REMOVAL OF HEAVY METALS FROM LANDFILL LEACH WATER USING PYROPHYLLITE AS ADSORBENT

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ABSTRACT
Leachate water from sanitary landfills represents one of the most complex global environmental problems. This paper examines the possibility of using aluminosilicate material, pyrophyllite, from the Parsovići deposit, as an adsorbent. It was researched the influence of two granulations of pyrophyllite (0-53 µm and 0-100 µm) on the degree of adsorption of heavy metals (Fe, Ni, Mn) from leachate water from the municipal landfill "Desetine", Tuzla. The adsorption experiment was performed using the Batch method, depending on the contact time between the adsorbent and the adsorbate, the mixing speed, and the mass of the adsorbent, pyrophyllite, through two treatments. The results indicate a higher efficiency of the finer fraction of pyrophyllite, and in the competition of the three examined metals, iron is completely removed in the first treatment with both granulations and then nickel with finer granulation and manganese with coarser. After the first treatment, the unpleasant smell was removed, which is certainly a consequence of the removal of ammonia compounds as the most abundant compounds in leachate water. In these pioneering researches, pyrophyllite proved to be effective, and at the same time, it is a cheap, easily available, and environmentally friendly material for leachate water purification.

1. INTRODUCTION

Leachate water from sanitary landfills represents highly polluted wastewater and can be defined as all water that has "been in contact" with waste disposed of at the landfill. Leachate landfill water is created by the percolation of precipitation through the layers of disposal of waste, then partly originates from water that is included in the composition of disposed waste, and partly arises during the process of decomposition of waste [1,2].

The amount and quality of leachate formed in the body of the landfill depends on the size of the landfill, age, working conditions, biological, chemical, and physical processes at the landfill, climatic conditions at the location, composition, and amount of waste that is disposed of, etc.

Landfill leachate water is mainly loaded with the following pollutants [3]:

- nitrogen compounds in organically bound form or in the form of ammonia,
- compounds with phosphorus,
- heavy metals
- cations - the most common cations that occur are Na^+, K^+, Mg^{2+}, Ca^{2+}
- anions - Cl^-, SO_4^{2-}, S^{2-} i HCO^{3-}
- organic pollution
- chlorinated hydrocarbons and pesticides
- specific organic compounds: aromatic hydrocarbons, phenols, chlorinated aliphatic compounds.

Conditions for the treatment of leachate water are prescribed by legal acts, and the application of treatment technology depends on the amount and composition of leachate water and the conditions of discharge into an open watercourse or public drainage system [4].

Mechanical, biological, and chemical purification procedures are used for wastewater treatment. Chemical purification processes are processes in which purification is carried out using certain chemical reactions or certain physical-chemical phenomena. The basic procedures of chemical wastewater treatment are the removal of certain dissolved substances: chemical precipitation, ion exchange, oxidation, aeration, and adsorption [5].

Adsorption is a diffusion operation by which one or more components are removed from the gas or liquid phase using solid porous materials, called adsorbents. A solid substance on the surface on which the adsorption process takes place is called an adsorbent, while the substance that binds is called an adsorbate [6].

Adsorption is performed under the influence of physical or chemical forces when the adsorbed ions or molecules come close enough to the adsorbent. Physical phenomena occur in the form of Van der Waals electrostatic forces. Chemical adsorption occurs when molecules on the surface of the adsorbent and adsorbate molecules react. The effect of adsorption depends on the total surface area of the grain by mass, i.e. of the specific surface area [7].

The most commonly used adsorbents in wastewater treatment are activated carbon, silica gel, zeolites, and more recently the so-called "low-cost" adsorbents (waste biomass such as sawdust of various types of wood, straws of various kinds of wheat, rice husks, walnut husks, hazelnut husks, stems and leaves of various types of plants, etc.) [8].

Clay minerals, including pyrophyllite, are highly valued for their adsorptive properties. The widespread use of clays in the industry for wastewater treatment applications is often recommended today due to their local availability, technical feasibility, engineering application, ions, and cost-effectiveness [9].

Clay minerals appear as colloidal aggregates of small particles. Their large surface area is responsible for a number of unique physical and chemical properties such as cation exchange and pH-dependent sorption [10].

Pyrophyllite has shown great efficiency in the adsorption of heavy metals from contaminated wastewater as well as wastewater from electroplating plants. According to current regulations, the allowed pH value in wastewater from industrial plants before its discharge should be 7, which dictates the need for its neutralization before discharge into waterways. Optimizing the process of adsorption of heavy metals from the wastewater of the electroplating plant, it was concluded that the adsorption of metals is most favorable at a mass of pyrophyllite of 10 g, a fraction size of 0.10 mm, at pH 7, and a contact time of 2 hours [11,12].

The results of the research into the effectiveness of raw and modified pyrophyllite (modified with boric acid) in the adsorption of heavy metals speak of the justification of further research, but also of the practical application of pyrophyllite in the purification of industrial wastewater. Analysis of waste and treated water also found that pyrophyllite treatment reduces: organic carbon, ammonia, total inorganic nitrogen, total phosphorus, and total alkalinity. The results showed the additional effectiveness of pyrophyllite on the reduction of organic compounds, indicating that pyrophyllite can be an effective agent for the treatment of wastewater in mines, the metal industry, and landfill leachate water [13].

Preliminary experimental results of heavy metal removal (Pb, Cu, Cd, Zn and Ni) with PIR (pyrophyllite), PIR-B (pyrophyllite modified with boric acid) and PIR-B-V (pyrophyllite modified with boric acid and washed with water) singled out pyrophyllite PIR as the most effective adsorbent, which has a particular affinity for lead: 47.25 mg/g, for the described

operating conditions. This capacity stands out in relation to pyrophyllites from other sites. During the conduct of the experiment, the pH value was not adjusted, and during the sorption of lead ions, there was the smallest deviation between the initial and final pH values. Due to the fact that unmodified pyrophyllite was used without adjusting the pH value, the application itself is more economically profitable and simpler. Based on these experimental results, pyrophyllite can be used to remove lead from wastewater [14].
Chemical stabilization of soil contaminated with heavy metals using natural aluminosilicate materials (pyrophyllite and zeolite) has generally been shown to be a very effective measure from the point of view of reducing the accessibility of heavy metals in the soil, and therefore also from the point of view of reducing the possibility of their entering the plant, i.e. into the food chain. The results of this research support the thesis that zeolite, and especially pyrophyllite, have the ability to firmly bind heavy metals to their structure, which, on the one hand, reduces the possibility of their uptake by plants, and on the other hand, contributes to environmental protection, because by immobilizing heavy metals of metals reduces the possibility of their leaching from the surface layers of the soil into underground water courses [15, 16].
During the research, pyrophyllite proved to be a good adsorbent for glyphosate (organophosphorus herbicide), so in the future, it could be used as a filter in many experiments where it is necessary to examine the possibility and efficiency of adsorption [17].
Taking into account all previous research that was carried out on a laboratory-prepared sample contaminated with heavy metals, the goal of this work was to examine the effectiveness of pyrophyllite, as a heavy metal adsorbent, in the process of purifying waste landfill water.

2. MATERIALS AND METHODS

The removal of toxic metals from wastewater through the process of adsorption on natural materials such as clays is an efficient, inexpensive, and environmentally friendly procedure for preserving the environment. The material used in this work is pyrophyllite shale (hereafter pyrophyllite) from the Parsovići deposit, Konjic, Bosnia and Herzegovina. Pyrophyllite belongs to the group of aluminosilicate minerals of the chemical formula $Al_2Si_4O_{10}(OH)_2$, and in nature, it is found in the form of shale. It got its name from the Greek words *pir*-fire and *philon*-leaf because it spreads like a fan when heated. It is part of the isomorphic order of aluminosilicates that contain bound water. It is characterized by a three-layer crystal lattice, which has a tetrahedral structure in the outer layer, and an octahedral structure in the inner layer. The crystals are plate-like, soft, and greasy to the touch. It is electroneutral and not reactive in its natural form. Pyrophyllite is not soluble in water and does not swell. It is thermally stable. Depending on the admixture, the color of pyrophyllite varies from white, and gray to purple. The chemical and mineralogical composition and physical properties of pyrophyllite are shown in Tables, 1, 2, and 3:

Table 1. Average chemical composition of pyrophyllite

Composition	SiO_2	Al_2O_3	Fe_2O_3	FeO	TiO_2	CaO	MgO	CO_2	Na_2O	K_2O	H_20^-	H_20^+	Other elements
%	61±	23.1±	1.1	0.25	0.12	1.85	1.94	4.30	0.61	1.44	0.61	4.66	<0.1

Table 2. Average physical properties of pyrophyllite

pH	8.0-9.0
Hardness (by Mohs)	1.0-1.5
Specific gravity g/cm^3	2.6-2.8
Volumetric weight without shaking (33 μm) u g/cm^3	0.380-0.420
Volumetric weight with shaking (33 μm) u g/cm^3	0.525-0.550
Volumetric weight without shaking (63 μm) u g/cm^3	0.508-0.530
Volumetric weight with shaking (63 μm) u g/cm^3	0.750-0.820

Table 3. Average mineralogical composition of pyrophyllite

Pyrophyllite	44-52 %
Quartz	12-18 %
Carbonates	10-12 %
Kaolinite	18-22 %
Serecit	6-12 %
Other minerals in smaller percentages	

Pyrophyllite has naturally hydrophobic properties on the surface in aqueous solutions, which acts as a neutral adsorption site, accessible for non-polar organic species. Edges are hydrophilic in aqueous solutions. Cation exchanges (e.g. Al^{3+} instead of Si^{4+} in the tetrahedral layer or Mg^{2+}, Fe^{2+}, Ti^{2+} instead of Al^{3+} in the octahedral layer) contribute to the negative charge which contributes to the adsorption of cations or organic polar pollutants.

A sampling of pyrophyllite was carried out at the site of the Parsovići mine, Konjic, Bosnia and Herzegovina. The pyrophyllite samples used were mechanically activated by crushing, grinding, and sieving. The effect of mechanochemical activation of pyrophyllite leads to significant changes in the mineral structure, i.e. to partial amorphization, due to an increase in the number of lattice defects and deformations in the crystal structure, which results in an increase in specific surface area and reactivity. During grinding, easy splitting of layers occurs, while ionic and covalent bonds in the structure are broken at the edges. This is why flat, layered surfaces are hydrophobic while edges are hydrophilic in aqueous solutions, forming negatively charged sites. Two granulation samples: 0-53 μm and 0-100 μm were used to test the adsorption of heavy metals in this work.

Leachate landfill water was sampled at the sanitary municipal landfill "Desetine", Tuzla. The basic characteristics of landfill soil are the structure of sediments: clay, marl, sandstone, conglomerate, and sand. Clays and marls, i.e. the zones they build act as a hydrogeological insulator, while the zone with conglomerates, sand, and sandstones represent a collector of integral porosity. The greater the thickness of the clay and the greater its density, the greater the effect of purifying the filtrate. All leachate water from the waste material and from the surface, porous soil located on the impermeable layer is collected by a drainage system and controlled under an earthen dam [18]. Collected wastewater does not undergo any purification treatment before discharge into the recipient, surface water.

Parameters that exceed the permitted limit value in relation to the current legal regulation are heavy metals: Fe, Ni, Mn, and biological oxygen consumption (BPK_5). In this paper, the focus of purification is on the removal of heavy metals to the satisfactory values prescribed by Regulation [4].

Heavy metal adsorption experiments were performed using the "Batch" method, direct contact of a certain amount of pyrophyllite, and a real sample of landfill leachate in the Laboratory of AD Harbi LLC, Sarajevo.

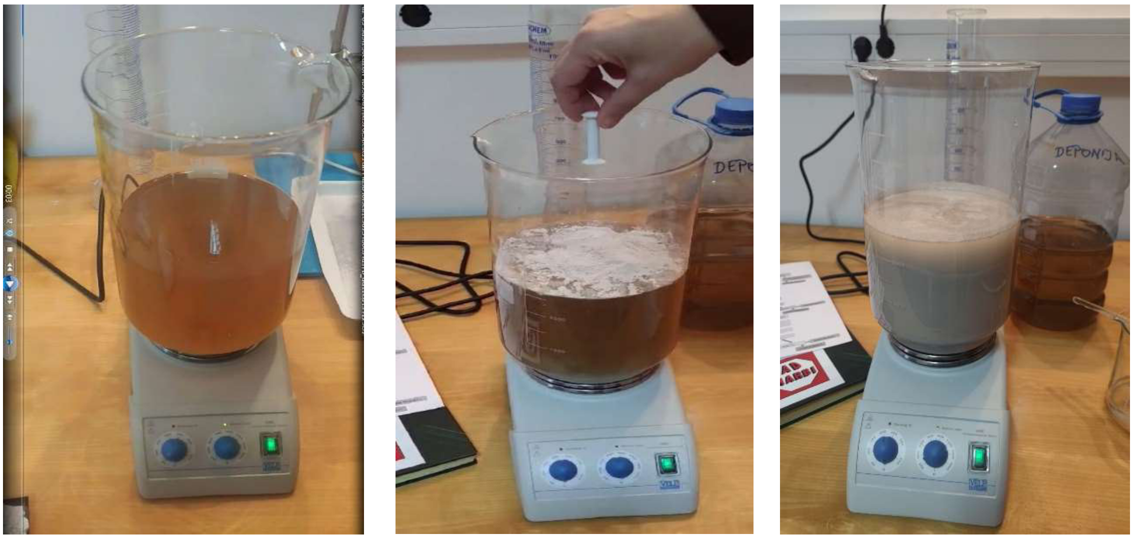
3. EXPERIMENTAL PART

Visual characteristics of the initial sample of landfill leachate water: dark yellow, slightly turbidity water with a very sharp and unpleasant smell.

The leachate water is divided into three parts for further treatment:

- **Sample 1** - landfill water without treatment,
- **Sample 2** - landfill water for treatment with pyrophyllite granulation 0-53 μm in a concentration of 5%,
- **Sample 3** - landfill water for treatment with pyrophyllite granulation 0-100 μm in a concentration of 5%.

The laboratory equipment used was a laboratory balance, a magnetic stirrer type Velp Scientifica, an electric vacuum pump type KNF Neuberger and other standard laboratory accessories and dishes. Pyrophyllite granulation 0-53 μm and 0-100 μm in a concentration of 5% were added to water samples 2 and 3, after which they were mixed on a laboratory stirrer at a speed of 200 rpm, for 2 hours (*Figure 1*).



a) *b)* *c)*

Figures1. Sample of landfill leachate water before a), during b), and after c) the addition of pyrophyllite

At the end of 2 hours, the mixture of wastewater and pyrophyllite was filtered on a Büchner funnel, through a filter paper blue strip with the use of an electric vacuum pump, for assisted filtration. The treatment was repeated twice with both granulations of pyrophyllite, by adding the same amount of pyrophyllite (concentration 5%) to the filtrates after the first treatment.

Laboratory determination of the content of iron, nickel, and manganese in leachate landfill water was done in cooperation with the Laboratory of the Institute of Chemical Engineering Tuzla, using standard methods EPA Method 7000 B and BAS ISO 11047:2000. Both mentioned methods are based on flame atomic absorption spectrophotometry, and instruments manufactured by Perkin Elmer, type Optima 2100 DV (optical emission spectrometer-plasma) and manufactured by VARIAN, type AA 200 (Atomic Absorption Spectrometer) were used for testing.

4. RESULTS AND DISCUSSION

Below is a tables and figures overview of experimentally obtained results.

Table 4. Initial and limiting pH values and metal values

Metal	Concentration in the initial water sample (mg/l)	* Limit value for surface water bodies (mg/l)
Fe	2.766	2.0
Ni	0.656	0.5
Mn	3.307	1.0
pH	7.12	6.5-9.0

* *in accordance with the applicable legislation, Annex 1. [4]*

Table 5. pH value, metal concentrations in the initial sample of landfill leachate water, and after I and II treatment with pyrophyllite granulation 0-53 μm

Metal	Concentration in initial sample (mg/l)	I treatment (mg/l)	II treatment (mg/l)
Fe	2.766	<0.006	<0.006
Ni	0.656	0.117	0.108
Mn	3.307	1.096	0.201
pH	7.12	7.42	7.63

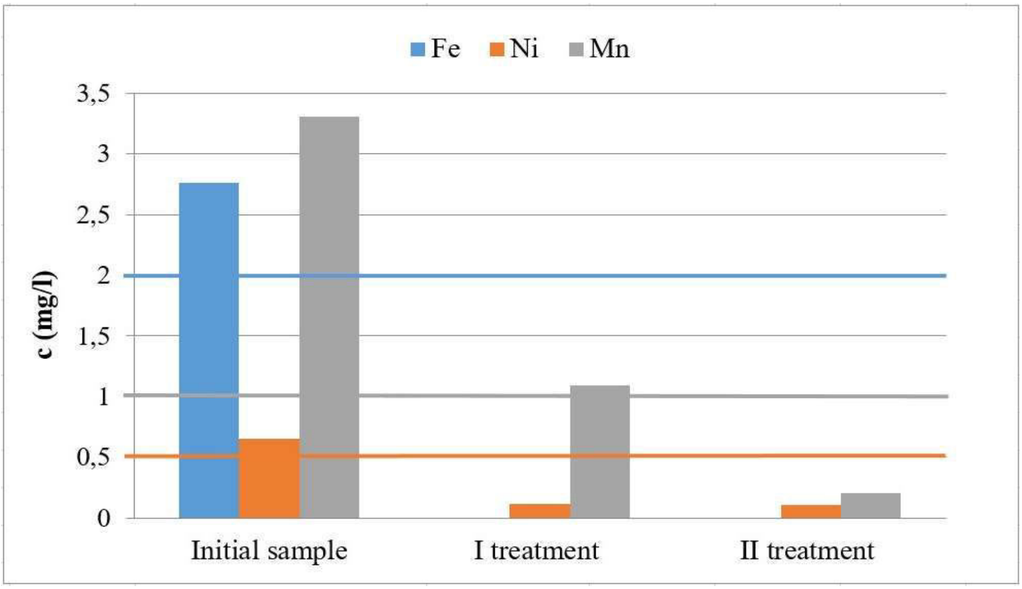


Figure 2. Presentation of limiting metal concentrations, metal concentrations in the initial sample of leachate landfill water and after I and II treatment with pyrophyllite granulation 0-53 μm

Table 6. pH value, metal concentrations in the initial sample of leachate landfill water after I and II treatment with pyrophyllite granulation 0-100 μm

Metal	Concentration in initial sample (mg/l)	I treatment (mg/l)	II treatment (mg/l)
Fe	2.766	0.231	<0.006
Ni	0.656	0.200	0.107
Mn	3.307	0.665	0.198
pH	7.12	7.37	7.44

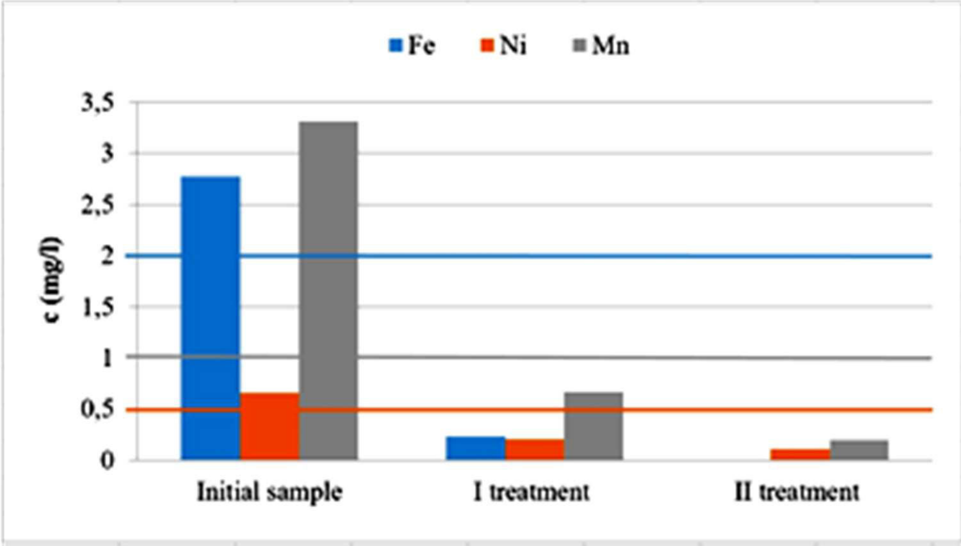


Figure 3. Presentation of limit concentrations of metals, the concentration of metals in the initial sample of landfill leachate water after Ist and IInd treatment with pyrophyllite granulation 0-100 µm

Table 7. Overview of adsorption efficiency depending on pyrophyllite granulation

Metal	% adsorption			
	I treatment 0-53 µm	I treatment 0-100 µm	II treatment 0-53 µm	II treatment 0-100 µm
Fe	100.0	91.6	0	100
Ni	82.2	69.5	7.7	46.5
Mn	66.9	79.9	81.7	70.2

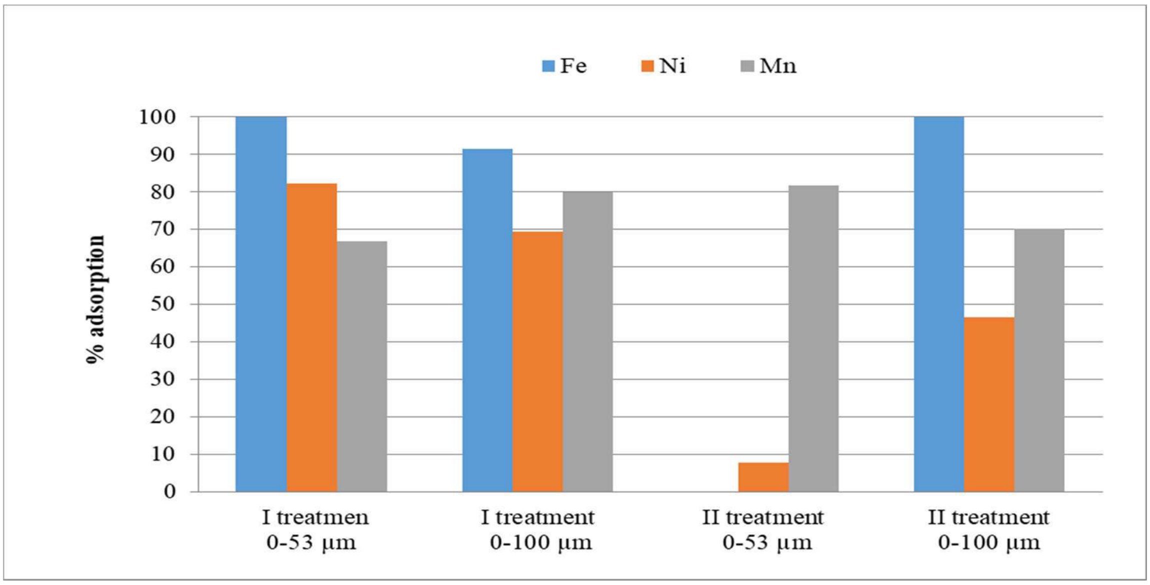


Figure 4. Presentation of adsorption efficiency depending on granulation

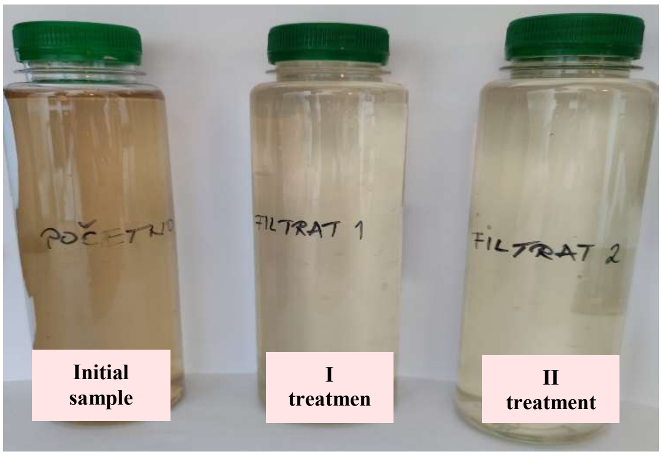


Figure 5. Visual representation of samples of landfill leachate before and after treatments

After the first treatment, the unpleasant smell was significantly reduced in both treated samples, and after the second it was almost gone. As leachate water is rich in ammonia compounds, with an intense smell, it is clear that pyrophyllite plays a role in binding them and neutralizing the smell. After both treatments of landfill leachate with pyrophyllite, a lighter color of the sample is observed, as seen in Figure 5.

When it comes to the change in pH value, the initial sample had a value of 7.12, and after the IInd treatment, the pH value was 7.63 (for granulation 0-53 μm) and 7.44 (for granulation 0-100 μm). An increase in pH, i.e. alkalinity of the environment, indicates an increase in hydroxyl ions and cations as a consequence of adsorption chemistry.

The results of the experiment conducted on Sample 1 (pyrophyllite granulation 0-53 μm) are shown in Table 5 indicate a decrease in the concentration of iron from the initial value of 2.766 mg/l to a value less than 0.006 mg/l immediately after the Ist treatment, the concentration of nickel from the initial value of 0.656 mg/l to a value of 0.117 mg/l after Ist treatment or 0.108 mg/l after the IInd treatment, and manganese concentration from the initial value of 3.307 mg/l to a value of 1.096 mg/l after the Ist treatment or 0.201 mg/l after the IInd treatment.

The results of the experiment conducted on Sample 2 (pyrophyllite granulation 0-100 μm) shown in Table 6 indicate a decrease in iron concentration from the initial value of 2.766 mg/l to a value of less than 0.231 mg/l after the first treatment, i.e. to a value of less than 0.006 mg/l after the II treatment, nickel concentrations from the initial value of 0.656 mg/l to a value of 0.200 mg/l after the Ist treatment, i.e. 0.107 mg/l after the IInd treatment, and manganese concentrations from the initial value of 3.307 mg/l to a value of 0.665 mg/l after the first treatment or 0.198 mg/l after the second treatment.

5. CONCLUSION

The results of the research prove that pyrophyllite from the "Parsovići" deposit, Konjic, Bosnia and Herzegovina, can be used as an effective agent (adsorbent) for removing iron, nickel, and manganese from the landfill leachate taken from the sanitary landfill "Desetine" in Tuzla. (Figures 2, 3, and 4).

The paper examined the effectiveness of two granulations of pyrophyllite (0-53 μm and 0-100 μm) on the degree of adsorption of heavy metals, Fe, Ni, and Mn present in landfill leachate water.

The research results indicate that the iron in the sample can be completely removed immediately after the first treatment with pyrophyllite of both pyrophyllite granulations (granulation 0-53 μm) and (granulation 0-100 μm).

The removal of nickel from landfill leachate water was achieved immediately after the first treatment with pyrophyllite in the amount of 82.2% (for granulation 0-53 μm) and 69.5% (for granulation 0-100 μm) in relation to the initial concentration. The stated efficiency in both cases indicates that the remaining concentrations of nickel in leachate landfill water are below the permitted limit value and that this leachate can be discharged into the final recipient without further treatment. The IInd treatment with pyrophyllite for the purpose of reducing nickel in this water was not even necessary.

Manganese in the landfill leachate sample exceeded the permitted limit value the most (up to 3 times) and its removal from the landfill leachate water required both treatments. Better adsorption efficiency in the amount of 79.9% was shown by the coarser granulation of the used pyrophyllite (0-100 μm) after the first treatment, while in the second treatment, the efficiency was better with the granulation 0-53 μm and was 81.7% compared to initial sample.

When using both granulations, manganese was removed from the landfill leachate water, and the remaining concentrations were below the legally prescribed values.

Bearing in mind the number of sanitary landfills in Bosnia and Herzegovina and the region, which represent an increasing environmental problem and challenge, and the fact that they do not have any leachate treatment, pyrophyllite as a valuable natural mineral with proven adsorption properties is emerging as an effective ecological and innovative solution to the problem of pollution heavy metals.

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