency of the aeration lagoon in removing heavy metals from the leachate.

Material and Method

Sampling

In order to determine the heavy metals content of the leachate from the Glina landfill, Ilfov County, the leachate samples collected during the period of 2013-2017 at the beginning of June and December were subjected to analysis.

The two sampling points were:

- the leachate collection chamber;
- the two-compartmented storage basin (located after the aeration lagoon that was introduced in 2015).

Measurements were performed on leachate samples in different stages, following a possible influence of factors on the concentration of heavy metals in the leachate, thus proposing methods to decrease their concentration.

The average samples were obtained by mixing two point samples of 250 ml each until the leachate had a strong turbulence, which was an indication of good mixing. The sampling points were located at the exit of the leachate from the transport pipe for the influent and at the exit from the lagoon for the effluent.

Methods of analysis

The analysis of the leachate was performed by means of flame atomic absorption spectrometry, proceeding according to the standardized methods set out in Table 2 and described below.

Table 2. Methods for determination of heavy metals

No.	Metal	Standard number
1	Chromium	SR ISO 11083:1998
2	Copper	SR ISO 8288/2001
3	Zinc	SR ISO 8288/2001
4	Cadmium	SR ISO 8288/2001
5	Manganese	SR 8662-2:1996
6	Lead	SR ISO 8288/2001
7	Iron	SR ISO 6332: 1996/C91:2006

Figure 1. Aspects during sampling moments in Glina landfill.
The samples were collected in sterile polyethylene vessels with a capacity of 250 ml.

The analysis was performed on a number of 7 heavy metals (Cd, Cr, Cu, Fe, Mn, Pb, Zn) using an ANALYST 700 atomic absorption spectrometer.

Results and Discussions

The processes of removing the heavy metals from the leachate were difficult, mainly because of the complexity of the physical, chemical and biological processes that took place on the purifying route of the leachate (E.Z. GOMAA [8]).

Chromium (Cr3 +) is an element that in a small amount aids animal and human metabolism. Hexavalent chromium (Cr 6+) has a toxic effect and is still used today in leather industry.

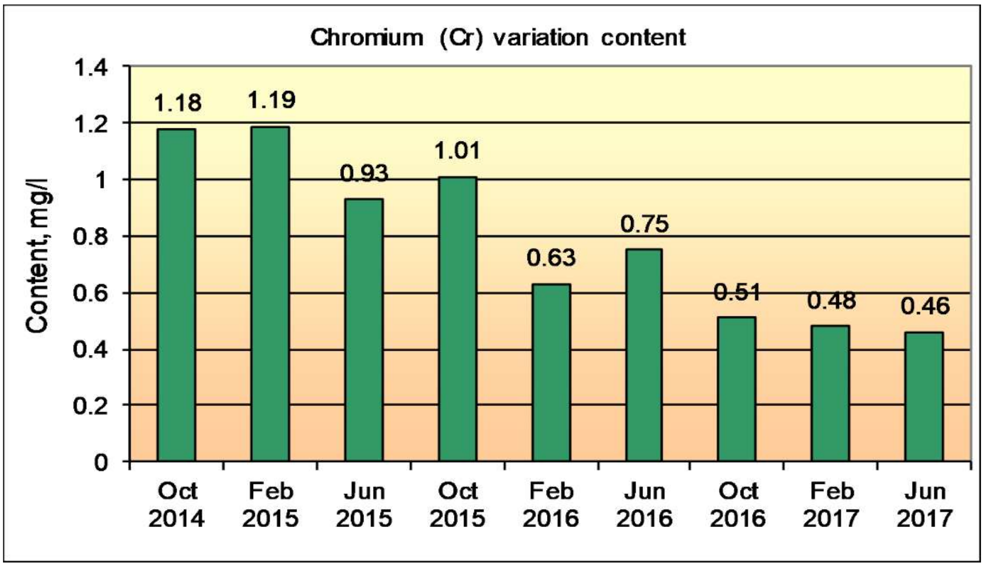

Figure 2. Variation of total chromium content of leachate in the Glina landfill between 2014 and 2017.

According to the experimental determinations, represented in Figure 2, the following characteristics resulted: a high chromium content of the leachate in the period 2014-2015, the maximum value being 1.19 mg / l in February 2015. Once the aeration lagoon became operational, the concentration of chromium decreased with percentages between 42% and 61%, the values recorded between June 2016 and June 2017 were between 0.46 mg/l and 0.75 mg/l.

Owing to their ability to assimilate and bind hexavalent chromium metal ions, the bacteria and fungi are used to remove this metal from the leachate, which explains the decrease of the chromium ion concentration after the leachate remains in the aeration lagoon.

Copper (Cu) in too high concentrations in water is toxic. It does not bioaccumulate in the human body (MOLEA A. & al [9]). In waste, copper can result from copper pipes, demolitions or repairs which are attacked by soft or acidic waters.

The results obtained experimentally for October 2014 and February 2015 (Figure 3) indicated a high content of copper in leachate of 3.12 mg/l and 3.22 mg/l, respectively, values well above the limits allowed for the discharge of leachate in the network of sewage.

Since 2015 the content decreased by over 60% from the maximum of 3.22 mg/l to 0.41 mg/l in June 2017, when the minimum value was registered. Regarding the copper content, Figure 3 shows levels of close values concentrations.

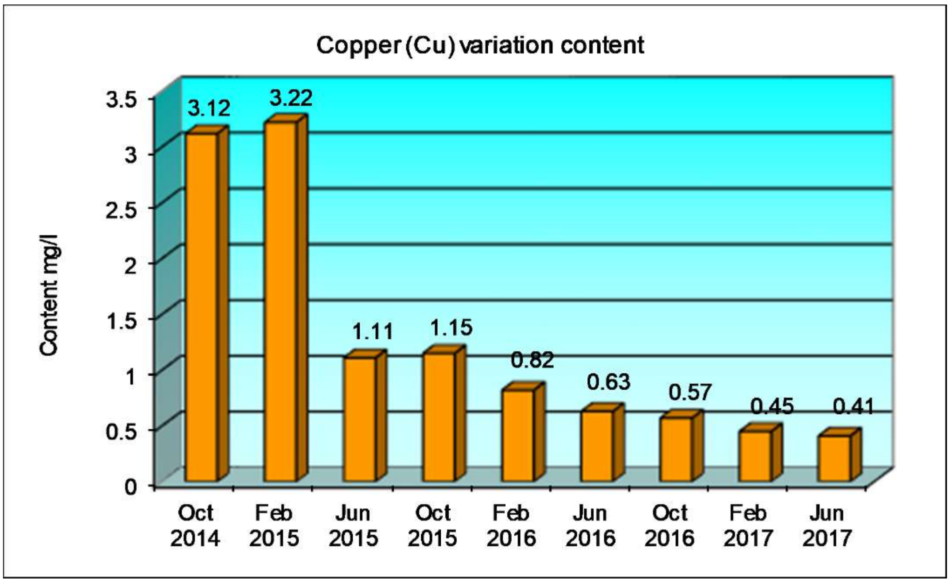

Figure 3. Variation of copper content of leachate in Glina landfill between 2014 and 2017.

The first level, October 2014 – February 2015, shows a very high copper content; the second level, lowered, corresponds to the period of introduction into the network of evacuation of the suspended basin and indicates a high precipitation of copper.

The assimilation and binding of copper ions, as well as of other metal ions, occurs on the surface of the cells (biosorption) or inside the cells by the active passage of the ions through the cell membrane (bioaccumulation). The bacteria have the ability to participate in the precipitation of metal cations as insoluble sulphides through the action of hydrogen sulphide on sulfates (bioprecipitation). These chemical-biological processes explain the decrease of the ionic metal concentration in the leachate.

Typically, *cadmium* is very rare in nature, but having many uses in the industry, especially in the electronics industry, it can be found in waste and leachate in higher concentrations than in soil or in natural waters (CORBU V. [4]).

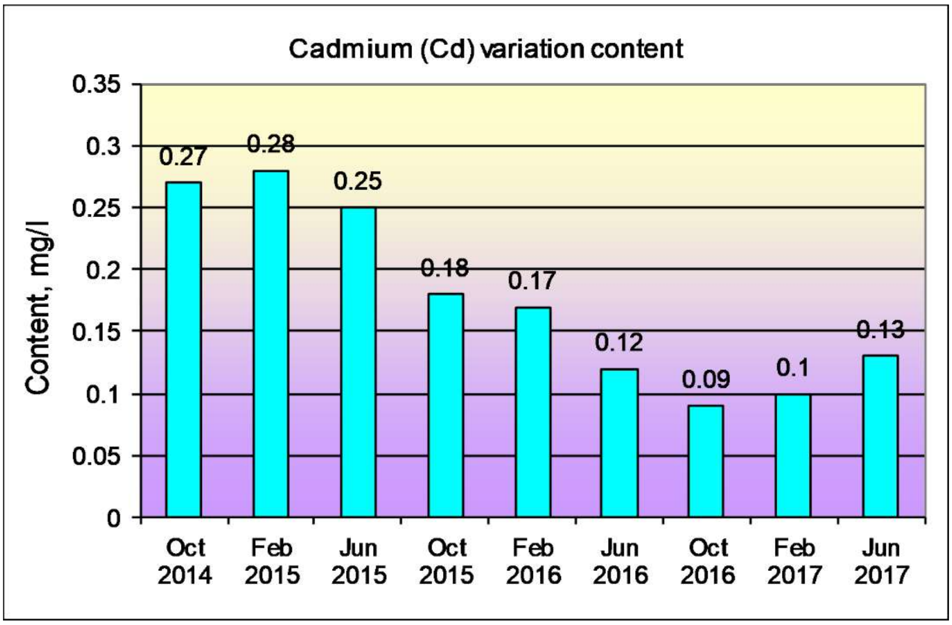

Figure 4. Variation of cadmium content of leachate in Glina landfill between 2014 and 2017.

Due to its high toxicity and high capacity of accumulation in the liver and kidneys, its presence is tracked both in waste and leachate, as well as in the environment near the landfills.

Following the experimental determinations, the maximum concentration was obtained for cadmium in February 2015 with a value of 0.29 mg/l and a minimum concentration of 0.09 mg/l in October 2016 (values shown in Figure 4), both values being below the limit imposed by the NTPA Regulation 002/2001.

The decreasing cadmium content in the leachate was mainly accounted for by sludge sedimentation in the leachate basins and in the aeration lagoon. This phenomenon was also noted by other researchers (CORBU V. & al [4]).

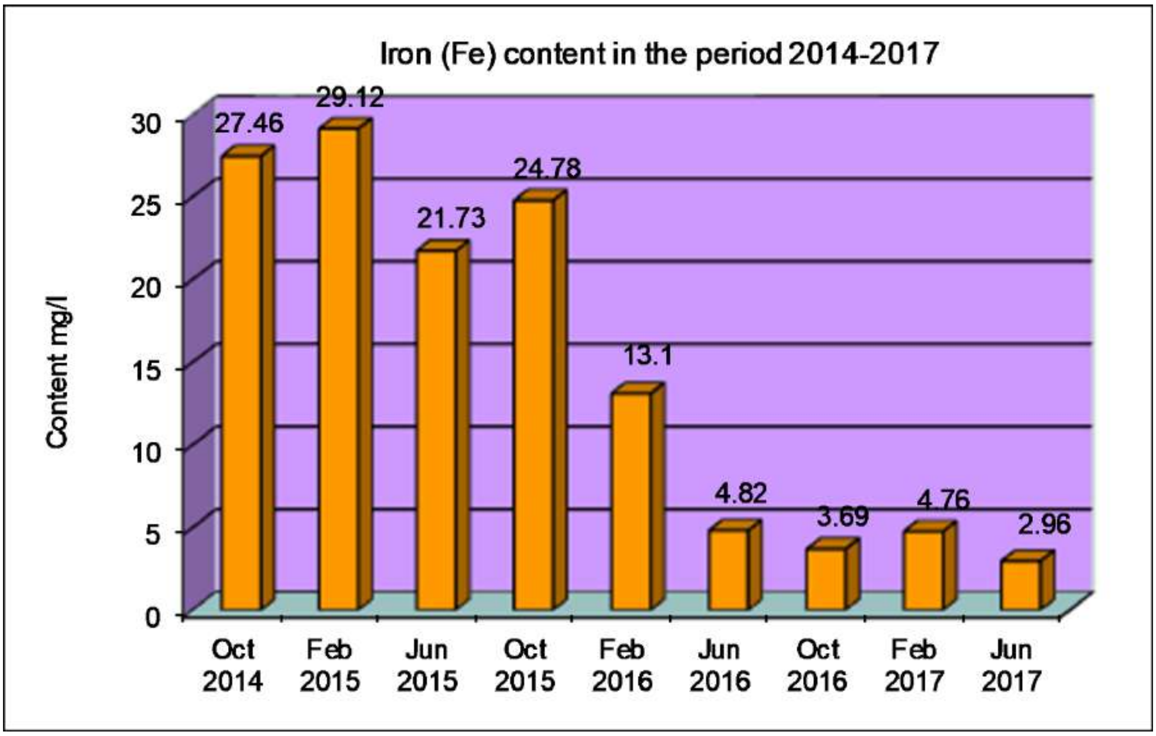

Figure 5. Variation of iron content of the leachate in Glina landfill between 2014 and 2017.

Iron is a widespread element in nature, important iron concentrations occurring naturally in surface waters, soils, sediments, etc. Its widespread use in industry leads to its frequent presence as a component of wastewater.

From the laboratory determinations made in the period of October 2014 – June 2017 and presented in the Figure 5 graph, the following can be noticed:

The iron content between October 2014 – February 2016 varied between 13.4 mg/l and 29.12 mg/l, all values being below the limit stipulated by the normative NTPA 002/2001.

Between June 2016 – June 2017 the concentration of iron ions decreased, reaching a maximum of 4.82 mg/l in June 2016 and a minimum of only 2.96 mg/l. All the values measured in this time interval were below the limit stipulated by the norm for the discharge of leachate in natural watercourses (NTPA 001/2001).

In the case of iron and manganese, the presence of microscopic fungi in the aeration lagoon was very important, as the biochemical processes of purification were related to the presence of the amine groups in the chitin of the cell wall, and to the presence of the phenolic groups in the pigments (melamine). The fungi had an advantage over the bacteria by the fact that the metal ions were rapidly bound only to the cell surface, independently from metabolism, and thus created the possibility of reusing biomass after the metals removal by treatment with an acid solution.

In the wastewater coming from landfills, *manganese* was found in small quantities, as shown by the results of determinations made during the observation period of the Glina landfill (Figure 6).

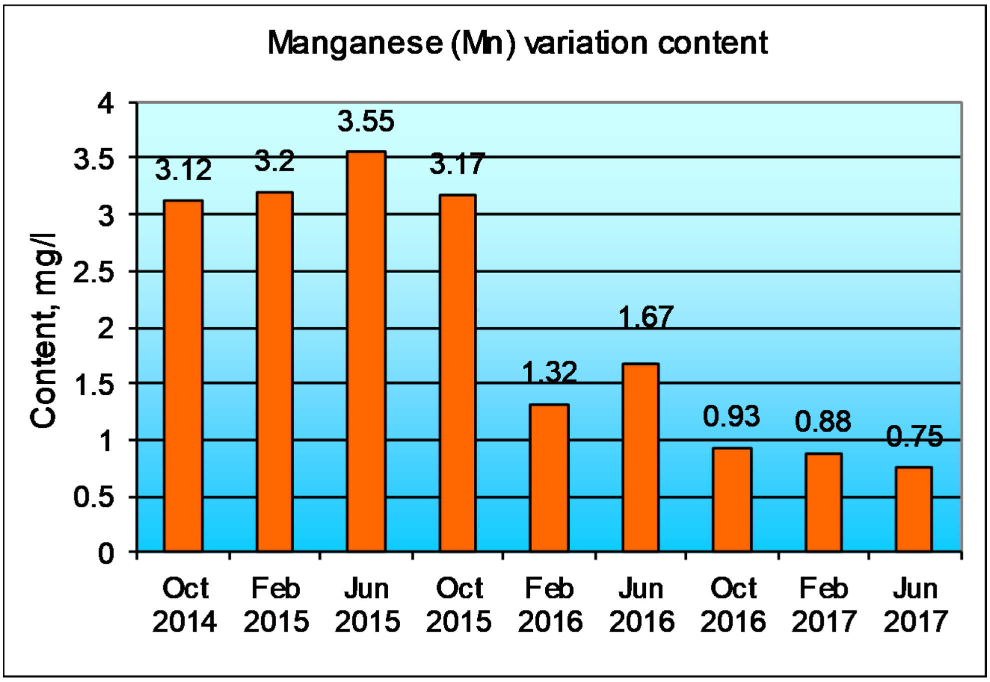

Figure 6. Variation of manganese content of leachate between 2014 and 2017.

The results obtained experimentally for 2014 and 2015 show a not very high content of manganese in leachate above the limits allowed for the discharge of leachate in the sewerage network. Starting with 2016, the content decreased by 2.8 mg/l from the maximum of 3.52 mg/l to 0.75 mg/l in June 2017 when the minimum value was registered.

Since the commissioning of the aeration lagoon, the concentration of manganese in leachate decreased with percentages between 46% and 74%, and since 2016 (year of commissioning) the concentration was reduced below the limit imposed by regulations (2 mg/l).

Lead can be present in leachate because of municipal waste through the disposal of old lead pipes, which were replaced with polyethylene pipes.

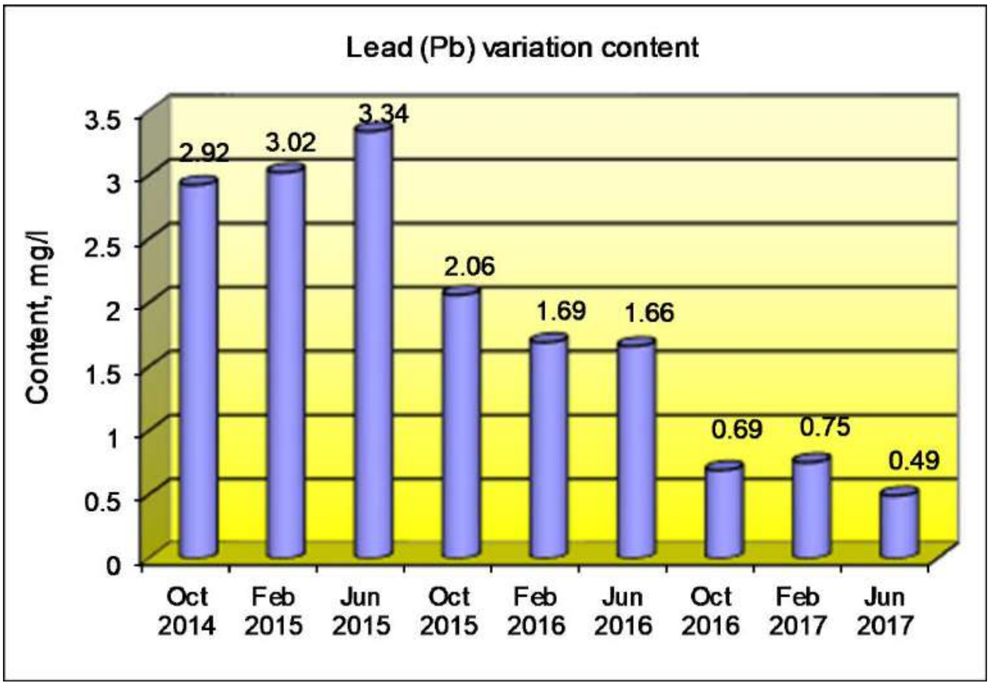

Figure 7. Variation of lead content of leachate in Glina landfill between 2014 and 2017.

Measurements regarding the lead content of the leachate carried out in the laboratory between October 2014 – February 2017 (presented in the Figure 7 graph) highlight the following aspects regarding the presence of this metal in the leachate:

The lead content ranged from 0.69 mg/l to 3.34 mg/l, all values being above the limit stipulated by NTPA 002/2001.

Between October 2015 – June 2016 the concentration of lead ions decreased, reaching a maximum of 2.06 mg/l in October 2015, being above the limit allowed by the normative NTPA 002 / 2001.

Starting with October 2016, the lead content of leachate registered a new reduction from 1.66 mg/l to 0.49 mg/l being between October 2016 – June 2017 slightly above the limit mentioned in the normative.

The binding of the lead and zinc ions to the cell walls occurred in specific groups that had a negative electrostatic charge, such as: phosphate groups, hydrophilic groups in extracellular polysaccharides and in wastewater with a slightly basic character such as leachate.

Zinc is a frequent pollutant of waters and sediments, being an important component of wastewater. Companies that deal with the production of materials containing zinc are considered as being possible pollutants. Above the toxic threshold, zinc alters the water taste (PLUGARU S.C.R. & al [11]).

Following the experimental determinations, a maximum concentration of 4.06 mg/l was obtained for zinc in October 2014 and a minimum concentration of 0.47 mg/l in June 2017. Except for the last three values that are below the limit imposed by the NTPA Regulation 002/2001, the rest of the determinations had values above this limit.

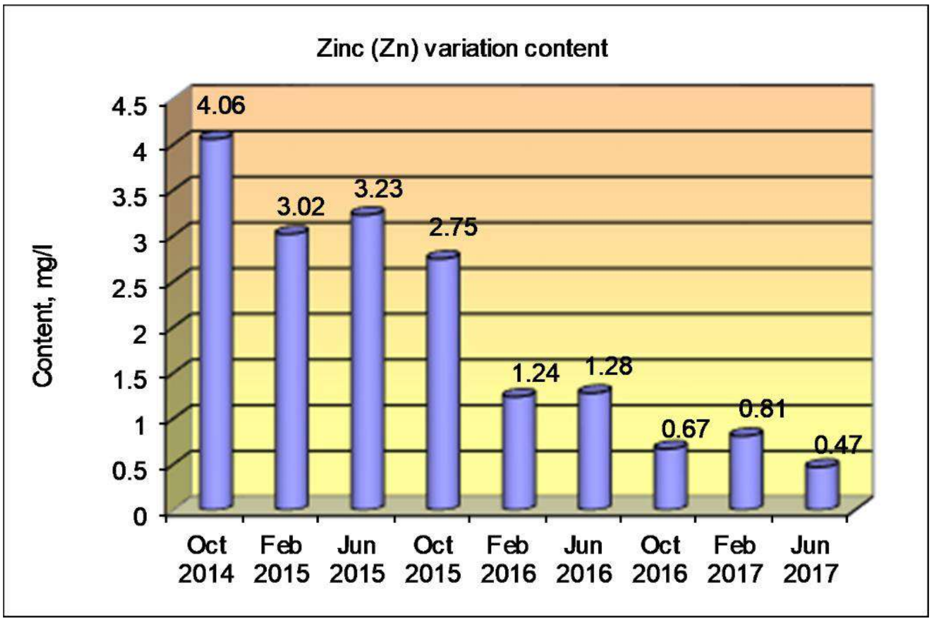

Figure 8. Variation of zinc content of leachate in the Glina ramp for 2013-2017.

It can be inferred from the results that regarding the zinc content, the execution of the aeration lagoon was efficient, the concentration values of zinc ions being between 0.47 mg/l and 0.81mg/l, which represented a retention efficiency of 71%. in the lagoon.

It can be observed that the biodegradation processes do not take place linearly because bacteria and fungi split the organic substances from the environment through reactions that follow certain pathways generated by their specific and specialized enzymatic equipment. Thus, the degradation products made by some microorganisms act as raw material for others; therefore, between different physiological groups of microorganisms, a series of interactions are realized which, in turn, depend on the activity of non-biodegradable microorganisms.

Through these interactions that occur in the process of biodegradation, some chains are formed that cause the creation of degradation cycles through which heavy metals, nitrogen, phosphorus, carbon and sulfur are eliminated from the leachate.

To remove heavy metals from leachate, numerous treatment systems are recommended in specialist literature; chemical precipitation (CHEN YN & al [3]), coagulation-flocculation (SYAFALNI & al [13]), flotation (ROBINSON J.M. [12]), ion exchange (CORTEZ S. & al [5], membrane filtration (DURENKAMP M. & al [7]), electrochemical oxidation (TURRO E. & al [14]), each method having advantages and limitations.

The latest research in the field of leachate purification (performed by YANAN REN & al [16]) highlighted a number of advantages for treatment by using microorganisms, especially fungi. (XIAOLI & al [15]) showed in their work that anaerobic processes comparable to the degradation of organic materials occured between the heavy metals and the humic substances from the leachate.

In the use of microbiological leachate purification systems it is of major importance to find, isolate and select strains of bacteria from the respective environment (BEJEN M & al [1]), which are already adapted to that polluted environment and therefore can be very effective in removing pollutants from leachate.

Other types of microorganisms that can accumulate significant amounts of heavy metals: Cd, Cr, Pb, Cu, Zn, Fe or others are cyanobacteria (BELINGHER ML & al [2]), (NECHIFOR ROXANA & al [10]) which can be developed in the laboratory to be introduced into the aeration lagoons or into the treatment tanks.

Conclusions

From the analysis regarding the content of heavy metals carried out on the effluent in the period 2014-2017, it resulted the total chromium content was below the limit imposed by the disposal norm of the leachate in the sewerage network (NTPA 002/2002).

After commissioning the aeration lagoon, the copper concentration decreased with percentages between 66% and 84%, but only in 2017 (one year since the beginning of the lagoon commissioning) the concentration below the limit imposed by regulations was reduced.

The reduction of cadmium content in leachate, experimentally found, was mainly accounted for by sedimentation in the sludge from the collection chimneys, the leachate basins and the one in the aeration lagoon.

The iron content was reduced after the installment of the aeration lagoon with percentages between 75% and 89.9%, reduction determined by the introduction into the leachate circuit of the aeration lagoon and the leachate basin.

The presence of manganese in leachate was beneficial because under the presence of organic substances, manganese was a suitable environment for the development of microorganisms.

The reduction of the lead content in the study period 2014-2017 was between 74% and 83%, a reduction determined by the introduction into the leachate circuit of the leachate basin and the aeration lagoon.

Even after the introduction of the aeration lagoon, the concentration of lead exceeded the permissible limits. Therefore, it is necessary to pass the leachate through the reverse osmosis treatment plant.

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