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Ground Water Quality Assessment Near Municipal Landfill and Characterization of Leachate in Kaniqrzhala Area, Kurdistan Region of Iraq

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Abstract:
The present study is to characterize the groundwater and leachate in the Kaniqrzhala landfill in Erbil City. Groundwater samples were collected from six wells and a leachate sample in order to evaluate the possible effect of leachate percolation into groundwater and assess the potential contamination. Several physicochemical parameters were analyzed to evaluate the groundwater and leachate characterizations, including (turbidity, pH, EC, total dissolved solids (TDS), total hardness (TH), Ca^{2+}, Mg^{2+}, total alkalinity (TA), Cl^-, SO_4^{2-}, PO_4^{3-}, NH_3^+, NO_3^-, Na^+, K^+) and heavy metals (Cu, Zn, Fe, Pb, Cr, and Cd). In addition, the evaluation of the water quality index (WQI) and leachate pollution index (LPI) were determined. All groundwater samples were determined to be below the permitted limits set by WHO guidelines, excluding EC, TDS, PO_4^{3-}, and NO_3^-, showing moderately high concentrations and leachate sample concentrations above allowed limits. The WQI values ranged from 74.833 to 88.463, meaning that all groundwater samples were deemed "good" and fit for drinking and other uses. The LPI value is high (23.938), indicating a high contamination potential in the leachate. The results showed *Hypericum triquetrifolium Turra, Tribulus terrestris*, and *Caper spinosa* plant leaves have varying capacities to adsorb heavy metal ions from leachate.

Keywords: *Ground Water; Water Quality Index; Heavy Metals; Leachate Pollution Index; Plant*

1. Introduction

In the Kurdistan region, landfills are the most popular method of garbage disposal, requiring vast spaces and good drainage. However, many landfills, like the Kaniqrzhala landfill, lack environmental protections. Landfill operations and leachate generations are the sources of contamination for underground and surface water sources. Surface and groundwater are used for drinking water; for instance, Erbil alone uses 5000 wells for this purpose. While most drinking water in the mountain region comes from surface and spring resources, Erbil City relies on wells for 40% of its irrigation water (1). Groundwater is a crucial natural supply needed for human intake, irrigation, urbanization, industrialization, home usage, etc. It changes according to the kind of soil, the volume of water mined, and geological and geomorphological factors (2). A liquid called landfill leachate is mostly created when precipitation percolates through an open landfill. Leachates may contain significant levels of suspended particles, heavy metals, inorganic salts, phenols, and other organic contaminants (3). Landfill leachate differs based on various factors such as landfill age, pH, type of municipal waste being buried, site weather, site hydrology, soil used for capping, decomposition, biodegradability ratio, moisture content, and stage of landfill (4). Water quality is a term used to describe how suitable a body of water is for consumption. It is based on the physical and chemical characteristics of the water sample (5). In previous studies, the impact of landfill leachate on groundwater in Kaniqrzhala has not been mentioned.

The water quality index (WQI) is the most useful active tool for providing information about each water body to policymakers in order to assess the drinking water quality for end users. The impact of leachate on groundwater and other water resources has recently received a lot of attention due to its enormous environmental importance. If not properly managed, leachate migration from waste disposal sites or landfills, as well as the discharge of pollutants from sediments (under certain conditions), pose a serious threat to groundwater resources (6). However, a very comfortable tool for indexing and comparing the potential to contaminate a landfill and to characterize it would be used (7), and this would also have potential uses in other areas, such as measuring the contamination capacity of leachate in landfills of different sizes, dimensions, and natures all around the world. This tool is known as the leachate pollution index (LPI). The LPI index indicates the contamination capacity of a proposed landfill area, and the numbers will range from a scale of 5 to 100. One single digit will highlight the pollution at a given point in time, and the severity increases with the numbers in the ascendancy. The proposed and agreed standard value of the leachate pollution index is 7.378 (8). The current study aimed to assess the levels of several physicochemical properties and heavy metals in groundwater in different wells located near landfill for drinking purposes by using WQI. The study also quantified the leachate contamination potential generated from landfills by applying LPI. Furthermore, the study evaluated the removal of heavy metals in leachate with the different plants was also evaluated.

2. Methods and Materials

2.1 Description of the Studied Area

The Kurdistan region has several types of landfills, including one located in the Kaniqrzhala area, west of Erbil city. The investigation focuses on six wells near this landfill. Elevation above sea level, latitude, longitude, and distance of the sites were determined using a global positioning system (GARMIN/GPS 72), which can connect with satellites (Table 1, Figures 1 and 2). The landfill, opened in 2001 and covering an area of 50 hectares (based on data from office employees and Ministry of Municipalities).

Table 1: Elevation, latitude, longitude and distance of studied area

Sites	Abbreviation	Elevation above sea level (m)	Latitude	Longitude	Distance (m) (Landfill-well)
Landfill	LF	472	36.1152	43.5224	-
Well $_1$	W_1	466	36.1213	43.5142	1001
Well $_2$	W_2	468	36.1154	43.5129	855
Well $_3$	W_3	440	36.1137	43.5144	739
Well $_4$	W_4	476	36.1224	43.5133	1144
Well $_5$	W_5	470	36.1145	43.5146	706
Well $_6$	W_6	478	36.1155	43.5249	227

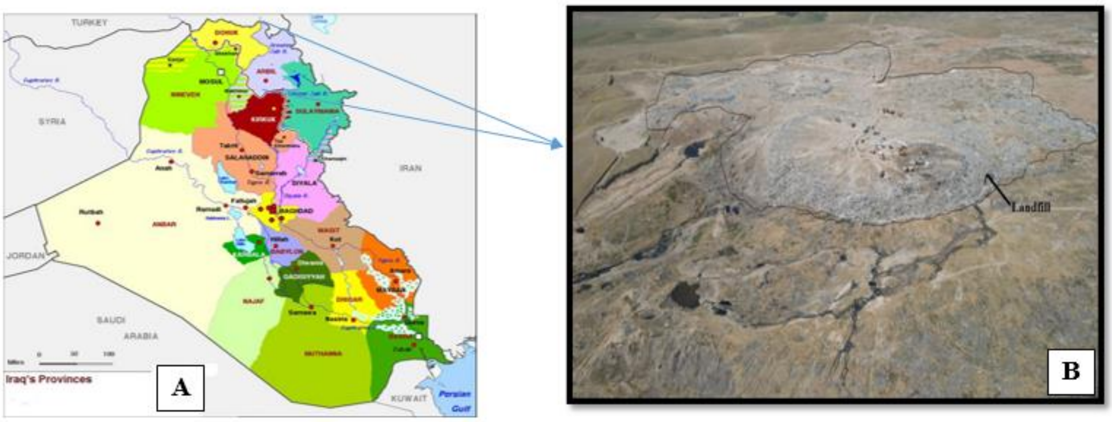

Figure1: A. Image of Iraq map B. Image of Kaniqrzhala landfill site.

Figure 2: Satellite image of studied area.

2.2 Sample Collection

- **Ground Water and Leachate Collection**

The glass bottles (1L) were used to collect groundwater samples from different wells ($well_1$, $well_2$, $well_3$, $well_4$, $well_5$ and $well_6$) in Kaniqrzhala near the landfill, with each well at a different distance from the landfill as shown from Table 1. This landfill is illegally and unhealthy. A municipal landfill leachate sample in liquid form was taken from the lower part of the landfill in the Kaniqrzhala area. In July 2021, glass bottles were deployed to collect the samples in a scientific manner and were then sent to the lab in cooler boxes. They were kept in the refrigerator until all analyses were carried out.

- **Plant Collection**

The leaves of *Hypericum triquetrifolium Turra, Tribulus terrestris L. and Caper spinosa* L. were collected in 2021 from Erbil in Iraq's Kurdistan area. The plant leaves were collected, washed properly, and allowed to dry entirely at room temperature (40-50°C) until they reached a constant weight. They were then progressively pulverized into a fine powder using grinders and kept in a specific bottle (9).

2.3 Analysis of Physicochemical Properties of the Samples

In order to examine physicochemical analysis, samples were analyzed by using standard procedures (9). The parameters considered include turbidity, pH, electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH), calcium (Ca^{2+}), magnesium (Mg^{2+}), total alkalinity (TA), chloride (Cl^{-}), sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), ammonia (NH_3^{+}), nitrate (NO_3^{-}), sodium (Na^{+}), potassium (K^{+}), copper (Cu), zinc (Zn), iron (Fe), lead (Pb), chromium (Cr), and cadmium (Cd). A turbidity meter was deployed in order to ascertain the turbidity (Palintest Micro 950); TDS, EC, and pH were determined on-site using a digital portable multi-parameter meter (Hanna HI 98130); titrimetric methods were deployed while measuring the important parameters such as TH, Ca^{2+}, Mg^{2+} and TA. Ammonia (NH_3^{+}), nitrate (NO_3^{-}), phosphate (PO_4^{3-}), and Sulfate (SO_4^{2-}) were measured using the UV-VIS spectrophotometer method (Jenway -6305), while the cations like (Na^{+}) and (K^{+}) were assessed using the flame photometer (Sherwood-410), heavy metals were measured using an atomic absorption spectrophotometer.

2.4 Water Quality Index (WOI) Calculation

The suitability of the water for drinking is determined by the water quality index (WQI), a mathematical parameter. (10, 11). It illustrates the combined effect of numerous water quality metrics on the total water quality. Out of total twenty-one important studied parameters, turbidity, pH, EC, TDS, TH, Ca^{2+}, Mg^{2+}, TA, Cl^{-}, SO_4^{2-}, PO_4^{3-}, NH_3^{+}, NO_3^{-}, Na^{+}, K^{+}, Cu, Zn, Fe, Pb, Cr, and Cd, were selected for water quality index (WQI) calculation in Table 2. WQI was calculated using the World Health Organization's drinking water quality standards (12). WQI is calculated in a detailed way by means of three steps, *wi*, which is the weight assigned to each of the 21 parameters based on their importance in determining the quality of the water for drinking purposes. The scores can from a minimum 1 to a maximum 5. The highest weight was given to nitrate parameter NO_3^{-} , Pb, and Cd due to the importance of their role in water quality compared to others, while a lesser weight was assigned to total alkalinity (13). In the second step, the following equation was used to compute the relative weight (*Rw*):

(1) $$Rw = wi / \sum_{i=1}^{n} wi$$

Rw stands for relative weight, *wi* for parameter weight, and n for the total number of parameters. Table 2 includes the determined relative weight (*Rw*) values for each parameter as well as the assigned weight (*wi*). In the third phase, a quality rating scale (*Qi*) was applied to all parameters except pH by dividing its concentration in each water sample by its corresponding reference and multiplying the result by 100:

(2) $$Qi = \left(\frac{Ci}{Si}\right) \times 100$$

(3) $$QpH = \left(\frac{Ci - Vi}{Si - Vi}\right) \times 100$$

where *Qi* represents the water sample's quality rating and *ci* represents each chemical parameter's concentration in mg/L, in accordance with the WHO standard for that parameter, and *vi* is the optimal pH value of 7.0. Equations 2 and 3 make sure that *Qi* is always equal to zero when a pollutant is absolutely absent from the water sample and always equal to 100 when the value of this parameter is just beyond the permissible range. The more contaminated the environment is, the higher the value of *Qi* (14). Each chemical parameter's *Si* value is first determined, and then it is applied to calculate the WQI as follows:

(4) $$SIi = Wi \times Qi$$

(5) $$WQI = \sum_{i=1}^{n} SIi$$

The estimated WQI values were then divided into five groups, as shown in Table 3, to assess the current state of the water quality.

Table 2: The assigned and relative weights of each parameter used to calculate WQI in accordance with WHO drinking water standards

Parameters	Unit Weight	WHO standard	Assign Weight (*wi*)	Relative Weight (*Rw*) (*Rw*) = *wi*/∑*wi*
Turbidity	NTU	5	3	0.046875
pH	-	6.5-8.5	4	0.0625
EC	(µs/cm)	1000	3	0.046875
TDS	(mg/L)	500	3	0.046875
Total hardness	(mg/L) as$CaCO_3$	200	2	0.03125
Calcium (Ca^{2+})	(mg/L)	100	2	0.03125
Magnesium (Mg^{2+})	(mg/L)	30	2	0.03125
Total alkalinity	(mg/L) as$CaCO_3$	200	1	0.015625
Chloride (Cl^-)	(mg/L)	250	2	0.03125
Sulfate (SO_4^{2-})	(mg/L)	250	4	0.0625
Phosphate (PO_4^{3-})	(mg/L)	0.25	3	0.046875
Ammonia (NH_3^+)	(mg/L)	3	3	0.046875
Nitrate (NO_3^-)	(mg/L)	50	5	0.078125
Sodium (Na^+)	(mg/L)	200	3	0.046875
Potassium (K^+)	(mg/L)	10	3	0.046875
Copper (Cu)	(mg/L)	2	2	0.03125
Zink (Zn)	(mg/L)	5	2	0.03125
Iron (Fe)	(mg/L)	0.3	3	0.046875
Lead (Pb)	(mg/L)	0.01	5	0.078125
Chromium(Cr)	(mg/L)	0.05	4	0.0625
Cadmium (Cd)	(mg/L)	0.003	5	0.078125
Total			$\sum_{i=1}^{n} wi = 64$	$\sum Rw = 1$

Note: Assign weight, and water quality standards (46)

Table 3: Classification of Drinking Water Quality based on WQI Value

Water Quality Index Level	Water Quality Status
<50	Excellent
50-100	Good
100-200	Poor
200-300	Very Poor
>300	Unsuitable

2.5 Leachate Pollution Index (LPI) Calculation

A number that ranges from number 5 to 100 is the LPI, which provides an indication of the landfill's potential for leachate contamination, which could be hazardous in the future. This index is based on several parameters connected to many parameters at a particular time. According to this index, a greater value implies bad environmental conditions (8). According to (7), the LPI requires eighteen chemical leachate pollutant parameters to be determined. The following equation can be used to compute the LPI.

(6) $$LPI = \sum_{i=1}^{n} wi\, pi$$

Where *LPI* is the weighted additive leachate pollution index, *wi* is the weight assigned to the *ith* pollutant variable, and *pi* is the sub-index value of the *ith* leachate pollutant variable taken from the curve and calculated using professional assessments, and *n* is the total number of leachate pollutant variables considered in the LPI computation. $\sum_{i=1}^{n} wi = 1$. When all of the pollutant variable values required for calculation were not available, the LPI was estimated using the measured concentrations of available leachate pollutants. Thus, the following equation may be employed for calculating LPI:

(7) $$LPI = \frac{\sum_{i=1}^{m} wi\, pi}{\sum_{i=1}^{m} wi}$$

Where *LPI* stands for the weighted additive leachate pollution index, *wi* for the *ith* pollutant variable, *pi* for the *ith* leachate pollutant variable's sub-index score, and *m* for the number of leachate pollutant variables for which data are available to calculate *LPI*. In the present study, (m < 18 and $\sum_{i=1}^{m} < 1$). Since not all of the 18 pollutant parameters provided by (7) were used, the LPI values for Kaniqrzhala leachate were thus determined using Equation (2).

2.6 Heavy Metals Removal From Leachate With Different Plants

Preliminary experiments were carried out to identify the optimal conditions for effectively removing the metal ions under study. In the experiment, 10 mL of leachate solution were combined with 1.0g of each *Hypericum triquetrifolium Turra, Tribulus terrestris* L. *and Caper spinosa* L. leaves powder. For 24 hours, the combinations were continually shaken in a water bath shaker at room temperature (30°C). The final step involved filtering the samples using Whatman 0.45µm filter paper, removing the adsorbent from the mixture, and using an atomic absorption spectrophotometer to measure the remaining metal ion levels in the solution(15).

(8) $$\text{Removal efficiency (\%)} = [(C_0 - C_e)/C_0] * 100$$

Whereas, C_0 represents the initial heavy metal ion concentration (mg/L), C_e displays the equilibrium concentration (mg/L).

2.7 Statistical Analysis

The analytical data of physicochemical parameters and heavy metals in ground water samples was subjected to descriptive statistical analysis using standardized statistical techniques and the SPSS (version 26) program (16).

3. Results and Discussion

3.1 Physicochemical Characteristics Of Groundwater Samples

The physicochemical characteristics of groundwater in the wells are presented in Tables 4 and Table 5. The World Health Organization's Drinking Water Quality Guidelines were used as reference values for analyzing the water quality of well water samples (12). Groundwater in the research area was used for drinking, household use, and other purposes in the research area. Table 4 provides the World Health Organization's recommended desirable and maximum permissible levels (12).

Turbidity measures the clarity or cloudiness of water and represents the suspended solids. The turbidity values of groundwater samples range from 0.38 NTU in W_4 to 3.25 NTU in W_3, with a mean value of 1.17 NTU shown in Tables 4 and Table 5. According to WHO standards, none of the groundwater samples exceed this limit, indicating that the water remains unaffected by landfill seepage and is safe to drink. The pH value of all groundwater samples was neutral, ranging from 7.46 in W_5 to 7.73 in W_6. The mean pH of the groundwater samples was found to be 7.59. The results show that all groundwater samples were found to be within limits (6.5-8.5) set by WHO standards (12). Electrical conductivity (EC) is the ability of a substance to conduct electricity. It is a valuable measure of the amount of material dissolved in water. In the study region, EC values ranged from 936.5 in W_2 to 1260 in W_1 µS/cm. The mean EC value was 1088 µS/cm. Excluding W_2, all of the groundwater samples exceeded the permitted level of 1000 µS/cm for drinking purposes, as shown in Table 4 and 5 based on the EC findings. Total dissolved solids (TDS) relate to the numerous minerals found in water and have an impact on its taste. In the study area, TDS levels range from 456.50 mg/L in W_2 to 572.00 mg/L in W_6, with a mean value of 527.33 mg/L. These levels were found to be higher than the WHO standard of 500 mg/L. The high value of TDS may be attributed to the close proximity and shallowness of the wells to the landfill, as well as the leaking of several contaminants from the Kaniqrzhala dump into the groundwater (17). Therefore, EC and TDS are widely used as quick indicators of water quality (18). Total hardness (TH) refers to the reaction with soap and scale formation that raises the boiling point of water. It is often expressed as the sum of the Ca^{2+} and Mg^{2+} concentrations in mg/L equivalent $CaCO_3$. In the study area, TH levels ranged from 126.00 mg/L in W_4 to 202.00 mg/L in W_3, with an average of 158.33 mg/L. The desired limit for TH, according to (12), is 200 mg/l. When compared to this limit, the values from the well water samples were determined to be within the acceptable range, indicating soft water that is appropriate for drinking and cleaning, exception of W_3, which shows a slightly higher value (202.00 mg/L), indicating slightly hard water. TH levels above 200 mg/L are not connected with severe health effects in humans, but they do indicate the leaching of Ca^{2+} and Mg^{2+} ions into groundwater (19). On the other hand, the source, geology, and soil formation of the catchment region, as well as different human actions and climatic conditions, may be responsible for the variance in TH (20). Ca^{2+} levels in all well water samples ranged from 26.45 to 35.27 mg/L in W_4 and W_3, respectively, whereas Mg^{2+} levels ranged from 13.60 to 27.70 mg/L in W_1 and W_3, with mean values of 31.66 and 19.27 mg/L, respectively. These results fell below the WHO standards of 100 mg/L for Ca^{2+} and 30 mg/L for Mg^{2+}. The Low Ca^{2+} and Mg^{2+} levels may be due to their low composition in the rocks of the study region. In the study, the concentration of Ca^{2+} dominates over the level of Mg^{2+} in general, which may be related to Erbil's predominantly limestone-based geological formation (21). Consequently, this implies that the groundwater samples are still secure and have not been polluted by landfill runoff. Total alkalinity (TA), a property of water, governs the buffering properties of the liquid. The presence of bicarbonate in the main contributor to TA as $CaCO_3$ in groundwater samples. TA levels range from 85.00 mg/L in W_6 to 119.00 mg/L in W_2. The TA of the groundwater samples was in compliance with the WHO threshold of 200 mg/L, with a mean value of 104.00 mg/L. This indicates that groundwater samples are still unaffected by landfill leachate and are safe.

The Cl^-content in the present study ranged from 7.40 mg/L in W_3, W_5 to 13.90 mg/L in W_6, with a mean value of 10.35 mg/L; these results reveal that no well water sample exceeded the 250 mg/L threshold set by the WHO in 2017 as the permissible limit (12). So, the water sources were of good quality with respect to chloride content and remain unaffected by landfill pollutants. One of the least dangerous anions in water is sulfate (SO_4^{2-}), but excessive amounts of it can give water an unpleasant taste. Out of W_3 and W_6, which reveal high concentrations of SO_4^{2-} were 268.64 and 291.72 mg/L respectively, the SO_4^{2-} concentrations in other groundwater samples ranged from 175.88 to 291.72 mg/L, with a mean value of 225.28 mg/L. All of these concentrations were found to be below the WHO-recommended drinking water acceptance threshold value of 250 mg/L. Agricultural fertilizers and industrial activities, and landfill leachate are the principal sources of SO_4^{2-} in groundwater (22). In the current study, increasing SO_4^{2-} levels in well waters revealed the impact of landfill leachate on groundwater in addition to surface runoff during rainy periods, which is a sign of leachate infiltration into the subsoil (23). Sources of Phosphate (PO_4^{3-}) may include various anthropogenic activities such as washing and laundering effluents, fertilizers, septic tank leaks, discharges of wastewater, waste from people and animals, industrial wastes, soil erosion, and decomposition activities (24). As indicated in Tables4 and 5, the findings of the current study showed that the level of PO_4^{-3} changed from 1.77 mg/L in W_1 to 2.35 mg/L in W_6, with a mean value of 2.14 mg/L. The suggested phosphate drinking water quality limits (0.25 mg/L) went exceeded in all groundwater samples. PO_4^{-3} is clearly attenuated in the groundwater downgrading of the landfill. This indicates a high level of detergent pollutants from landfills (25). Groundwater with a minute concentration of (PO_4^{-3}) as low as 0.01 mg/L may become slimy and promotes the growth of algae (26). Ammonia (NH_3^+) is a sign of elevated organic compound pollution. Ammonia values ranged from 0.48 in W_1 to 1.49 in W_3 mg/L, with a mean value of 1.05 mg/L. The present study revealed that all well water samples had NH_3^+ levels below the 3.00 mg/L permissible standard for drinking water. The presence of NH_3^+ in water indicates ammonification. The lack of effect of leachate pollutants from the landfill site on NH_3^+ levels in groundwater assessments could be due to the leachate's low organic pollutant concentration. The permissible limit for nitrate (NO_3^-) is 50 mg/L, according to (12) guidelines. The mean value of the water samples, which ranged from 42.31 mg/L in W_1 to 52.41 mg/L in W_4, was 47.95 mg/L. According to the findings, all the samples were within the acceptable range, with the exception of W_3 and W_4, which showed slightly high NO_3^- levels of 51.93 and 52.41 mg/L, respectively. These results could be due to waste disposal leakage, excessive inorganic nitrate fertilizer use, sanitary landfills, fertilizer, or inadequate manure management techniques (27). Accordingly, elevated NO_3^- concentrations are an indication of leachate percolation into the groundwater. The cations sodium (Na^+) and potassium (K^+) are vital metals because they are nutritionally important to life, supporting a variety of metabolic activities in the human body. The Na^+ concentration ranges from 20.69 to 33.56 mg/L in W_5 and W_1 respectively, with a mean value of 26.69 mg/L, while K^+ concentration ranges from 0.72 to 0.91 mg/L with a mean value of 0.81 mg/L. These minerals, Na^+ and K^+, which are among the minerals that characterize plain sands, most likely developed as a result of the chemical degradation of feldspars and micas. Na^+ and K^+ are two cations that interact with the components of aquifers and undergo cation exchange often (28). Compared to the WHO limits of 200 mg/L for Na^+ and 10 mg/L for K^+, all of the groundwater samples in the current investigation had very low levels of Na^+ and K^+, indicating that neither Na^+ nor K^+ were affected by landfill leachate. Hence, they remain safe for drinking purposes.

Table 4: Physicochemical characteristics of groundwater in different wells

Parameters/Sites	Units	W_1	W_2	W_3	W_4	W_5	W_6	WHO
Turbidity	NTU	1.39	0.88	3.25	0.38	0.58	0.56	5
pH	-	7.67	7.595	7.62	7.48	7.46	7.73	6.5-8.5
EC	(µs/cm)	1260	936.5	1050	1052.5	1066	1163	1000
TDS	(mg/L)	529.5	456.5	542.5	525.5	538	572	500
Total hardness	(mg/L) as$CaCO_3$	128	158	202	126	182	154	200
Calcium (Ca^{2+})	(mg/L)	28.85	33.66	35.27	26.45	34.46	31.26	100
Magnesium (Mg^{2+})	(mg/L)	13.6	17.98	27.7	14.58	23.32	18.46	30
Total alkalinity	(mg/L) as$CaCO_3$	91	119	111	109	109	85	200
Chloride (Cl^-)	(mg/L)	13.3	7.8	7.4	12.3	7.4	13.9	250
Sulfate (SO_4^{2-})	(mg/L)	216.31	175.88	268.64	192.86	206.31	291.72	250
Phosphate (PO_4^{3-})	(mg/L)	1.77	2.3	2.02	2.12	2.3	2.35	0.25
Ammonia (NH_3^+)	(mg/L)	0.48	0.84	1.49	0.94	1.39	1.13	3
Nitrate (NO_3^-)	(mg/L)	42.31	49.75	51.93	52.41	48.83	42.48	50
Sodium (Na^+)	(mg/L)	33.56	24.29	24.81	28.41	20.69	28.41	200

Potassium (K^+)	(mg/L)	0.82	0.72	0.82	0.82	0.82	0.91	10

Table 5: Descriptive Statistics for physicochemical characteristics of groundwater in different wells.

Parameter	Minimum	Maximum	Mean	Standard Error	Standard Deviation	Variance	Range
Turbidity	0.38	3.25	1.17	0.439	1.075	1.157	2.87
pH	7.46	7.73	7.59	0.044	0.107	0.011	0.28
EC	936.5	1260	1088	45.221	110.770	12269.9	323.5
TDS	456.5	572	527.33	15.668	38.378	1472.867	115.5
Total hardness	126	202	158.33	12.181	29.837	890.267	76
Calcium (Ca^{2+})	26.45	35.27	31.66	1.415	3.466	12.016	8.82
Magnesium (Mg^{2+})	13.61	27.7	19.27	2.190	5.365	28.784	14.09
Total alkalinity	85	119	104	5.335	13.069	170.8	34
Chloride (Cl^-)	7.4	13.9	10.35	1.278	3.131	9.803	6.5
Sulfate (SO_4^{2-})	175.89	291.72	225.28	18.462	45.223	2045.107	115.84
Phosphate (PO_4^{3-})	1.78	2.35	2.14	0.090	0.220	0.048	0.58
Ammonia (NH_3^+)	0.49	1.5	1.05	0.152	0.373	0.139	1.01
Nitrate (NO_3^-)	42.32	52.42	47.95	1.839	4.505	20.295	10.1
Sodium (Na^+)	20.69	33.56	26.69	1.811	4.436	19.682	12.87
Potassium (K^+)	0.72	0.91	0.81	0.025	0.060	0.004	0.19

3.2 Physicochemical Characteristics of Leachate Sample

Table 6 summarizes the results of the physicochemical analysis of the leachate. For assessing characteristics of the leachate, we adopted the reference values of the World Health Organization Guidelines (12). The mean turbidity value is 50.2 NTU; which was above the limit threshold because of landfill age and leachate stabilization (29). The pH of landfills varied depending on their age. with stabilized leachate generally having a higher pH than young leachate (30). In the present study, the average pH value was 7.85, falling within the neutral pH range (31). This result may be due to the mature methanogenic state of the Kaniqrzhala landfill, the biological composition of wastes, or rainfall (22). The EC value was above the limit at 45300 µS/cm. High concentrations of anions and cations, such as compounds of Na^+, K^+, Cl^-, NO_3^-, SO_4^{2-}, and NH_3^+, are responsible for the extremely elevated EC value (23). The TDS value was high at 22700 mg/L. The TH of the leachate samples was over the limit, averaging 1800 mg/L. High hardness is caused by calcium and magnesium carbonate and bicarbonate (32). The mean Ca^+ and Mg^+ values were 480.96 mg/L and 145.8 mg/L, respectively. These values were higher than the WHO thresholds. These cations are formed in waste via mass transfer processes, and their concentration in leachate is influenced by the waste mass's composition and the landfill's present level of stabilization (33). The Total alkalinity was 9600 mg/L, exceeding the WHO guideline. The leachate sample's alkalinity was mostly caused by the presence of HCO_3^- ions since it had a mean pH of 7.855, which aided in buffering the leachate system and the processes of liquefaction and decomposition (22). The mean Cl^- level in the leachate sample was 1110.00 mg/L, which was greater than the permissible limit of 250 mg/L. The researcher (34) believe that chlorides are conservative pollutants since they are unaffected by biochemical processes, naturally occurring decontamination processes inside the landfill, or leakage into the Kaniqrzhala area (35). The mean SO_4^{2-} contents were determined to be 1241.415 mg/L, exceeding the recommended range of 250 mg/L. Leachate's sulfate content is primarily determined by its degradation of organic waste compounds (29). The phosphate concentration was higher at 397.50 mg/L. The high PO_4^{3-} levels in the leachate sample are attributable to the waste's organic load, which contains phosphorus. As this organic material mostly phospholipids and phosphoproteins, decomposes, it releases phosphorus, increasing the phosphate concentrations (22, 34). PO_4^{3-} in leachate is hazardous because it encourages eutrophication in water, which leads to the growth of algae (35). The NH_3^+ levels reveal a high mean value of 221.00 mg/L. High NH_3^+ levels indicate the dominance of anaerobic and reduction conditions in the landfill's leachate, which could accelerate the conversion of nitrate to ammonia gas phase, a long-term pollutant (33, 35). The mean NO_3^- content in the leachate sample was 3691.057 mg/L, which was higher than WHO limits. The presence of NO_3^- is caused by the nitrification process, which oxidizes ammonium to nitrite and then to nitrate (12). Na^+ and K^+ mean concentrations in the leachate sample were 45.92 mg/L and 11.783 mg/L, respectively. Na^+ value in leachate was within the threshold limit, however, the K^+ content in the leachate sample revealed higher concentrations, indicating that microbial activity at the waste site did not immediately impact them (25, 32).

Table 6: Physicochemical Characteristics of Leachate

Parameters	Units	Leachate	WHO
Turbidity	NTU	50.2	5
pH	-	7.855	6.5-8.5
EC	(µs/cm)	45300	1000
TDS	(mg/L)	22700	500
Total hardness	(mg/L) as$CaCO_3$	1800	200
Calcium (Ca^{2+})	(mg/L)	480.96	100
Magnesium (Mg^{2+})	(mg/L)	145.8	30
Total alkalinity	(mg/L) as$CaCO_3$	9600	200
Chloride (Cl^-)	(mg/L)	1110	250
Sulfate (SO_4^{2-})	(mg/L)	1241.415	250
Phosphate (PO_4^{3-})	(mg/L)	397.5	0.25
Ammonia (NH_3^+)	(mg/L)	221	3
Nitrate (NO_3^-)	(mg/L)	3691.057	50
Sodium (Na^+)	(mg/L)	45.92	200
Potassium (K^+)	(mg/L)	11.783	10

3.3 Heavy Metal Concentration In Groundwater And Leachate

Samples of groundwater taken from wells and leachate were analyzed to assess the presence of heavy metals such as Cu, Zn, Fe, Pb, Cr, and Cd. The descriptive statistics and analytical results of heavy metals are shown in Tables 7 and 8. Except for Zn and Cu metals, most of the heavy metals examined were little or no detectable (Table 7). The levels of copper range from 0 to 1.25 mg/L, with a mean of 0.49 mg/L, whereas the levels of zinc range from 0 to 0.025 mg/L, with a mean of 0.0158 mg/L. According to WHO guidelines, heavy metals in leachate samples from the Kaniqrzhala landfill were found at a higher level. According to Table 7, the heavy metal sequence in the leachate sample determined in this study is as follows: Zn>Fe>Cu>Pb>Cr>Cd.

Cu concentrations were found to be high with a mean value of 3.00 mg/L. Cu in leachate could be generated by the corrosion of copper-containing components in the environment, copper-based electrical wire and communication equipment, and nearby electromagnetic waste (36). High Zn concentrations were present with a mean value of 4.00 mg/L. Zn in leachate indicates the presence of battery and fluorescent light wastes, and the primary sources of Zn are agrochemicals such as fertilizers and pesticides (35). The presence of Fe and steel-based scrap was found to have a mean value of 3.80 mg/L for total Fe (37). The Leachate sample revealed a high mean value of Pb of 2.30 mg/L. A high Pb level indicates that the wastes were mostly of municipal sources and included metallic objects, paint products, leftover batteries, etc. (23). The leachate of landfill showed an elevated mean value of total Cr of 1.00 mg/L. The sources of Cr in the leachate samples may involve Pb-Cr batteries, colored polythene bags, wasted plastic items, and empty paint containers (33). The mean Cd content was 0.20 mg/L, which was higher than the 0.003 mg/L WHO standard. Cd is discharged into the environment through welding and electroplating, as well as pesticides, fertilizer, and Cd-Ni batteries (37, 38).

Table 7: Heavy metals concentration (mg/L) in groundwater and leachate

Parameter/Sites	W_1	W_2	W_3	W_4	W_5	W_6	Leachate	WHO
Copper (Cu)	1.25	ND	0.27	ND	0.82	0.6	3	2
Zink (Zn)	0.015	0.025	0.015	0.02	0.02	ND	4	3
Iron (Fe)	ND	ND	ND	ND	ND	ND	3.8	0.3
Lead (Pb)	ND	ND	ND	ND	ND	ND	2.3	0.01
Chromium (Cr)	ND	ND	ND	ND	ND	ND	1	0.05
Cadmium (Cd)	ND	ND	ND	ND	ND	ND	0.2	0.003

ND: Not Detected

Table 8: Descriptive Statistics for heavy metals characteristics of groundwater

Parameters	Minimum	Maximum	Mean	Standard Error	Standard deviation	Variance	Range
Copper (Cu)	0.00	1.25	0.49	0.490	0.495	0.245	1.25
Zink (Zn)	0.00	0.03	0.0158	0.016	0.009	0.00	0.03
Iron (Fe)	0.00	0.00	0.00	0.000	0.000	0.00	0.00
Lead (Pb)	0.00	0.00	0.00	0.000	0.000	0.00	0.00
Chromium (Cr)	0.00	0.00	0.00	0.000	0.000	0.00	0.00
Cadmium (Cd)	0.00	0.00	0.00	0.000	0.000	0.00	0.00

3.4 Water Quality Index (WQI)

WQI was utilized to combine several parameters and dimensions into a single score, providing a picture of the water quality at the Kaniqrzhala site. The WOI findings of the groundwater samples in this investigation ranged from 74.833 to 88.463. Table 9 shows the WQI of all well water samples. Accordingly, the overall results revealed that all water samples were classified as a “Good” category and without any significant variation in the groundwater quality from the landfill effects, and they still remain suitable for drinking consumption.

Table 9: Water quality index (WQI) of various wells

Sites	WQI	Water Type
W_1	74.833	Good water
W_2	80.883	Good water
W_3	85.338	Good water
W_4	76.832	Good water

W_5	83.880	Good water
W_6	88.463	Good water

3.5 Characteristics of Leachate

- **Leachate pollution index (LPI)**

LPI is a helpful tool for standardizing and comparing the data obtained, as well as evaluating the contamination risk connected to landfill leachate on a scale (39). The greatest numbers demonstrate worse environmental circumstances (8). The characteristics of the selected leachate and the LPI value of the Kaniqrzhala leachate are shown in Table 10. Based on the available data, the LPI was determined. Nine out of the 21 variables were used for the LPI analysis (29). Therefore, Equation (2) above was used to calculate LPI. According to (7), the leachate disposal standards had a value of 7.378. This means that any LPI value less than the required threshold (7.378) is acceptable, while any value greater than the standard is not acceptable and indicates polluted leachate. In the present study, higher LPI levels were observed as 23.938, which is above the LPI value of the leachate standards published by (8), but quite low in comparison to the 5-100 LPI scale. The higher the LPI value, the less stable the landfill leachate. However, it should be noted that the LPI value is influenced by a variety of factors, including the type of waste, the age of the landfill, the temperature, humidity, and the amount of rainfall (40). A higher LPI value at the Kaniqrzhala landfill could be attributed to the inflow of extra rainfall into the waste during the rainy season, resulting in more soluble elements enter the leachate. This is in agreement with the findings of previous research (25). Furthermore, landfill's age and the period of operating, as in the case of the Kaniqrzhala landfill, which has been in operation for 22 years according to (3), could affect the composition of leachate and thus the LPI value (39), as confirmed by the analyses conducted. The predicted LPI values, however, were impacted by several of factors, including the low concentration of heavy metals in the leachate, which is associated with the age of the landfills. The proportion of heavy metals in leachates reduces over time due to the acidic-to-basic reaction induced by organic acid consumption by methane bacteria and the formation of insoluble metal forms (41). In the current study, higher contaminant levels of TDS, ammonia, chloride, and heavy metals were detected, which contributed to higher LPI values. Comparable to the report of researchers (42), who reported LPIs of 13.7 and 16.7 for two aged municipal solid waste dumpsites in Pakistan, another study (7) reported LPI was 15.97 for a landfill in China. The LPI value of the current study was 23.938, which implied that the leachate of this landfill has the potential to contaminate and subsequently pollute the environment when released. This poses an enormous threat to public health and the environment; thus, there is an urgent need for Erbil City to take remedial action in the interests of people, particularly those who come into everyday contact with it.

Table 10: Characteristics and LPI calculation of leachate from Kaniqrzhala landfill.

Serial	Leachate	Observed	Sub-Index	Pollutant	Overall pollutant

Number	characteristics	value (ci)	value (Pi)	weight (wi)	rating ($pi\ wi$)
1	pH	7.855	5	0.055	0.275
2	TDS	22700	18	0.05	0.9
3	Ammonia (NH_3^+)	221	23	0.051	0.969
4	Chloride (Cl^-)	1110	9	0.049	0.441
5	*Nitrate (NO_3)	3691	*100	0.053	5.3
6	Copper (Cu)	3	19	0.05	0.95
7	Zinc (Zn)	4	6	0.056	0.336
8	Iron (Fe)	3.8	5	0.045	0.225
9	Lead (Pb)	2.3	19	0.063	1.197
10	Chromium (Cr)	1	6	0.064	0.384
Total	$\frac{\sum_{i=1}^{m} wi\ pi}{\sum_{i=1}^{m} wi}$			$\sum_{i=1}^{m} = 0.536$	$\sum_{i=1}^{m} wipi = 12.831$
LPI			LPI= 23.938 > 7.378		

Note: All values are in mg/L except pH, pollutant weight (wi), and sub-index value (pi) which are from the study of (7), excluding * nitrate (NO_3^-) from (43).

- **Removal of heavy metals from leachate with different plants**

Table 11 shows the level of metal ions removed from leachate, which demonstrates a direct correlation with the types of plants. *Tribulus terrestris* L plant had a high percentage removal of Cu (73%), whereas *Caper spinosa* L had 83% removal rates for Fe and both plants had 100% removal rates for Pb. However, *Hypericum triquetrifolium Turra, Tribulus terrestris* L and *Caper spinosa* L had 100% removal rates for Cr and Cd. The heavy metal ions Cu, Fe, Pb, Cr, and Cd were removed from the leachate sample in this study using a variety of plants. Plant biomass is cheaper and more readily available in huge numbers, and it has a remarkable capacity to absorb heavy metals. The results showed that Cu, Fe, Pb, Cr, and Cd were strongly adsorbed on plant leaves, suggesting that this could be a less expensive alternative to expensive adsorbents for the removal of the examined metal ions from leachate. In general, the findings revealed that different plant leaves have varying capacities to adsorb heavy metal ions. This variability is influenced by several factors, including changes in pH, competitive adsorption (15, 44), and the chemical structure of the plant leaves (45).

Table 11: Removal efficiency of heavy metals with different plants

Plants	Removal efficiency (%)				
	Cu	Fe	Pb	Cr	Cd
Hypericum triquetrifolium	60	50	0	100	100
Tribulus terrestris	73	68	100	100	100
Caper spinosa	10	83	100	100	100

4. Conclusion

The present study was conducted to assess the impact of the Kaniqrzhala landfill in Erbil City on the surrounding environment. From this investigation, it can be concluded that:

- The physicochemical characteristics and heavy metal concentrations in groundwater samples collected near the Kaniqrzhala landfill were found to be lower than the allowable levels recommended by WHO standards, with the exception of EC, TDS, PO_4^{3-}, TH, and NO_3^-, which showed moderately high concentrations. This indicates that the leachate had no effect on groundwater in numerous wells located far from the landfill site.
- Leachate characteristics from the landfill site have higher levels of contamination potential with respect to analyzed physicochemical and heavy metal parameters.

- The overall computed WQI values of groundwater samples ranged from 74.833 to 88.463, and classified as "good" quality, suitable for drinking and other domestic purposes.
- The calculated LPI value of the Kaniqrzhala landfill leachate revealed a high LPI of 23.938, which was above the leachate disposal standard 7.378. A high LPI value indicated that the leachate was highly polluted and the waste deposited had been stabilized. Therefore, adequate treatment should be guaranteed before disposing of the leachate, and leachate pollution in the Kaniqrzhala landfill must be limited.
- The results revealed that different plant leaves have varying capacities to adsorb heavy metals from the leachate of the landfill, suggesting a potential for biological treatment of the leachate.

5. Author's Contribution:

We certify that each author listed has read and approved the document. Furthermore, we vouch for the fact that each author made the same contribution to the paper. Additionally, we can attest that each author has accepted the manuscript's order of authors.

6. Conflicts of Interest:

There is no conflict of interest stated by the authors.

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