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Assessment of Lead and Cadmium in Some Industrial Wastewater in Kirkuk City

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Abstract The current article concerns wastewater contamination with lead and cadmium due to their toxicity and negative impacts on living creatures and the ecosystem. The study included the assessment of the physiochemical properties and the concentrations of some ions in the wastewater of some industrial plants in Kirkuk governorate Coded (Area 1 to Area 5). The physiochemical properties include temperature, pH, total dissolved solids (T.D.S.), total suspended solids (T.S.S.), electrical conductivity ($E.C^{\circ}$), total hardness, and turbidity. The concentration of ions includes nitrate (NO_3^-), magnesium (Mg^{2+}), calcium (Ca^{2+}), sulphate (SO_4^{2-}), chloride (cl^-), sodium (Na^+), phosphate (PO_4^{3-}), lead (Pb) and cadmium (Cd). The findings demonstrated that the phosphate (PO_4^{3-}) and lead (Pb and Cd) concentrations were more than the permitted limits. All the physiochemical properties have shown elevated levels compared to the normal values except for those related to total hardness and turbidity, which were unacceptable.

Key Words Wastewater contamination, Lead, Cadmium, Physiochemical properties, Industrial plants

1. Introduction

Human well-being, economic progress, and the global ecosystem's health rely on a continuous supply of high-quality water. However, increasing development and urbanization have raised water demand and introduced harmful contaminants and waste chemicals into water sources [1]. The large volumes of wastewater produced due to population growth and industrial activities pose a serious threat to environmental sustainability on a global scale, particularly the escalation of heavy metal pollution [2]. This industrialization-induced pollution disrupts marine systems, affecting fish and their ecosystems [3]. Urgent measures are needed to address this critical issue and preserve the environment's delicate balance [3].

The complete elimination of organic and heavy metal contaminants from water presents a major challenge for the global water treatment industry. The complexity arises from the diverse mix of effluent pollutants with varying concentrations and properties. Interestingly, the impact of these pollutants remains consistent regardless of their unique effluent matrix, which is influenced by specific industrial activities or locations [4].

According to reports, these contaminants may have synergistic or antagonistic qualities that make it difficult to remove them all at once from water [5], [6]. Some of these instances may be found in various sectors, including paint, pesticide, and petroleum/refinery industries, as well as power plants [7]. Singh et al. (2005) [3] categorized Gomti River water contamination into three stages based on 24 factors. Their study revealed that employing Principal Component Analysis (PCA) could enhance the robustness of statistical studies by reducing the number of required factors for water quality assessment. Similarly, a multivariate statistical approach was used to evaluate the water quality of the Fuji River in Japan. They also classified pollution levels into low, moderate, and high categories. They identified Biochemical oxygen demand (BOD), pH, Electrical conductivity ($E.C^{\circ}$), nitrate ion (NO_3^-), and ammonium (NH4+) as the most influential metrics impacting water quality [8], [9]. The more concentrated heavy metals are present, the more harm they will do to the environment and water resources. If the environment and water sources are too polluted with heavy metals, health risks, and concerns are inevitable [10].

Of all the industries, five have been shown to pose the biggest threat to human health and the environment: the pharmaceutical, petrochemical, coal-making, textile and paper, and pulp sectors [11]. Batteries, electroplating, mining, metallurgical processing, petrochemical processing, paper

Figure 1: A map showing the locations of the industrial areas where wastewater samples were collected. Reference: Google Maps

and pulp, plastics, brewing, and paint are among significant businesses that emit metals (such as copper, lead, nickel, zinc, aluminum, and cadmium) into the environment as a byproduct [12]. Water bodies commonly include Cd, Pd, and Cu. Lead exposure can have harmful effects on a person's neurological system, kidneys, cardiovascular system, and reproductive system; it can also induce hyperactivity and mental retardation in children in particular [13]. When cadmium interferes with an enzyme, such as acetylcholinesterase, it can lead to behavioral problems and cholinergic neurotransmission in people [14], [15]. The complexity of many contaminants makes it challenging to treat wastewater to reduce its toxicity and raises the cost of treatment [16]. This article concerns the assessment of Pb and Cd in wastewater of oil companies, including Northern Oil Company and Northern Gas Company, as well as Kirkuk Cement Factory; the assessment has been done using different measurements, including total hardness, turbidity, total dissolved salts (T.D.S.), total suspended solids (T.S.S.), pH, electrical conductivity ($E.C^{\circ}$), and temperature. Also, many ions like nitrate (NO_3^-), sulphate (SO_4^{2-}), phosphate (PO_4^{3-}), magnesium (Mg^{2+}), calcium (Ca^{2+}), sodium (Na^+), and chlorine (cl^-) were assessed in this research.

2. Experimental Part

A. Study Locations

This study has been conducted in Kirkuk governorate, Iraq. Latitude and longitude are (35.478565) and (44.041932) respectively. The selected areas in which the wastewater samples were collected and coded as follows; Kirkuk Cement Factory inlet-outlet sewage, coded (Area 1), Kirkuk Cement Factory wastewater, coded (Area 2) (latitude: 35.3407217) and (longitude: 44.4764001), North Oil Company coded (Area 3) (latitude: 35.517098) and (longitude: 44.3136205), North Gas Company, coded (Area 4) (latitude: 35.3862227) and (longitude: 44.2194695), North Gas Company/Qadir Karam plant, coded (Area 5) (latitude: 35.1965418) and (longitude: 44.893221), as in Figure 1 and Table 1.

Sample No.	Location	Sample Code
1	Kirkuk Cement Factory (inlet-outlet) sewage	Area 1
2	Kirkuk Cement Factory (Factory wastewater)	Area 2
3	Northern Oil Company (Main company)	Area 3
4	Northern Gas Company (Main company)	Area 4
5	Northern Gas Company (Qadir Karam plant)	Area 5

Table 1: Samples collected from different locations and sample codes

B. Preparation and Collection of Samples

Finding the physicochemical properties of drinking tap water, such as its pH, total dissolved solids (T.D.S.), electrical conductivity ($E.C^{\circ}$), and temperature (C°), is the first step. The pH of the drinking tap water samples was ascertained using two reference solutions (pH 4.0 and 7.0) and a calibrated pH meter. The samples' temperature, total dissolved solids, and electrical conductivity were measured using an electrical conductivity meter. A reference solution with known electrical conductivity was used to calibrate the probe. The second phase involved utilizing an AA-6800 AAS combined with a GFA-EX7 graphite furnace atomizer and an ASC-6100 autosampler from a Shimadzu Flame atomic absorption spectrophotometer (Koyoto, Japan) to analyze two heavy metals (Cd and Pb) for the prepared samples in a laboratory setting. Prior to evaluating each water sample, the standard solution for each studied element was adjusted to match its contents and used to calibrate the apparatus. The device automatically generates the Relative Standard Deviation (RSD) and the Standard Deviation (SD) based on the subject matter and statistical analysis results.

Elemental concentrations were determined using ICP-OES SPECTROSCOPY for both (Cd and Pb) and air as a catalyst for all elements at wavelengths of 228.8 and 216.9 (nm), the liquid spray rate was (4 ml/min), as well as the Inductively Coupled Plasma ICP-OES SPECTROSCOPY/HORIBA. In addition, the (Ca^{2+}) and total hardness were measured using the standard analytical chemical method and EDTA, while the (cl^-) and (Mg^{2+}) were calculated using the Argentometric method. The phosphate was determined using the Vanadomolybdo phosphoric acid colorimetric and Flame emission methods. The gravimetric method is used to measure sodium and sulfate using a photometer. The turbidity was measured with a turbidity meter. The gravimetric approach was used to quantify total suspended solids (T.S.S.). Lastly, the Brucine technique is used to test nitrate [17].

C. Methods

Electrical conductivity, pH, T.D.S, T.S.S., and temperature were estimated according to the procedure [18]. Turbidity, total hardness, calcium Ca^{2+}, chlorine cl^-, magnesium Mg^{2+}, sodium Na^+, phosphate PO_4^{3-}, and sulphate SO_4^{2-} procedures were conducted according to the procedure [19]. Nitrate ion was assessed following the procedure [20].

3. Results and Discussions

The values of the examined physiochemical characteristics of wastewater from various Kirkuk region industrial sites are displayed in Table 2.

The measured pH values spanned from 6.14 to 8.7 with a mean of 7.42; IQS/417 specifies the acceptable pH range as (6.5-8.5). The areas southeast of Kirkuk City, including North Gas Company (Area 4) and Northern Gas Company plant in Qadir Karam (Area 5), have shown the highest and lowest pH values of 8.7 and 6.14, respectively. The effluent from the industrial complexes may occasionally be alkaline (pH>7). Furthermore, there were no notable differences among the sampling locations, leading to the conclusion that the wastewater has little impact on the concentration of hydronium ions [21]. According to the temperature data, (Area 5) had the highest wastewater temperature (Area 5) while the lowest was found in (Area 2); the temperature varies from 28.8 to 29.7 degrees Celsius, with an average of 29.28 degrees Celsius, depending on the weather. Measurement is required because it influences several water parameters, including bacteriological activity, density, viscosity, and chemical solubility [22]. After measuring the electrical conductivity (E.C°) of the wastewater areas inside and outside of Kirkuk city, it was discovered that Area 3 had the highest value, while Area 2 had the lowest value.

The $E.C.^{\circ}$ ranged from 624 to 1825 μs/cm, with an overall mean of 1014 μs/cm, as indicated in Table 1. The permissible limit of $E.C.^{\circ}$ is 1000 μg/cm by IQS/417, marginally higher than the specified values. Turbidity and water quality are correlated, as are turbidity and bacterial content. Turbidity reduces chlorine's ability to sanitize water, necessitating higher chlorine concentrations to eradicate bacteria and pathogens [23]. According to Table 1, the turbidity range value was between 0.1 and 1.7 NTU, with an overall mean of 0.98 NTU. Of the wastewater regions in Kirkuk City, Area 4 had the most outstanding value and Area 3 had the lowest value. According to IQS/417, the allowable maximum of turbidity is 5 NTU, and this value has been determined to comply with the requirements. This study indicated that the wastewater regions of Kirkuk City had T.S.S. values ranging from 4 to 12 mg/L, with an overall mean of 8 mg/L. The greatest value was discovered in Area 3, and the lowest level in Area 2, as illustrated in Table 2. According to IQS/417, the allowable limit of T.S.S. is 0 mg/L; nevertheless, this value does not meet the specified limits. After measuring the T.D.S. of wastewater sources, it was discovered that Area 3 had the highest value while Area 2 had the lowest value. The T.D.S. varied from 410 to 1220 mg/L, with an overall mean of 679 mg/L, as shown in Table 2.

Table 3 shows the chemical analysis of the collected wastewater from the industrial areas that have been studied, the values in Table 3 can be discussed as follows:

The concentrations of phosphate (PO_4^{3-}) varied across the studied areas. (Area 3) has shown the highest phosphate concentration at 4.60 mg/l, while (Area 5) showed the lowest concentration at 2.76 mg/l. This difference in phosphate concentrations could be attributed to variations in agricultural runoff or sewage discharge in (Area 3) [23], which may contribute to higher phosphate levels. The total hardness levels were different among the studied areas, ranging from 232 mg/l to 760 mg/l in (Area 3), which has shown the highest level. Total hardness is influenced by the presence of calcium and magnesium ions in the water [24].

The variation in total hardness suggests that these areas' geological composition and water sources may be similar. The concentrations of calcium (Ca^{2+}) varied across the studied areas. (Area 3) the highest calcium concentration is 140 mg/l, while (Area 2) has the lowest concentration is 41 mg/l. These variations in calcium concentrations could be attributed to differences in geological formations or the presence of calcium-rich minerals in the water sources. The concentrations of magnesium (Mg^{2+}) have also shown variation among the studied areas, ranging from 32 mg/l in (Area 2) to 100 mg/l in (Area 3).

This suggests that the sources of magnesium in the water may be consistent across these areas. The concentrations of chloride (cl^{-}) varied across the studied areas. (Area 3) has shown the highest chloride concentration at 50 mg/l, while (Area 1) had the lowest concentration at 20 mg/l. These variations in chloride concentrations could be influenced by geological formations, industrial activities, or saltwater intrusion in the area [25]. The concentrations of sodium (Na^{+}) also varied across the studied areas. (Area 5) had the highest sodium concentration at 14.70 mg/l, while (Area 1) and (Area 4) showed the lowest concentration at 9.30 mg/l. These variations in sodium concentrations could be influenced by factors such as geological formations, industrial activities, or saltwater intrusion in the area [25].

The concentrations of sulfate (SO_4^{2-}) in the studied areas ranged from 164 mg/l to 474 mg/l. (Area 3) the highest sulfate concentration was 474 mg/l, while (Area 1) had the lowest concentration at 164 mg/l. These variations in sulfate concentrations could be attributed to differences in geological formations, industrial activities, or agricultural practices in the different areas. The concentrations of nitrate (NO_3^{-}) in the studied areas range from 0.171 mg/l to 15.303 mg/l. There were significant variations in nitrate concentrations among the areas, with (Area 2) having the highest concentration at 15.303 mg/l and (Area 5) having the lowest concentration at 0.171 mg/l. These similar nitrate concentrations suggest that the sources of nitrate pollution may be consistent across the studied areas.

In conclusion (Table 3), the concentrations of different ions in the studied areas varied, indicating potential differences in wastewater quality and sources of pollution. Understanding these variations is important for assessing wastewater analysis and identifying potential impacts on aquatic ecosystems and human health. In addition, (Area 3) was the most contaminated among the studied areas.

Table 4 shows the analytical assessment of tap water according to the Iraqi Quality Standards (IQS 417/2001) along with the minimum and maximum acceptable concentrations

Physiochemical Properties	Areas					Acceptable range ***
	Area 1	Area 2	Area 3	Area 4	Area 5	
pH	7.2	7.5	7.5	8.7	6.14	6.5-8.5
Temperature (C○)	29.2	28.8	29.3	29.4	29.7	—-
Electrical Conductivity (µs/cm)	794	624	1825	1002	825	1000
*T.D.S (mg/l)	552	410	1220	635	578	1000
Turbidity (NTU)	1.3	0.2	0.1	1.7	1.6	5
**T.S.S (mg/l)	6	4	12	10	8	0
*T.D.S.: Total Dissolved Solids, **T.S.S.: Total Suspended Solids. *** According to (IQS 417/2001).						

Table 2: Physiochemical properties of collected wastewater sample

Studied Ions	Areas					Acceptable range*
	Area 1	Area 2	Area 3	Area 4	Area 5	
PO_4^{3-} (mg/l)	2.82	3.53	4.60	3.32	2.76	3.00
Total Hardness (mg/l)	280	232	760	363	320	500
Ca^{2+} (mg/l)	47	41	140	78	53	50
Mg^{2+} (mg/l)	40	32	100	34	35	50
cl^- (mg/l)	20	24	50	44	32	250
Na^+ (mg/l)	9.30	9.33	9.50	9.30	14.70	200
SO_4^{2-} (mg/l)	164	168	474	232	320	250
NO_3^- (mg/l)	1.515	15.303	6.762	1.786	0.171	50
* According to (IQS 417/2001).						

Table 3: The chemical analysis of wastewater samples from the studied areas

Parameters	Unit	(IQS 417/2001)	Min	Max	Average
pH	-	6.5-8.5	6.14	8.7	7.9
T.D.S.	mg/l	1000	410	1220	679
T.S.S.	mg/l	0	4	12	8
NO_3^-	mg/l	50	0.171	15.303	5.1074
Mg^{2+}	mg/l	50	32	100	48.2
Ca^{2+}	mg/l	50	41	140	71.8
SO_4^{2-}	mg/l	250	164	474	271.6
cl^-	mg/l	250	20	50	34
Na^+	mg/l	200	9.3	14.7	10.426
PO_4^{3-}	mg/l	3	2.76	4.6	3.406
Cd	mg/l	0.003	0.94	6.85	2.962
Pb	mg/l	0.1	0.83	2.64	1.738
E. C°	mg/l	1000	624	1825	1014
Total hardness	mg/l	500	232	760	391
Turbidity	NTU	5	0.1	1.7	0.98

Table 4: Analyzing the quality attributes of tap water samples in the examined areas

and measured parameter.

Table 4 states that the permissible range for Cd (cadmium) content in water is 0.001–0.005 mg/l, with an average of 0.0025 mg/l, which means that Cd concentrations in water should have exceeded 0.005 mg/l and do not meet the acceptable Iraqi standards. However, a study by Abdullah et al. [26] showed Cd level was more than the acceptable concentration in an industrial beverage company in Kirkuk governorate. Globally, the acceptable concentration of Cd should not exceed 0.003 mg/l. Regarding Pb, the acceptable levels in wastewater ranged between 0.0076-0.1 mg/l, with an average of 0.0055 mg/l. The average Pb level is 1.738 mg/l, representing the typical concentration found in wastewater samples. The concentration of Pb reached 2.46 mg/l, indicating that the concentration of Pb was way above the acceptable values, which overcame the upper limit for Pb concentration in water. However, drinking tap water has been measured to be pure in terms of lead contamination, according to the study by Al-Jumaily [27]. The concentrations of Cd and Pb in the studied areas have also been investigated using the inductively coupled plasma (ICP) technique as shown in Table 5 below:

Sample No.	Sample Code	Cd (mg/l)	Pb (ng/l)
1	Area 1	0.94	2.64
2	Area 2	1.76	0.83
3	Area 3	6.85	2.13
4	Area 4	3.21	1.79
5	Area 5	2.05	1.34

Table 5: Concentrations of Cd and Pb estimated using ICP-OES technique

From Tables 4 and 5, It can be noticed that the concentrations of Cd and Pb estimated by ICP-OES are much higher than the acceptable levels. However, measuring the heavy metal concentration using ICP-OES can be considered a more accurate measuring method due to the advanced and powerful enhancement introduced in this technique [28].

4. Conclusions

This study studied different parameters in wastewater samples from different industrial areas in the Kirkuk governorate, including oil companies and a cement factory. Parameters concentrations such as turbidity, cl^-, Na^+ and T.S.S were within the acceptable levels. However, our study showed that (Area 3) has shown the most elevated level of ions, as well as high physiochemical properties compared to other areas and also in comparison to the acceptable IQS 417/2001 Iraqi standards of water.

Conflict of interest

The authors declare no conflict of interests. All authors read and approved final version of the paper.

Authors Contribution

All authors contributed equally in this paper.

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