applied sciences

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Investigation of the Effect of Leachate on Permeability and Heavy Metal Removal in Soils Improved with Nano Additives

Mehmet Şükrü Özçoban [1] and Seren Acarer [2,*]

[1] Department of Geotechnical, Yildiz Technical University, Davutpasa, Istanbul 34220, Turkey; ozcoban@yildiz.edu.tr

[2] Department of Environmental Engineering, Istanbul University-Cerrahpasa, Avcilar, Istanbul 34320, Turkey

* Correspondence: seren.acarer@ogr.iuc.edu.tr

Abstract: Soils with low permeability are widely used in solid waste landfills to prevent leakage of leachate into groundwater. By adding nanomaterials to clay soils, the permeability of the clay can be reduced as well as the retention of pollutants in the leachate. In this study, three different nanomaterials, iron oxide, aluminum oxide, and Oltu clay, were added to kaolin at two different rates (1% and 5%), and the effect of nanomaterials on permeability and heavy metal (iron, manganese, zinc, copper, and lead) removal rate was investigated. According to the experimental results, permeability decreased, and the heavy metal removal rate increased with increasing nanomaterial content in kaolin. With the addition of 5% iron oxide, 5% aluminum oxide, and 5% Oltu clay to kaolin, the average permeability decreased by 63%, 81%, and 96%, respectively. Iron (90–93%), manganese (47–75%), zinc (39–50%), copper (33–41%), and lead (36–49%) removal rates of nanomaterial-added kaolin samples were found to be higher than the removal rates of kaolin without nanomaterial addition. Oltu clay, which has the smallest size and high surface area, performed better than aluminum oxide and iron oxide in reducing the permeability of kaolin and retaining heavy metals.

Keywords: compacted clay; heavy metal; leachate; nanomaterial; permeability

Citation: Özçoban, M.Ş.; Acarer, S. Investigation of the Effect of Leachate on Permeability and Heavy Metal Removal in Soils Improved with Nano Additives. *Appl. Sci.* **2022**, *12*, 6104. https://doi.org/10.3390/app12126104

Academic Editor: Francisco José Alguacil

Received: 20 May 2022
Accepted: 13 June 2022
Published: 16 June 2022

1. Introduction

Landfilling, one of the final disposal methods for solid waste, is the most used method worldwide [1]. Control of leachate generated in landfills is of great importance for the environment and human health. The use of soil with low permeability in a landfill prevents leachate contaminants from easily leaking from the ground and mixing with groundwater [2,3]. Clayey soils are widely used in landfill areas due to their low permeability [4]. However, the properties of the clay change as a result of interactions such as cation exchange, dissolution/precipitation, and redox reactions between the clay and leachate [5]. It has been reported by many researchers that pH [6], salt solutions [7,8], organic matter [9,10], and heavy metals [9,11,12] increase the permeability of clayey liners used in landfills. The resulting increase in permeability raises great concern about the environmental fate of leachate pollutants such as heavy metals.

Heavy metals are defined as metals with a density higher than 5 g/cm^3, and heavy metals include iron (Fe), manganese (Mn), zinc (Zn), lead (Pb), copper (Cu), arsenic (As), cobalt (Co), nickel (Ni) [13,14]. Electronic devices, batteries, pesticides, fertilizers, paints, and varnishes in the landfill are among the materials that increase heavy metal content [15–17]. Heavy metals are highly threatening pollutants due to their persistence, non-degradability, and toxicity [18]. Clays have high specific surface areas and small particle sizes that increase chemical and physical interaction with heavy metals [17]. Mirzaei et al. reported that Cd^{2+}, Cr^{3+}, Pb^{2+}, and Ni^{2+} heavy metals in leachate can be adsorbed more strongly in clay loamy texture than in loamy sand textured soil [19].

The voids of soils vary from micrometer to nanometer [20]. Filling the voids of clayey soils with nanomaterials changes the permeability. Studies have been carried out to reduce the permeability and/or hydraulic conductivity of soils by using different nano-sized materials by many researchers. Kananizadeh et al. investigated the changes in the properties and permeability of clayey soil resulting from the addition of nano clay with high aspect ratio and good thermal and physical properties. Kananizadeh et al. reported that soil permeability decreased from 3×10^{-9} cm/s to 9.4×10^{-11} cm/s with the addition of 3% nano clay to clay soil [21]. Ng and Coo added nano gamma-aluminum oxide (γ-Al_2O_3) and nano copper oxide (CuO) into kaolin clay because they are insoluble in water and chemically stable, and investigated the changes in the properties and hydraulic conductivity of kaolin clay. Ng and Coo reported that the pores of kaolin clay were clogged with the addition of γ-Al_2O_3 and nano CuO, and the hydraulic conductivity decreased by 30% and 45%, respectively, with the addition of 2% γ-Al_2O_3 and CuO into kaolin clay [22]. Fakhri et al. added 1–8% nano clay to kaolinite in order to improve the hydraulic properties of kaolinite. Kaolinite was investigated concerning the effect on the permeability coefficient of nano clay addition of up to 8%, and it was found that the permeability decreased gradually with increasing nano clay content. The experimental results showed that the addition of 8% nano clay to kaolinite reduced the permeability coefficient by 300 times [23]. Reginatto et al. carried out a study to find the appropriate nanoparticle concentration for reducing the permeability of clay soils of zero-valent nano iron particles, which have lower costs and lower toxicity than other metallic nanoparticles. In the study by Reginatto et al., the changes in the hydraulic conductivity of clay soil in suspensions with different concentrations nano iron varying in the range of 1–10 g/L were investigated. It was reported that 1 g/L and 4 g/L nano iron concentrations did not cause a significant change in the hydraulic conductivity of the soil, but 10 g/L nano iron concentration decreased the hydraulic conductivity from 6.1×10^{-6} m/s to 2.5×10^{-7} m/s [24]. Taha and Alsharef investigated the effect of carbon nanofibers (CNF) and multi-walled carbon nanotubes (CNTs) in the same carbon family, which are relatively inexpensive and readily available on the market, on the hydraulic conductivity of clay soils. The hydraulic conductivity of the soil sample (2.16×10^{-9} m/s) decreased with increasing CNT and CNF ratio, and the hydraulic conductivity decreased to 9.46×10^{-10} m/s and 7.44×10^{-10} m/s with the addition of 0.2% CNT and CNF, respectively [25]. Ochepo and Kanyi treated a lateric soil with nano silica, which has superior properties such as large surface area, small particle size, and porous structure, and showed that the permeability coefficient decreased at pressures above 40 kN/m^2 [26]. Bhadra and Leander investigated the geotechnical properties of fly-ash-doped soils with different nano calcium silicate (NCS) doses (0.2–1%). With the addition of 1% NCS to soil containing 6% fly ash, the permeability decreased from 6.2×10^{-6} cm/s to 4.8×10^{-6} cm/s [27].

In this study, the effects of three different nanomaterials (iron oxide, aluminum oxide, and Oltu clay) at two different rates (1% and 5%) on the permeability and heavy metal removal rate of the compacted kaolin through which the leachate was passed were investigated. The Fe, Mn, Zn, Cu, and Pb removal rates, as well as the permeability of compacted kaolin and compacted kaolin/nanomaterial clay samples, were determined. Identifying the compacted clayey soil sample possessing the lowest permeability and the greatest inhibition of the transmission of heavy metals to the groundwater is beneficial for the design of soil to be used in landfill areas. In addition, the final product obtained by adding natural Oltu clay and a small amount of nanomaterials to kaolin, which is abundant in nature, is a more economical and simple material that is able to compete with the expensive geomembranes used in landfills, but which have tearing problems.

2. Materials and Methods

2.1. Materials

The leachate used in the study was obtained from Şile Kömürcüoda Landfill Area on the Anatolian Side of Istanbul. Fe, Mn, Zn, Cu and Pb concentration values in the leachate were 59.6 mg/L, 1.1 mg/L, 3.07 mg/L, 2.68 mg/L and 0.68 mg/L, respectively. Kaolin clay was obtained from Esan Eczacıbaşı Industrial Raw Materials Inc. The chemical composition of kaolin determined by X-Ray Fluorescence (XRF) analysis and Carbon-Sulphur Analysis is presented in Table 1, and the particle size distribution results determined by the laser diffraction method are given in Table 2. Nano iron oxide and nano aluminum oxide were obtained from Sigma-Aldrich. Oltu clay was obtained from the Oltu district of Erzurum in Turkey. The properties of the nanomaterials used in the study are given in Table 3. The chemical composition of Oltu clay used in the study is given in Table 4.

Table 1. Chemical composition of kaolin.

Component	Content (%)
Loss on ignition (LOI)	10.0 ± 1.0
SiO_2	57.5 ± 1.0
Al_2O_3	27.0 ± 1.0
Fe_2O_3	1.5 ± 0.3
TiO_2	1.2 ± 0.1
CaO	0.2 ± 0.1
MgO	0.45 ± 0.1
Na_2O	0.2 ± 0.1
K_2O	1.7 ± 0.2
Soluble Salt	0.4 ± 0.1
Soluble SO_4	0.2 ± 0.1
SO_3 *	0.15 ± 0.1
C *	1.5 ± 0.1

* Carbon-Sulphur Analysis.

Table 2. Particle size distribution of kaolin.

Size (μm)	Percentage (%)
<2	65
<10	80
>63	2

Table 3. Properties of nanomaterials.

Material	Chemical Formula	Purity (%)	Particle Size (nm)	Surface Area (m^2/g)	Form
Iron oxide	Fe_3O_4	97	50–100	6–8	Nano powder
Aluminum oxide	Al_2O_3	99.8	13	85–115	Nano powder
Oltu clay	-	-	5–10	>110	Nano clay

Table 4. Chemical composition of Oltu clay [28].

Component	Content
LOI	13
SiO_2	41.48
Al_2O_3	12.22
MgO	8.10
Na_2O	0.20
K_2O	1.23
CaO	11.14
TiO_2	0.53
Fe_2O_3	9.88

2.2. Compaction Test

For the preparation of nanomaterial-added kaolin samples, 1% and 5% iron oxide, aluminum oxide, and Oltu clay were mixed separately with kaolin until a homogeneous mixture was obtained. Then, the samples were brought to the appropriate water content to reach the desired moisture content. The samples taken into the Proctor container were compacted in three stages by the standard compaction method. At each stage, 25 strokes were applied from a height of 30 cm with a 2.5 kg hammer [29].

2.3. Experimental Setup

A constant-head permeameter experimental method was used in this study [30]. Plexiglas reactors were used in the study. The reactors were filled with compacted kaolin and compacted kaolin/nanomaterial samples. The kaolin clay height in the reactor was 11 cm. Filters were formed at the bottom and top of the reactors to prevent soil particles from being washed away. To prevent the clay samples from swelling, a coarse-grained gravel soil layer was formed on the filter. The leachate was fed to the reactor containing compacted kaolin clay from the top of the reactor at a pressure of 0.3 bar. The schematic view of the experimental setup is given in Figure 1.

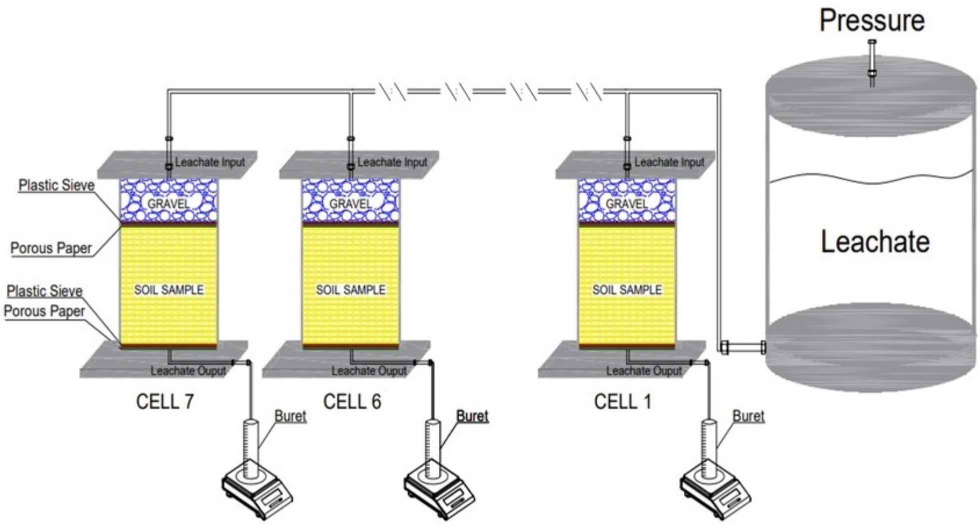

Figure 1. Schematic view of the experimental setup.

2.4. Permeability

A constant-head test was performed to determine the permeability of the kaolin and kaolin/nanomaterial samples that were compacted and placed in reactors. The leachate given over the reactors was collected in a beaker after passing through the kaolin samples. Permeability was calculated according to the following equation:

$$k = \frac{Q\,L}{A\,t\,(h1 - h2)} \tag{1}$$

where k is permeability (cm/s), A is surface area (cm^2), L is the distance between the manometers (cm), Q is the total discharge (cm^3/s), and t is the elapsed time (s).

2.5. Heavy Metals Analysis

The concentrations of heavy metals in the leachate at the reactor inlet and the reactor outlet on the 30th, 60th, and 90th days were measured. Metal analyses were performed according to the standard methods [31]. The Fe, Mn, Zn, Cu, Pb removal rates of the samples containing compacted kaolin, kaolin/iron oxide and kaolin/aluminum oxide, and kaolin/Oltu clay were investigated for 90 days at 30-day intervals.

3. Results

3.1. Permeability

The liner structure used in landfills is an important factor affecting permeability [32]. The permeability of an effective liner must be low to prevent groundwater contamination by minimizing the leakage of leachate from waste in landfills [32–34].

Figure 2 shows the permeability results of kaolin containing different amounts of iron oxide, aluminum oxide, and Oltu clay over 90 days. The initial permeability of kaolin was determined to be 2.87×10^{-8} cm/s. The permeability of kaolin samples with all nanomaterials added was lower than that of kaolin without nanomaterials. The addition of 1% iron oxide, 1% aluminum oxide, and 1% Oltu clay to kaolin decreased the initial permeability of kaolin to 2.15×10^{-8} cm/s, 1.78×10^{-8} cm/s, and 3.66×10^{-9} cm/s, respectively. The addition of 5% iron oxide, 5% aluminum oxide, and 5% Oltu clay to kaolin decreased the initial permeability of kaolin to 1.93×10^{-8} cm/s, 6.74×10^{-9} cm/s, and 9.8×10^{-10} cm/s, respectively. This reduction in permeability can be attributed to the nanomaterials reducing the large voids of kaolin [21,22,25].

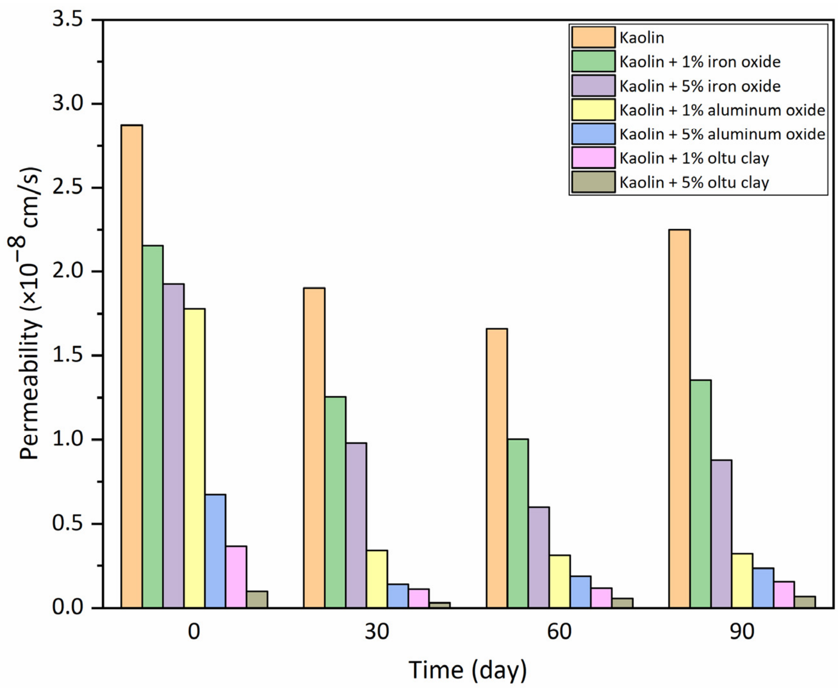

Figure 2. Permeability of kaolin and kaolin/nanomaterial samples.

The permeability decreased gradually with increasing ratio of nanomaterials added to kaolin. The addition of 1% iron oxide, 1% aluminum oxide, and 1% Oltu clay to kaolin reduced permeability by 25.11%, 38.09%, and 87.25%, respectively; 5% iron oxide, 5% aluminum oxide, and 5% Oltu clay reduced the permeability by 32.99%, 76.54%, and 96.59%, respectively. The permeability decreased with increasing nanomaterial ratios, as increased ratio of all nanomaterials caused more clogging of the porous structure of kaolin.

The permeability of all kaolin and kaolin/nanomaterial samples decreased until day 60, but increased on day 90. The decrease in permeability until the 60th day can be attributed the adsorption of contaminants such as heavy metals, suspended solids, and microorganisms in the leachate to the kaolin and nanomaterial surfaces or clogging of the voids in the soil structure by these pollutants [9,32,35]. On the other hand, permeability increased in all kaolin samples due to desorption on the 90th day. In addition, the results of the increase or decrease in the permeability as a function of the number of days were found to be in harmony with the heavy metal removal efficiency described in Section 3.2.

The maximum reduction in permeability was achieved in the case of the combination of kaolin + 5% Oltu clay on the first day, day 30, day 60, and day 90. For both 1% nanomaterial addition and 5% nanomaterial addition, the performance of the nanomaterials in terms of reducing permeability was determined to follow the following order from high to low on all days: Oltu clay > aluminum oxide > iron oxide. The order of the size of the nanomaterials included in kaolin, from largest to smallest, was Oltu clay > aluminum oxide > iron oxide. Oltu clay (5–10 nm), which has a smaller size than the other nanomaterials, clogged the pores of the kaolin more, causing a further decrease in the permeability of the leachate. The permeability results showed that the permeability decreased with decreasing size of the nanomaterial added to the kaolin.

Figure 3 shows the results for the average permeability of kaolin with the addition of 1% and 5% nanomaterials over 90 days. With the addition of 5% iron oxide, 5% aluminum oxide and 5% Oltu clay to kaolin, the average permeability decreased by 63.36%, 81.26%, and 96.89%, respectively. The improved performance of Oltu clay, aluminum oxide, and iron oxide in reducing permeability can be explained by the increased packing density due to their smaller size, as well as their structural properties. Results similar to those suggesting that smaller-diameter nanomaterials reduce the permeability more reported in this study dan be found in Bahmani et al. [36] and Taha and Taha [37].

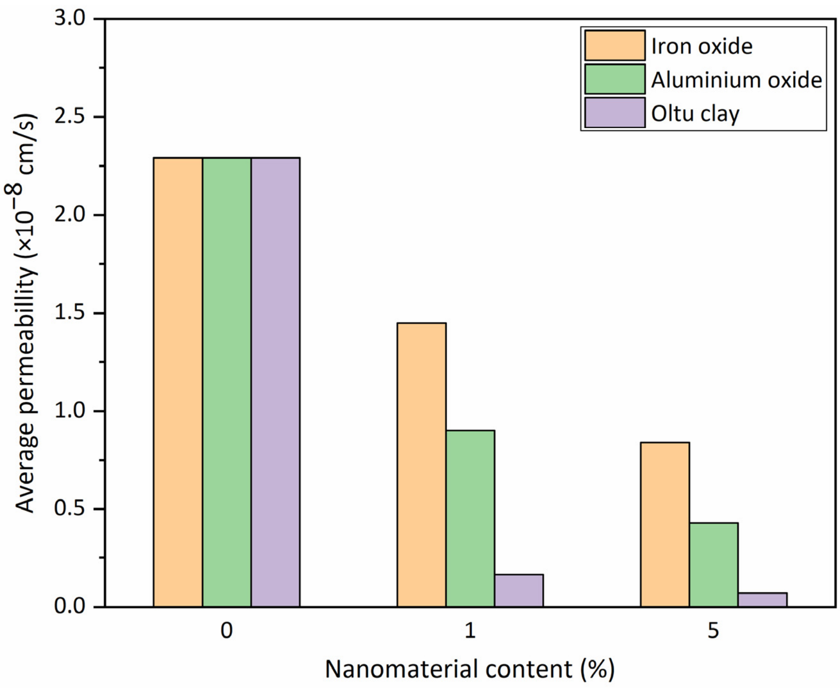

Figure 3. Average permeability of kaolin with different nanomaterial content.

3.2. Heavy Metal Removal

3.2.1. Iron Removal Rate

Figure 4 shows the iron removal efficiencies over 90 days for kaolin and nanomaterial-added kaolin samples compacted using standard methods. The initial iron concentration in the leachate was measured as 59.6 mg/L. On the 30th day, the lowest iron removal rate was 68.65% for kaolin, while the iron removal rates of nanomaterial-added kaolin samples varied between 70.09% and 80.63%. Iron removal rates continued to increase at a decreasing rate until the 60th day, and the iron removal rate of all kaolin samples reached a maximum on the 60th day. While the removal rate for the kaolin sample was 87.23% on the 60th day, the iron removal efficiencies of the nanomaterial-added kaolin samples ranged from 90.15% to 93.33%. As the ratio of nanomaterial in kaolin increased, the rate of iron removal also increased. On the 60th day, the iron concentration values were 7.61 mg/L for kaolin, and 5.63 mg/L, 4.21 mg/L and 3.97 mg/L for 5% iron oxide, 5% aluminum oxide and 5% Oltu clay added kaolin, respectively. The results showed that the nanomaterial performance in kaolin, in terms of increased iron removal rate, was Oltu clay > aluminum oxide > iron oxide, respectively.

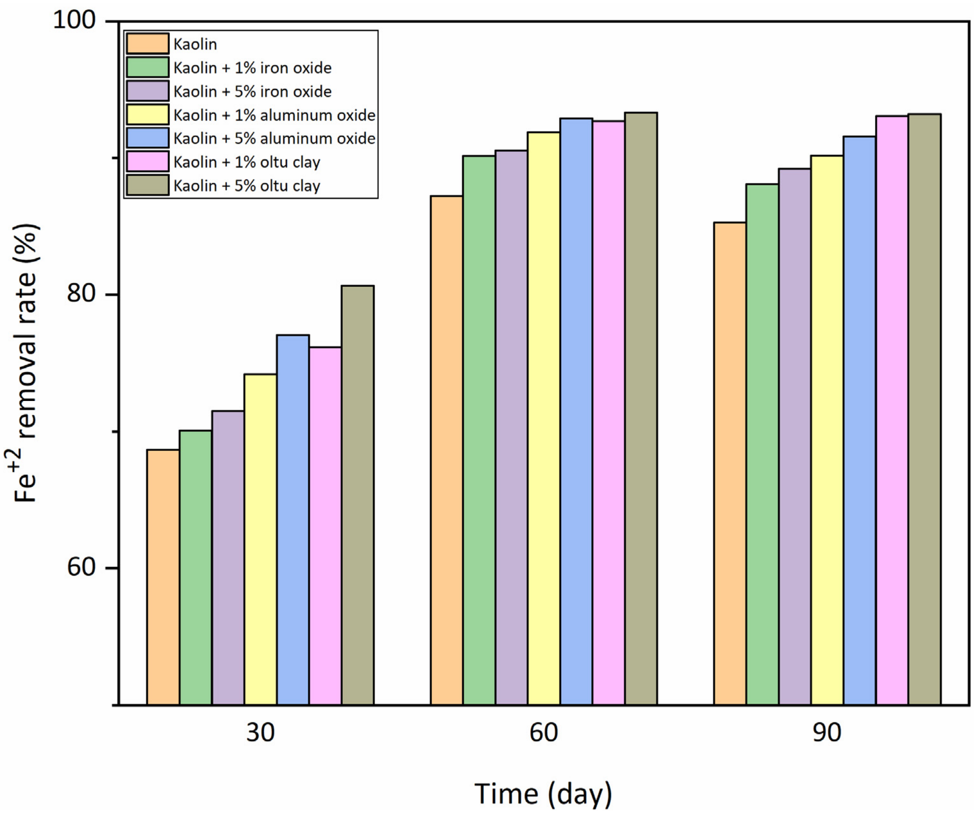

Figure 4. Iron removal rate of kaolin and kaolin/nanomaterial samples.

Over 90 days, the kaolin + 5% Oltu clay sample showed the best performance in terms of iron removal. The large specific surface area of the nanomaterials plays an important role in increasing the heavy metal adsorption capacity from water [38,39]. The smaller size and higher surface area of Oltu clay compared with aluminum oxide and iron oxide enabled the Oltu-clay-added kaolin samples to retain more iron in the leachate.

On the 90th day, the iron removal efficiencies of kaolin and kaolin/nanomaterial samples decreased slightly, and the iron concentration at the outlet increased. The decrease in the iron removal rate can be explained by the loss of heavy metal retention as a result of the saturation of the surface area of kaolin and nanomaterials with heavy metals and the separation of the heavy metals from the surface [40,41].

Iron was retained in higher amounts in all kaolin samples than other heavy metals in the leachate. This is related to the high concentration of iron in leachate compared to other metals. Moreover, the reaction of oxygen with iron in leachate and between the cavities of compressed kaolin samples in reactors causes the formation of iron hydroxide flocs, which contribute to the adsorption of iron [42].

3.2.2. Manganese Removal Rate

Figure 5 shows the manganese removal rate for kaolin and kaolin/nanomaterial samples over 90 days. The manganese removal rates of kaolin on the 30th and 60th days were 23.63% and 43.63%, respectively. The manganese removal rates of kaolin/nanomaterial samples varied between 31.81 and 58.18% and 47.27 and 75.45% on the 30th and 60th days, respectively. The lowest manganese concentration in the outlet of the reactors was obtained on the 60th day. When the ratio of all nanomaterials included in the kaolin was increased from 1% to 5%, the manganese removal rates also increased.

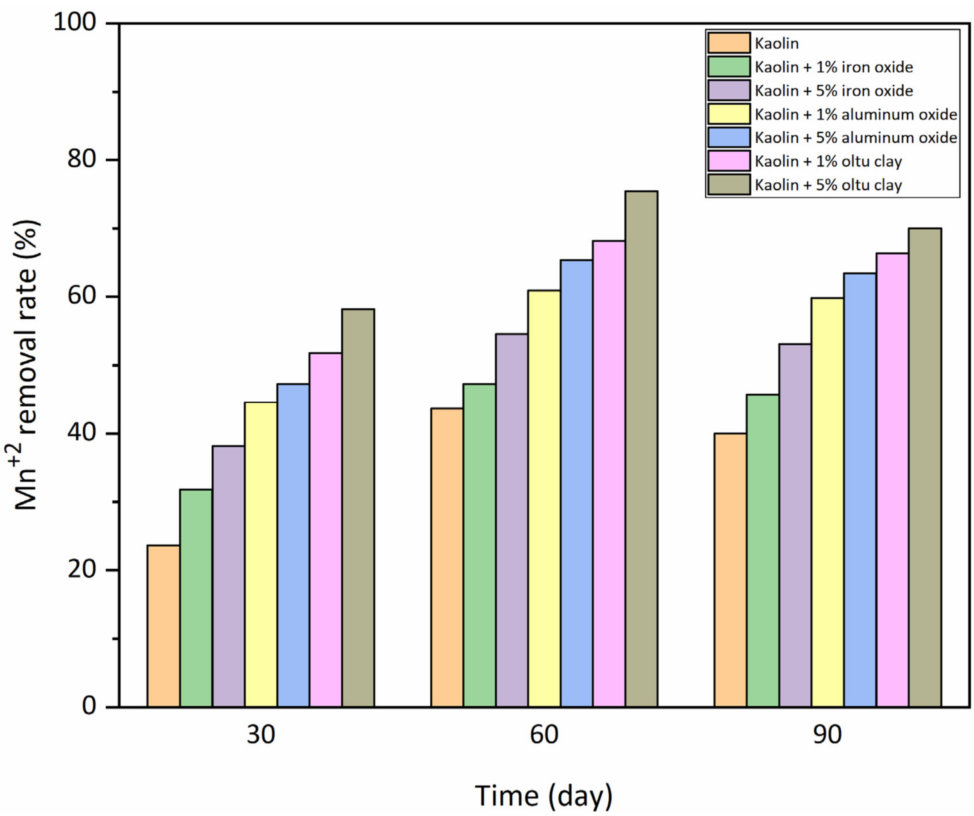

Figure 5. Manganese removal rate of kaolin and kaolin/nanomaterial samples.

The manganese removal rate increased with the addition of iron oxide, aluminum oxide, and Oltu clay to kaolin, respectively. The relatively large size and small surface area of iron oxide resulted in lower manganese removal, while Oltu clay with small size and high surface area allowed higher manganese removal. In addition, even if the amount of nanomaterials with higher surface area in kaolin was small, it showed better manganese removal performance compared to nanomaterials with higher amount and low surface area. For example, the addition of 1% aluminum oxide (85–115 g/m^2) into kaolin provided better manganese removal than with the 5% iron oxide additive (6–8 g/m^2).

With the addition of 5% iron oxide, 5% aluminum oxide, and 5% Oltu clay to kaolin, the manganese values at the exit of the reactor were 0.5 mg/L (54.54% removal), 0.38 mg/L (65.45% removal), and 0.27 mg/L (75.45% removal), respectively. On the 90th day, there was a slight decrease in the manganese removal rate due to desorption. The samples with the lowest and highest manganese removal rates on the 90th day were found to be kaolin (40% removal) and kaolin + 5% Oltu clay (70% removal), respectively. In this study, manganese is the heavy metal with the highest removal rate after iron. Similar to the removal rate of iron, iron hydroxide and manganese dioxide flocks formed in the upper part of the kaolin samples, and the cavities contributed to the adsorption of manganese, thereby increasing the removal rate [42].

3.2.3. Zinc Removal Rate

Figure 6 shows the zinc removal efficiencies of kaolin and kaolin/nanomaterial samples over 90 days. The initial zinc value in the leachate was measured as 3.07 mg/L. On the 30th day, the zinc removal rate of all kaolin samples was below 25%. On the 60th day, the zinc removal efficiencies of kaolin samples increased, and the zinc removal rate varied between 35.83% and 50.16%. The lowest zinc concentration and the highest zinc removal rate were 1.53 mg/L and 50.16%, respectively, for kaolin + 5% Oltu clay at day 60. At the end of the 90th day, the zinc removal efficiency of the samples decreased. When the ratio of nanomaterials in kaolin increased from 1% to 5%, the zinc removal rates also increased.

In terms of zinc removal rate, Oltu clay, aluminum oxide and iron oxide added to kaolin showed better performance, respectively. The small size and high surface area of Oltu clay provided the best zinc removal performance among all of the nanomaterials.

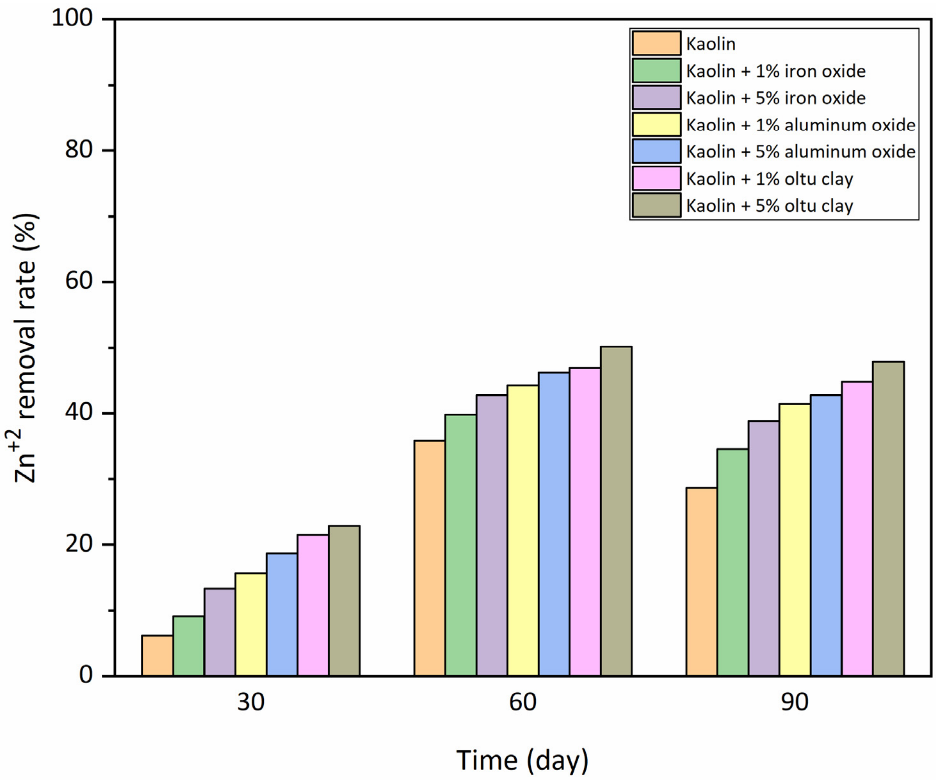

Figure 6. Zinc removal rate of kaolin and kaolin/nanomaterial samples.

The addition of 1% Oltu clay to kaolin showed higher performance in terms of zinc removal rate than kaolin with 5% iron oxide and 5% aluminum oxide. For example, even over a long operating time (90 days), kaolin with 1% Oltu clay offered 6% and 2% higher zinc removal performance than kaolin with 5% iron oxide and 5% aluminum oxide. These results show that the use of a lower amount of Oltu clay is more beneficial than the use of higher amounts of iron oxide or aluminum oxide in terms of increasing the zinc removal rate.

3.2.4. Copper Removal Rate

Figure 7 shows the copper removal rates of kaolin and kaolin/nanomaterial samples over 90 days. The initial copper concentration in the leachate was measured as 2.68 mg/L. While the copper removal rate of all kaolin samples was below 35% on the 30th day, it varied between 26% and 42% on the 60th day. On the 90th day, copper concentrations at the reactor outlet increased. The addition of Oltu clay to kaolin showed better performance in copper removal at all times than both kaolin and other kaolin samples with the addition of nanomaterials. The highest copper removal rate was obtained for 5% Oltu-clay-added kaolin. This is related to the fact that Oltu clay provides relatively more numerous active sites for Cu^{+2} to be adsorbed than aluminum oxide or iron oxide, respectively, due to its high surface area.

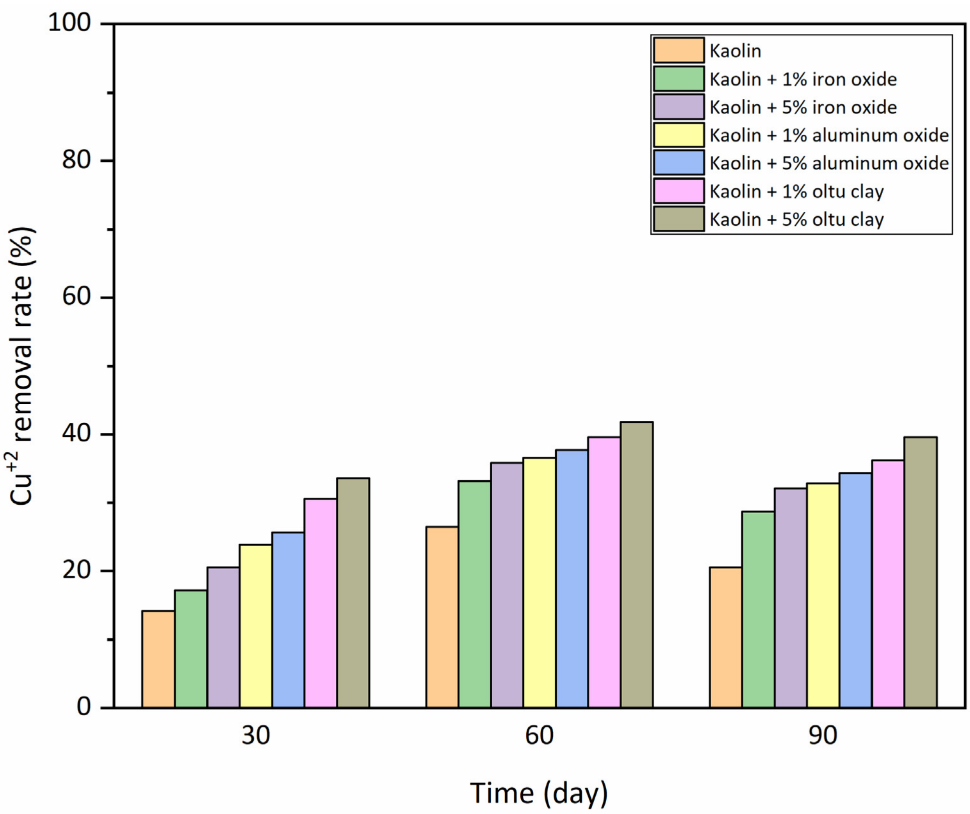

Figure 7. Copper removal rate of kaolin and kaolin/nanomaterial samples.

3.2.5. Lead Removal Rate

Figure 8 shows the lead removal rates of kaolin and kaolin/nanomaterial samples over 90 days. Initially, the lead concentration in the leachate was 0.68 mg/L. Kaolin samples with nanomaterial added for 30–90 days had a higher lead removal rate than kaolin. The lead removal rates increased with increasing ratio of all nanomaterials in kaolin. Similar to other heavy metal removal results, the highest lead removal rates in the 1% and 5% nanomaterial additives were achieved by adding Oltu clay, aluminum oxide, and iron oxide to kaolin, respectively. On the other hand, slightly different from the other heavy metal removal results, the lead removal rate of 5% aluminum-added kaolin was found to be higher than that of 1% Oltu-clay-added kaolin. However, the kaolin + 5% Oltu clay sample showed the best performance in terms of lead removal at all times examined. The highest lead removal rate was 48.52% for kaolin + 5% Oltu clay at day 60.

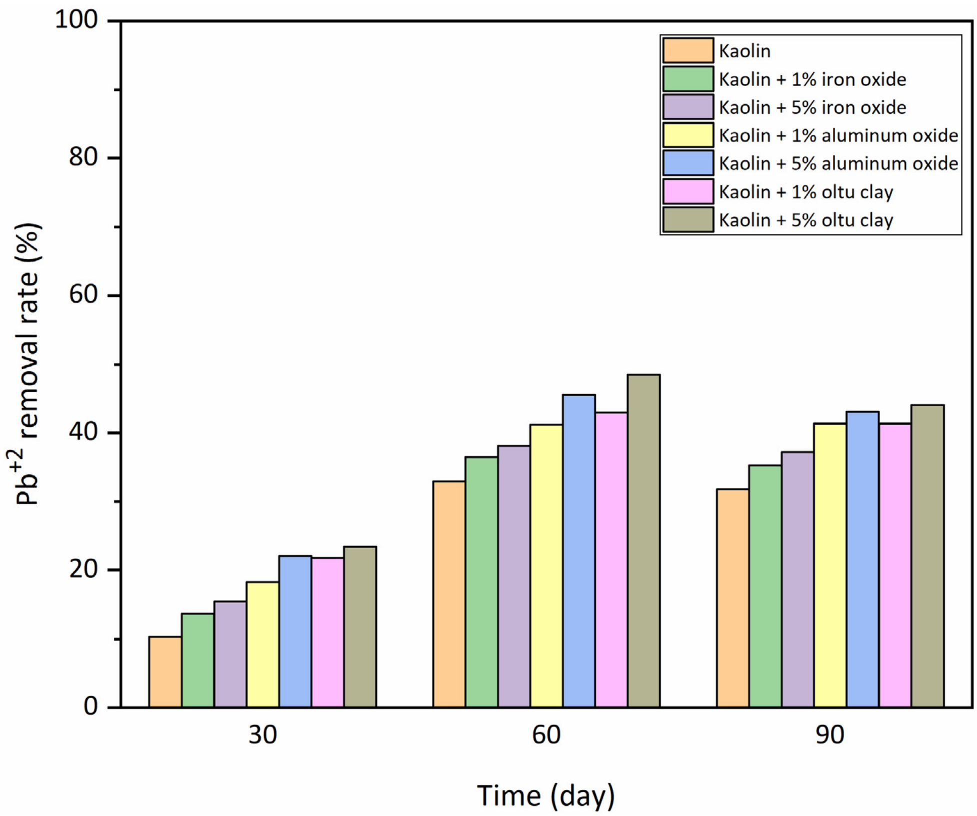

Figure 8. Lead removal rate of kaolin and kaolin/nanomaterial samples.

4. Conclusions

In this study, three different nanomaterials, iron oxide, aluminum oxide, and Oltu clay, were added to kaolin, and the permeability and heavy metal removal rates of kaolin samples passed through leachate were determined. On the basis of this study, the following results were obtained:

(1) The concentration of heavy metals in the leachate obtained from the solid waste landfill was determined to be Fe > Zn > Cu > Mn > Pb, from high to low.

(2) Nano-sized iron oxide, aluminum oxide, and Oltu clay caused the clogging of the large-sized pores of the kaolin and reduced the leachate permeability of the kaolin. The permeability decreased with increasing amounts of all nanomaterials in kaolin. In terms of reducing the permeability of kaolin, Oltu clay with the smallest size and high surface area exhibited the best performance, followed by aluminum oxide and iron oxide, respectively. The permeabilities of 5% Oltu clay, 5% aluminum oxide, and 5% iron oxide added kaolin samples decreased by 96.89%, 81.26%, and 63.36%, respectively, compared to the permeability of kaolin without nanomaterial additives.

(3) All of the kaolin samples containing nanomaterials exhibited a higher heavy metal removal rate over the 90-day measurement period than the undoped kaolin. The removal rate of heavy metals increased with increasing amounts of nanomaterials in the kaolin. While the highest removal rate of heavy metals (lead, copper, zinc, manganese, and iron) of kaolin over 90 days varied between 27 and 87%, for 5% Oltu-clay-added kaolin, this value varied between 41% and 93%. The highest heavy metal removal rates were obtained in kaolin + 5% Oltu clay sample, since Oltu clay has the highest surface area.

This study is promising in terms of reducing the permeability of solid waste leachate with high pollutant content by adding nanomaterials to clayey soils used in landfills and preventing the risk of reaching groundwater by keeping heavy metals in the soil structure more. This study reveals that if the permeability of the kaolin clay used in landfills does not meet the desired standards, the kaolin clay will mix with small amounts of nanomaterials (iron oxide, aluminum oxide, and Oltu clay), which will contribute to a significant reduction in permeability and increase the retention rate of heavy metals.

Author Contributions: Conceptualization, M.Ş.Ö.; methodology, M.Ş.Ö., S.A.; validation, M.Ş.Ö; formal analysis, M.Ş.Ö., S.A.; investigation, S.A.; resources, M.Ş.Ö., S.A.; data curation, M.Ş.Ö., S.A.; writing—original draft preparation, M.Ş.Ö., S.A.; writing—review and editing, M.Ş.Ö., S.A.; visualization, M.Ş.Ö., S.A.; supervision, M.Ş.Ö.; project administration, M.Ş.Ö.; funding acquisition, M.Ş.Ö. All authors have read and agreed to the published version of the manuscript.

Funding: This research is funded by the Research Fund of Yildiz Technical University, grant number FBA-2017-3158.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Luo, H.; Zeng, Y.; Cheng, Y.; He, D.; Pan, X. Recent advances in municipal landfill leachate: A review focusing on its characteristics, treatment, and toxicity assessment. *Sci. Total Environ.* **2020**, *703*, 135468. [CrossRef] [PubMed]
2. Visentin, C.; Zanella, P.; Kronhardt, B.K.; da Silva Trentin, A.W.; Braun, A.B.; Thomé, A. Use of geosynthetic clay liner as a waterproofing barrier in sanitary landfills. *J. Urban Environ. Eng.* **2019**, *13*, 115–124. [CrossRef]
3. Uma Shankar, M.; Muthukumar, M. Comprehensive review of geosynthetic clay liner and compacted clay liner. *IOP Conf. Ser. Mater. Sci. Eng.* **2017**, *263*, 032026. [CrossRef]
4. Khalid, N.; Mukri, M.; Kamarudin, F.; Abdul Ghani, A.H. Effect of compaction characteristics on hydraulic conductivity performance for sedimentary residual soil mixed bentonite as compacted liners. *IOP Conf. Ser. Earth Environ. Sci.* **2020**, *498*, 012003. [CrossRef]
5. De Soto, I.S.; Ayora, C.; Cuevas, J. Geochemical processes in compacted clay in contact with an acid landfill leachate: Laboratory experiments and modelling results. *Clay Miner.* **2014**, *49*, 443–455. [CrossRef]
6. Faraghati, S.N.; Sadeghpour Haji, M.; Ghadimi Hamzeh Kolaei, A.; Haji, M.S.; Ghadimi, A.; Kolaei, H.; Sadeghpour Haji, M.; Ghadimi Hamzeh Kolaei, A. Effect of PH Changes on the Geotechnical Properties of Clay Liners in Landfill. *Adv. Res. Civ. Eng.* **2019**, *1*, 49–57.
7. Shariatmadari, N.; Salami, M.; Fard, M.K. Effect of inorganic salt solutions on some geotechnical properties of soil-bentonite mixtures as barriers. *Int. J. Civ. Eng.* **2011**, *9*, 103–110.
8. Mishra, A.K.; Ohtsubo, M.; Li, L.Y.; Higashi, T.; Park, J. Effect of salt of various concentrations on liquid limit, and hydraulic conductivity of different soil-bentonite mixtures. *Environ. Geol.* **2009**, *57*, 1145–1153. [CrossRef]
9. Wang, S.; Zhu, W.; Xu, H.; Shu, S.; Fan, X. *Effects of Leachate Concentration (Na^+, Pb^{2+}, COD) on Non-Darcy Flow of Compacted Clay*; Springer: Singapore, 2019; ISBN 9789811322235.
10. Moon, C.H.; Lee, J.Y.; Oh, B.T.; Choi, S.I. Organically modified low-grade kaolin as a secondary containment material for underground storage tanks. *Environ. Geochem. Health* **2007**, *29*, 271–280. [CrossRef]
11. Ban, R.; Chen, X.; Song, Y.; Bi, P.; Yang, X.; Zhang, X. Study on Permeability and Electrical Resistivity of Red Clay Contaminated By Cu2+. *Stavební Obz. Civ. Eng. J.* **2021**, *30*, 312–322. [CrossRef]
12. Dutta, J.; Mishra, A.K. Influence of the presence of heavy metals on the behaviour of bentonites. *Environ. Earth Sci.* **2016**, *75*, 993. [CrossRef]
13. Kahraman, H. Heavy Metals and Bacteria; Example of P. aeruginosa. *Biomed. J. Sci. Tech. Res.* **2020**, *29*, 22444–22446. [CrossRef]
14. Srivastava, V.; Sarkar, A.; Singh, S.; Singh, P.; de Araujo, A.S.F.; Singh, R.P. Agroecological responses of heavy metal pollution with special emphasis on soil health and plant performances. *Front. Environ. Sci.* **2017**, *5*, 64. [CrossRef]
15. Al-Raisi, S.A.H.; Sulaiman, H.; Suliman, F.E.; Abdallah, O.; Abdul, S.; Al, H.; Sulaiman, H.; Suliman, F.E.; Abdallah, O.; Al-Raisi, S.A.H.; et al. Assessment of heavy metals in leachate of an unlined landfill in the Sultanate of Oman. *Int. J. Environ. Sci. Dev.* **2014**, *5*, 60–63. [CrossRef]
16. Sankhla, M.S.; Kumari, M.; Sharma, K.; Kushwah, R.S.; Kumar, R. Heavy Metal Pollution of Holy River Ganga: A Rev Ganga is the largest riverine syste. *Int. J. Res.* **2018**, *5*, 421–436.
17. Gu, S.; Kang, X.; Wang, L.; Lichtfouse, E.; Wang, C. Clay mineral adsorbents for heavy metal removal from wastewater: A review. *Environ. Chem. Lett.* **2019**, *17*, 629–654. [CrossRef]
18. Hussein, M.; Yoneda, K.; Mohd-Zaki, Z.; Amir, A.; Othman, N. Heavy metals in leachate, impacted soils and natural soils of different landfills in Malaysia: An alarming threat. *Chemosphere* **2021**, *267*, 128874. [CrossRef]
19. Mirzaei, S.M.J.; Heidarpour, M.; Tabatabaei, S.H.; Najafi, P.; Hashemi, S.E. Immobilization of leachate's heavy metals using soil-zeolite column. *Int. J. Recycl. Org. Waste Agric.* **2013**, *2*, 20. [CrossRef]

20. Taipodia, J.; Dutta, J.; Dey, A. Effect of nano particles on properties of soil. In Proceedings of the Indian Geotechnical Conference, Kochi, Japan, 15–17 December 2011; pp. 105–108.
21. Kananizadeh, N.; Ebadi, T.; Khoshniat, S.A.; Mousavirizi, S.E. The Positive Effects of Nanoclay on the Hydraulic Conductivity of Compacted Kahrizak Clay Permeated With Landfill Leachate. *Clean Soil Air Water* **2011**, *39*, 605–611. [CrossRef]
22. Ng, C.W.W.; Coo, J.L. Hydraulic conductivity of clay mixed with nanomaterials. *Can. Geotech. J.* **2015**, *52*, 808–811. [CrossRef]
23. Fakhri, Z.; Pourhoseini, R.; Ebadi, T. Improvement in the Hydraulic Properties of Kaolinite with Adding Nanoclay. *AJSR Civ. Enviromental Eng.* **2015**, *47*, 17–20. [CrossRef]
24. Reginatto, C.; Cecchin, I.; Carvalho, R.L.R.; Heineck, K.; Thomé, A.; Reddy, K.R. Influence of Iron Nanoparticle Concentration on the Hydraulic Conductivity of a Residual Clayey Soil. In Proceedings of the Geo-Chicago 2016, Chicago, IL, USA, 14–18 August 2016; pp. 458–466.
25. Taha, M.R.; Alsharef, J.M.A. Performance of soil stabilized with carbon nanomaterials. *Chem. Eng. Trans.* **2018**, *63*, 757–762. [CrossRef]
26. Ochepo, J.; Kanyi, I.M. Effect of Nano-Silica on Consolidation and Permeability Properties of Lateritic Soil. *Lautech J. Civ. Environ. Stud.* **2020**, *5*, 60–72. [CrossRef]
27. Bhadra, S.M.; Leander, T. Effect of Fly Ash and Nano Calcium Silicates in Clayey Soil used as Clay Liner. *Int. Res. J. Eng. Technol.* **2020**, *7*, 2451–2455.
28. Kurt Albayrak, Z.N. *Investigation of Some Geotechnical Properties of Nanoclay-Composites Developed in the Laboratory*; Ataturk University: Erzurum, Turkey, 2014.
29. ASTM. *Annual Book of ASTM Standards, Soil and Rock, Building Stone*; American Society for Testing and Materials: Philadelphia, PA, USA, 1982; Volume 04.08, part 19.
30. Daniel, D.E.; Anderson, D.C.; Boynton, S. *ASTM Special Technical Publication 874*; American Society for Testing and Materials: Philadelphia, PA, USA, 1985.
31. APHA. *Standard Methods for the Examination of Water and Waste Water American Public Health Association*, 22nd ed.; Rice, E.W., Baird, A.B., Eaton, A.D., Clesceri, L.S., Eds.; American Public Health Association: Washington, DC, USA, 2012; ISBN 9780875530130.
32. Özçoban, M.Ş.; Acarer, S.; Tüfekci, N. Effect of solid waste landfill leachate contaminants on hydraulic conductivity of landfill liners. *Water Sci. Technol.* **2022**, *85*, 1581–1599. [CrossRef]
33. Messaouda, D.; Hassiba, M. Waterproofing a Heterogeneous Soil (Sand-Bentonite) with Water and Leachate. In *Advances in Geosynthetics Engineering*; Springer International Publishing: Berlin/Heidelberg, Germany, 2018; Volume 1, ISBN 9783030019440.
34. Bouazza, A. Geosynthetic clay liners. *Geotext. Geomembr.* **2002**, *20*, 3–17. [CrossRef]
35. Ajitha, A.R.; Chandrakaran, S.; Sheela Evangeline, Y. Impact of Lead on the Geotechnical Properties and Adsorption Characteristics of Landfill Liner. *Int. J. Appl. Eng. Res.* **2019**, *14*, 3104–3110.
36. Bahmani, S.H.; Huat, B.B.K.; Asadi, A.; Farzadnia, N. Stabilization of residual soil using SiO2 nanoparticles and cement. *Constr. Build. Mater.* **2014**, *64*, 350–359. [CrossRef]
37. Taha, O.M.E.; Taha, M.R. Soil-water characteristic curves and hydraulic conductivity of nanomaterial-soil-bentonite mixtures. *Arab. J. Geosci.* **2016**, *9*, 1–14. [CrossRef]
38. Manyangadze, M.; Chikuruwo, N.H.M.; Narsaiah, T.B.; Chakra, C.S.; Radhakumari, M.; Danha, G. Enhancing adsorption capacity of nano-adsorbents via surface modification: A review. *South Afr. J. Chem. Eng.* **2020**, *31*, 25–32. [CrossRef]
39. Yang, J.; Hou, B.; Wang, J.; Tian, B.; Bi, J.; Wang, N.; Li, X.; Huang, X. Nanomaterials for the removal of heavy metals from wastewater. *Nanomaterials* **2019**, *9*, 424. [CrossRef] [PubMed]
40. Tang, J.; He, J.; Liu, T.; Xin, X. Removal of heavy metals with sequential sludge washing techniques using saponin: Optimization conditions, kinetics, removal effectiveness, binding intensity, mobility and mechanism. *RSC Adv.* **2017**, *7*, 33385–33401. [CrossRef]
41. Hu, S.; Zhou, Y.; Zhou, L.; Huang, Y.; Zeng, Q. Study on the adsorption behavior of cadmium, copper, and lead ions on the crosslinked polyethylenimine dithiocarbamate material. *Environ. Sci. Pollut. Res.* **2020**, *27*, 2444–2454. [CrossRef] [PubMed]
42. Türkoğlu Demirkol, G.; Çelik, S.Ö.; Güneş Durak, S.; Acarer, S.; Çetin, E.; Akarçay Demir, S.; Tüfekci, N. Effects of $Fe(OH)_3$ and MnO_2 Flocs on Iron/Manganese Removal and Fouling in Aerated Submerged Membrane Systems. *Polymers* **2021**, *13*, 3201. [CrossRef] [PubMed]