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Statistical Indicators for Evaluating the Effect of Heavy Metals on Samaraa Drug Industry Water Exposed to the Sun and Freezing

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ABSTRACT

Heavy metal poisoning is a worldwide problem caused by various human industrial activities such as battery and paint manufacturing, as well as occupational exposure of individuals working at petrol stations. Contaminated water and wastewater contain higher amounts of heavy metals such as chromium (Cr), aluminum (Al), copper (Cu), manganese (Mn), zinc (Zn), and iron (Fe), which may pose a risk to wastewater treatment plant workers. However, only a few studies have been conducted to assess the level of heavy metals and their subsequent effects. This study was therefore conducted to measure Samaraa pharmaceutical factory (SPF) work efficiency and predict the most important characteristics that affect water quality using the multiple linear regression (MLR) model. The case study location was the Samaraa Drug Industry, situated in Iraq. Water samples exposed to the sun and freezing were collected Pre and post factory operation. The concentrations (mg/L) of heavy metals (Cr, Al, Cu, Mn, Zn, and Fe) in the water samples were measured. Also, the influent, effluent, and samples exposed to sun and freezing were analyzed according to Iraqi standards for drinking water (ISL). The results show that the heavy metal data were normally distributed because the p-value was equal to 0.05 and the concentrations of substances in the river water were within the ISL acceptable limits. Meanwhile, Fe exceeded the ISL during the study period, but excellent results were obtained when the samples were exposed to the sun and freezing. Based on the coefficient of correlation, the MLR model (R^2 of 91.4 %) proved efficient.

Keywords: Freezing, Heavy metals, Multiple linear regression, Wastewater, Effluent, Pollution.

Introduction

Human activities and industrial expansion have led to a rise in water use. Wastewater discharge has polluted water resources. An environmental and health risk is posed to human and aquatic life by unregulated industrial effluent discharges that which contain levels of pollutants.[1] Water contamination is a global issue that poses a significant threat to the environment and water quality. Therefore, it is important to investigate the impact of toxins from wastewater and other sources on water quality.[2] Chemicals, suspended materials, pathogenic microbes, any other thing that can degrade water quality must be avoided.[3] More than 16% of the world's population still suffers from contaminated and polluted water, according to several studies.[4,5] Tigris river water quality has deteriorated during the last twenty years as a result of numerous factors, including dams and lakes, increased use of water for domestic, industrial, and commercial purposes, and harsh environmental conditions. Consequently, both the rate at which safe drinking water in Iraq and the quality of the drinking water decreased.[6] Heavy metals, which have a relatively high density in comparison to water, are among these pollutants and can be hazardous even at minute levels.[7] Toxic inorganic heavy metals found in the Earth's crust include Fe, Al, Cr, Cu, Mn, and Zn. They are discharged to the environment through human industrial activities such as metal plating, mining, battery manufacturing, smelting operations, and paint production.[8] All living organisms may quickly absorb heavy metals due to their high solubility in water.[9] Because of these two properties, inorganic pollutants may be found in nearly all tissues and organs because of these two properties.[10] Various forms of industrial and human waste, which may be toxic to a wide range of living organisms, are the most significant sources of water pollution.[11] Many heavy metals pose a significant risk to public health due to their stability and non-biodegradable fast and easily.[12] Heavy metals are resistant to microorganisms, as well as damaging life cycles and cellular structures. [13] Many studies have found that heavy metals cause or contribute to human health problems.[14] Furthermore, several research have been conducted in the field of water treatment assessment to determine the efficiency of the system. The most common method is the efficiency of contaminant removal, in which their performances at different times of the year can be compared to determine which sites require more treatment.[15] Al-Hassen et al.,[16] discovered in their investigation of the level of heavy metals in the environment that Basra city water samples taken from different places included varying concentrations of the elements iron, copper, lead, cobalt, and nickel. The study found that all of the identified elements had an impact on the general health of the population if this water was drank without treatment, which is a solid guarantee that the percentage of minerals in it is reduced. Abdullah,[17] assessed the quality of Shatt al-Arab water heavy elements such as iron, zinc, copper, lead, cadmium, and nickel and discovered that the waters of the Shatt al-Arab are not polluted by these elements. In addition, statistical analysis is a useful tool for processing vast amounts of data by describing the link between two or more variables. As a result, the number of potential confounding factors was reduced without surrendering crucial information.[18] To treat contaminated water, different methods and techniques such as chemical precipitation, ozonation, coagulation-flocculation, filtration, reverse osmosis, oxidation, adsorption, and so on are suggested.[19] Among these techniques, adsorption is useful due to its simplicity, efficiency, lack

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of previous preparation, and low cost.[20] The well-known medium of adsorption is activated carbon.[21] Despite its high efficiency and large surface area, the cost of activated carbon synthesis is relatively high, and it loses 10-15% of its mass after each regeneration process.[22] As a result, researchers are looking for new materials that can be used to manufacture activated carbon or as an adsorbent medium. The best alternative materials are agricultural wastes and industrial residues. These materials are characterized by availability, low cost, activity, and negligible toxicity.[23] Many studies have been conducted using natural materials such as rice husk,[24] watermelon rinds,[25] eggshells,[26] water hyacinth,[27] orange peels,[28] aluminum foil,[9] nanoparticles,[29,30] to remediate polluted aqueous solutions. Also, these wastes have the potential to eliminate cobalt and lithium metals from the soil,[31] and nickel from petroleum,[32] in addition, to remove nonmetallic elements e.g. hardness,[2] dyes,[33,29] sulfur from heavy naphtha,[34] and light naphtha.[35] The residue is not only used for adsorption but is also used to manufacture beneficial compounds such as acetone,[36,30] or drugs.[37] The only disadvantage of the adsorption process is the presence of toxic residues after the treatment is completed. This problem can currently be solved by transforming these harmful compounds into beneficial substances and leaving no residue.[38] currently there are several studies dealing with the statistical side of removing contamination from environmental elements,[25] and the effect of drugs on humans.[39,40]

Therefore, the present study was aimed at evaluating SPF work efficiency and predicting the most significant parameters that affect water quality using multiple linear regression (MLR) model.

Materials and Methods

Case study description

Samaraa Drug Industry is a laboratory of the General Company for the manufacturing of medicines and medical appliances (a governmental pharmaceutical company) established in 1959 in Iraq based on the Treaty of Economic and Technical Cooperation between Iraq and the Soviet Union. It is one of the oldest pharmaceutical companies in the Middle East and produces most of the pharmaceutical products used in Iraq. The industry is located in the district of Samarra as shown in Figure 1. It produces about 200 pharmaceutical preparations such as tablets, capsules, ointments, pharmaceutical syrups, disinfectants, and sterilizers. The Samaraa Drug Industry consists of five departments that are regarded as crucial in the company, in addition to two buildings that were built, one of which is nearing completion and the other is still awaiting adequate financial allocations. The first is the Ibn Sina Department, which manufactures antibiotics such as penicillin capsules and saturated suspensions. The second department is Ibn al-Nafis, which manufactures syrups, liquid suspensions, oral drops, and ANTA ionic water. The third is the Al-Yahrawi Department, which produces pills and tablets of various sizes and shapes.

Figure 1: The location of Samaraa Drug Industry on the Tigris river.

The fourth is the Ibn Hayyan Department, which manufactures antibiotic-free vials, eye drops, ampoules, and capsules, as well as Vitals, oral rehydration salts, antacid wipes, ointments and creams, & suppositories. The fifth structure is the New Antiquities Building, which manufactures cephalosporin capsules, suspensions, and vials.

Data collection

In this study, data were collected for three months (November and December 2021 and January 2022), containing six heavy metals in water, i.e., Cr, Fe, Cu, Al, Mn, and Zn (all measured in mg/l) from the Samaraa Drug industry. The data were collected for the water samples before and after the factory, as well as samples exposed to the sun and freezing. The Excel 2021 program was used. The regression analysis was performed using IBM SPSS 24 software.

Estimation of heavy metal concentrations

The concentrations (mg/L) of heavy metals including chromium, aluminum, copper, manganese, zinc, and iron were estimated according to the method described in APHA,[41] using a Perkin Elmer Analyzer 200 Spectrometer Atomic Absorption (Singapore). The samples were filtered with filter paper, and 100 ml of sample water was taken in a glass beaker. An aliquot of 5 ml of concentrated nitric acid was added to the solution and then placed on a hot plate to boil until its quantity reached 10 ml. The watch bottle was washed, and the volume was brought to 100 ml with distilled water. Afterward, a lamp was installed in the atomic spectrometer for each element at the appropriate wavelengths. The device was turned on and then the measurement was taken.

The heavy metals

Iron: Iron is one of the most abundant elements in soil and the earth's crust, and it has several industrial, domestic, and agricultural applications, as well as in other fields.[42]

Aluminum: Aluminum is one of the most abundant elements in the earth's crust, ranking third only to silicon and oxygen.[43] Unlike aluminum, which is absorbed by humans when dissolved in water, other nutrient components cannot be absorbed into the bloodstream.[44]

Copper: Copper is one of the elements present in nature in modest amounts, with a ratio of less than 0.05 mg/L. It arises from a variety of sources, including industrial, such as the electrical and textile sectors, through the release of copper salts into rivers via sewage water, and its advantages include the fact that it does not dissolve in water.[45] It is a significant element for animals and plants because it is involved in respiration, which is important in the transfer of electrons,[46] and has numerous benefits, such as producing protein and tissues for the organism's body, and its shortage causes many illnesses, such as blood diseases. Copper salts, such as copper sulfate and copper chlorides, dissolve quickly and completely in water. In the presence of a moderate medium, copper hydroxides and copper carbonate tend to precipitate. This is due to the weak ability of these compounds to dissolve. Copper toxicity is affected by aqueous medium components and properties such as temperature and oxygen. The solute, as well as the other elements, such as nitrates, play an important role in decreasing toxicity, in contrast to cadmium and mercury, which increase their toxicity.[47]

Zinc: Zinc is one of the elements found in trace amounts in the earth's crust, and it is a nutritive element for many organisms, however, it is required in modest amounts in comparison to the other elements. DNA-RNA polymerase and zinc may negatively affect living organisms when their concentration increases, as zinc, is harmful to plants at concentrations greater than 5 mg/liter due to its negative impact on the chlorotic sections of the plant.[48]

Manganese: Because of its role in digestion, absorption of nutrients, wound healing, bone growth, and immune system defense, manganese is an essential trace element for the human body. Manganese deficiency or excess may have negative health consequences. Manganese deficiency is unlikely in humans due to the presence of manganese in many typical diets. Osteoporosis, muscle and joint pain, and other major health issues may arise as a result of a vitamin D shortage. As a consequence of long-term exposure to excessive levels of manganese, a person's nervous system may be permanently affected

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by symptoms similar to Parkinson's disease. Underground water contamination by manganese may be traced back to human activity since this element naturally exists in rocks and soil.[49]

Chromium: Despite its critical role in human bodies, chromium is not toxic in and of itself; however, certain of its derivatives are. As an essential component of metabolic processes, chromium metal regulates blood sugar levels and aids insulin in transporting glucose into cells, where it may be used for energy. Chromium is required by human bodies in minute amounts. Chromium plays a role in the metabolism of lipids and other nutrients for its function in avoiding cardiovascular disease. Hypoglycemia, tiredness, increased cholesterol, and anxiety are just a few of the symptoms of chromium deficiency. Hexavalent (+6) chromium is more harmful than trivalent (+3) chromium because it is a byproduct of industrial contamination. If too much chromium is consumed, the skin and digestive system may become irritated, leading to lung cancer. Table 1 shows the maximum allowable quantities of heavy metals in water based on Iraqi specifications from 2001.

Multiple linear regression (MLR)

Multiple linear regression (MLR) is utilized to approximate the linear relationship between one definite dependent variable of the Iraqi limits for each element (ISL) and several quantitative independent variables (monthly readings). The classification functions listed below were calculated using the parameters as independent variables in the MLR linear equation:[18]

$$Y_i = A + a_1x_1 + a_2x_2 + \cdots + a_nx_n \quad (1)$$

Where Y_i represents the function of the dependent variable (ISL), x represents the independent variable (any reading of heavy metals), and A represents the constant of the equation.

Results and Discussion

Variation in the concentration of heavy metals in samples

The copper element can also migrate in acid-oxidizing environments. It enters the environment through mining and causes water pollution as a result of incorrect additions to canning containers.[50] The copper values before and after the factory ranged between 0.14-0.4 mg/L in the water samples. The highest concentration of 0.4 mg/L was recorded in January while the values were recorded within the ISL when the samples were exposed to the sun and freezing during the study period from November 2021 to January 2022 as shown in Table 2. Zinc concentrations were somewhat low due to the dominance of heavy metals that were less soluble in natural waters. One of the main sources of zinc in water is mining and coal burning.[51] Table 3 shows the zinc levels in the fourth stage of the current investigation within the ISL, with the maximum value recorded before the factory at 0.66 mg/L in November and the lowest value at 0.35 mg/L in December. The results of the zinc values for the various samples are similar to the previous study.[6] The aluminum values in the studied stages ranged between 0.01 and 0.1 mg/L, with the highest value of aluminum reaching 0.1 mg/L in the freezing stage in November, as shown in Table 4. Also, the results are in agreement with the findings of Ghawi.[52] The samples were drinkable and met the standards of Iraqi drinking water specifications. The iron levels in the water samples studied ranged from 0.1 to 0.9 mg/L, with the highest value reaching 0.9 in the freezing stage during November, as shown in Table 5, and the chromium levels in the water samples ranged from 0.03 to 0.16 mg/L, with the highest value reaching 0.16 before the factory during January, as shown in Table 6. These results were similar to those obtained by Alluhaiby,[13] while analyzing the quality of drinking water in Al-Alam and Al-Bu Ajil. The prepared drinking water from these units met Iraqi drinking water standards. Finally, the manganese levels in the water samples analyzed ranged from 0.01 to 0.085 mg/L, with the highest value reaching 0.01 at the freezing stage in November (Table 7).

Table 1: Iraqi standard specification of drinking water, 2001.[1]

Heavy metal	The Maximum allowable limit (mg/L)
Aluminum	0.20
Copper	1.00
Iron	0.30
Zinc	3.00
Manganese	0.10
Chromium	0.05

Table 2: The values and concentrations of copper during the study period

Cu	SPF		Sun	Freeze
	Before	After		
Nov.	0.144	0.224	0.094	0.034
Dec.	0.159	0.140	0.217	0.593
Jan.	0.156	0.397	0.053	0.095

Table 3: The values and concentrations of zinc during the study period

Zn	SPF		Sun	Freeze
	Before	After		
Nov.	0.66	0.61	0.65	0.5
Dec.	0.57	0.35	0.69	0.42
Jan.	0.477	0.45	0.55	0.44

Table 4: The aluminum values and concentrations during the study period

Al	SPF		Sun	Freeze
	Before	After		
Nov.	0.02	0.08	0.05	0.1
Dec.	0.02	0.02	0.02	0.01
Jan.	0.02	0.01	0.01	0.01

Table 5: The iron values and concentrations during the study period

Fe	SPF		Sun	Freeze
	Before	After		
Nov.	0.402	0.207	0.138	0.9
Dec.	0.297	0.188	0.221	0.155
Jan.	0.254	0.26	0.221	0.195

Table 6: The chromium values and concentrations during the study period

Cr	SPF		Sun	Freeze
	Before	After		
Nov.	0.088	0.069	0.052	0.03
Dec.	0.09	0.13	0.145	0.13
Jan.	0.166	0.07	0.07	0.064

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Descriptive statistics and MLR model

SPSS is a statistical application that analyzes data entered by the researcher via questionnaires, interviews, and notes using a series of lists and tools. It is one of the most widely used statistical data analysis software programs in sociology. The software explains the variables and consequently generalizes the findings of the research group. The statistical analysis of the data analyzed in this study, including mean and standard deviation, is shown in Table 8, which explains the statistical analysis with high confidence. Table 9 displays the results of the variable selection process using the SPSS regression tool and following the stepwise approach. The greatest coefficient of determination (R^2) in the final model was found to be 91.4%, as presented in Equation 2.

$$y = -0.013 + 3.01\,x \quad (2)$$

The sample mean population may differ from the real population mean by a large margin of error and all of the parameters have an acceptable error of the mean. Skewness values for heavy metals indicate that the distribution of data on the right of the curve contains a large number of samples with high concentrations, implying that the majority of the concentrations are greater than the mean.[53] Because the data for heavy metals was normally distributed, as indicated by the p-value of 0.05 in Table 10, the parametric test could be employed to determine the difference between the values of dependent variables (readings) and ISL (independent variable).[54]

Table 7: The manganese values and concentrations during the study period

Mn	SPF		Sun	Freeze
	Before	After		
Nov.	0.069	0.055	0.024	0.01
Dec.	0.055	0.135	0.024	0.068
Jan.	0.058	0.061	0.124	0.085

Table 8: Descriptive statistics for examinations data

	Mean	Std. Deviation
Iraqi Standard	1.0875	1.33690
Cr	0.0985	0.05862
Al	0.0650	0.09000
Cu	0.3648	0.42355
Mn	0.0680	0.02305
Zn	1.1768	1.21779

Table 9: Model summary of MLR

Model	R	R^2	Adjusted R^2	Std. Error of the Estimate	Durbin-Watson
1	0.956[a]	0.914	0.871	0.47954	1.835

[a] Predictors: (Constant), Cu

[b] Dependent Variable: Iraqi Standard

Table 10: ANOVA details

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	4.902	1	4.902	21.317	0.054[b]
	Residual	0.460	2	0.230		
	Total	5.362	3			

a. Dependent Variable: Iraqi Standard

b. Predictors: (Constant), Cu

The dependent variable can be accurately predicted when the independent variables are used together. This is an overall significance test that does not look at individual independent factors' ability to predict the dependent variable. Finally, statistical analysis demonstrated that the efficiency of SPF in heavy metal removal was significantly higher (p-value 0.05).

Conclusion

The concentrations of commodities in river water are within ISL, but when exposed to sunlight and freezing, the results are outstanding. The concentrations of elements in sediments are higher than in river waters, giving these sediments environmental significance. Due to an excellent correlation coefficient (R^2) of 91.4%, the inclusion of statistical indicators produced good results in the mathematical model of MLR.

Conflict of Interest

The authors declare no conflict of interest.

Authors' Declaration

The authors hereby declare that the work presented in this article is original and that any liability for claims relating to the content of this article will be borne by them.

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