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Article

Assessment of Heavy and Essential Elements in Drinking Water from of the Shirqat District, Salah Al-Din, Iraq

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Abstract: The major challenge in Iraq, particularly the river Tigris is surface water due to heavy metal contamination. The paper was applied in the identification of the effectiveness of a water treatment plant- Al- Shirqat, Saladin Governorate by the analysis of 6 samples, comprised of 3 samples of raw water influent and 3 samples of treated water effluent. The trace and vital elements were identified using the Flame Atomic Absorption Technology in order to find out the quality of water and the risks posed by water to human health. The results revealed that treatment process was quite effective in enhancing all the physicochemical parameters ($p < 0.01$), and the percentages of removing were 33% by Total Dissolved Solids (TDS) and 87% by Copper (Cu). Removal rates were 75% and 57% in the case of Magnesium and Calcium respectively. Water Quality Index (WQI) also had an improvement of 34.2 and Hazard Index (HI) was also reduced to 0.08 than 0.17. Since the HI was still considerably less than unity (HI < 1), it is ensured that there were no serious non-carcinogenic health effects with the treated water and that the water would be able to match the WHO recommendations of drinking water. The plant was discovered to be very stable in its operations with a coefficient of determination of R2 =.94.

Keywords: Heavy Elements, Essential Elements, Shirqat, Water Treatment, Iraq, Water Quality, Flame Atomic Absorption Technology

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1. Introduction

Water is one of the most basic natural resources to the life of human beings and sustainable development [1]. This is significant, as safe drinking water plays a vital role in the sustenance of the health of the people since it forms a significant aspect in many biological and chemical functions in the human body [2]. However, the consumption of water has been a matter of debate of great concern given the increasing level of pollution given the industrial practices, agricultural effluents, population and urban sprawl. These activities can introduce various contaminants to the water bodies like organic pollutants, microorganisms and heavy metals [3]. The heavy metals had considered as among the most detrimental pollutants of water bodies because they are toxic, persistent and accumulative in the living organisms [4].

Lead (Pb), cadmium (Cd), copper (Cu), iron (Fe) and manganese (Mn) metals may be found in nature in both geological and anthropogenic (by anthropogenic discharge, mining and agricultural fertilizers) and wastewater disposal [5]. The heavy metals are not biodegradable and can be harmful to the environment and human health as it had known to take long before the environment unlike other organic pollutants [6] can dispose of it.

As one consumes water, they might have various health issues as far as exposure to heavy metals is concerned. Such include the fact that the exposure to cadmium has been linked to damage to the kidney and malformation of the bone though the lead may lead to neurological disorders, blood deficiency or mis-development of children. Overabundance of some metals like copper and iron can also influence the taste, color among other general composition of drinking water. The concentration of the heavy metals available in the source of drinking waters should thus be monitored to consolidate the safety of water as well as in order to protect the human health [7].

Most of the developing countries like Iraq are depending on rivers as the primary source of drinking water. The river Tigris is one of the most important themes on the surface water resource in Iraq that provides the population with the water that should be used in domestic, agricultural and manufacturing industries. However, as the environmental requirements swell (and the human activities flourish in the river) the questions of the falling water quality and the risk that the heavy metals and other pollutants deposits of sediments brought about questions the water treatment plants as one of the legality of the drinking water quality enhancement. Those conventional methods of treatment are the coagulation, sedimentation, filtration and disinfection that were employed in the procedure of minimization of the pollutants and enhancement of the water safety. Such treatment processes may not be effective to get rid of hard metals and other parameters related to physicochemical parameters depending on the quality of raw water and the conditions within which such a treatment plant is operating. Hence, there is the necessity of having a continuous review and analysis of the operations of the water treatment plants concerning the protection of the drinking water supplies [9]. Certain studies were conducted on the frequency of the heavy metal in drinking water and evaluated the health risks that may manifest itself due to such contaminants. The health threat of the consumption of metal using the drinking tap water in Poland was highlighted as well as the necessity of continuously guarding the quality of the drinking water in Nigeria when dramatic variations were reported in the concentrations of the heavy metals in drinking water there [10]. It had highlighted by another study that the process of water treatment should be regularly reviewed to facilitate the process of ensuring that it is meeting the international drinking water requirements like the ones that are established by the world health organization [12]. Although the number of researches related to the water quality issue continues to rise in the global community, a minimal number of researches had carried out concerning the effectiveness of the water treatment plants in guaranteeing the decrease in the content of heavy metals in the drinking water sources in the Al-Shira city, Salah Al-Din Governorate, Iraq [13].

Therefore, further studies are necessary to test the efficiency of the water treatment procedures in the region and estimate whether people, according to the acceptable safety standards, can consume the water treated.

The study will determine the effectiveness of Al-Shirqat water treatment plant in improving the quality of drinking water using the chosen physicochemical parameters and heavy metals of the sampled water prior to and after the treatment process. The performance of the treatment plant was gauged by analyzing the flame atomic absorption spectrometry to ascertain the efficiency of the treatment plant as well as to ascertain the health risks that may be operated by taking water.

2. Materials and Methods

All chemicals used in the work can be tracked in following Table 1.

Subject Name	Chemical formula	Purity and Concentration	Company
Nitric acid	HNO_3	69%	Fluka
Water free of ions	DI-H_2O		Chemistry Lab

Standard solution for heavy elements	Cd, Fe, Cu, Pb, Zn	1000 ppm	Merck

2.1. Study Area and Sampling

It was done in the Al-Shiquat Water Treatment Plan (WTP) in the Saladin Governorate (Iraq). 6 water samples were run in it such as: 3 raw water samples (influent-Tigris River) and 3 end sample water (effluent). Sampling of the samples was done at 10cm of the water surface of 1 liter polyethylene bottles. The bottles were washed with 5% nitric acid ($HNO3$) and deionized water prior to rinsing with the same sample water twice in all the collection sites [14].

2.2. Sample Preparation and Acid Digestion

The acid digestion procedure was used in such a way that maximum release of the heavy metals in the organic complexes was achievable. Immediately, samples were collected and preserved by the addition of concentrated HNO3 to neutralize the pH to < 2 [15]. All the samples were combined with 5 mL of concentrated HNO3 (69% purity, Fluka) in a laboratory and boiled in a hot plate at about 95ºC until 20 mL of solution was obtained and the solution became clear. Filtering was done using Whatman No. 42 filter paper, the solutions were digested and allowed to cool down, and the deionized water was added to reach 100mL final volume [16].

2.3. Analytical Technique

The wt. of heavy metals (Cu, Fe, Pb, Cd, Mn) and important elements (Ca, Mg, K, Na) were measured by the Flame Atomic Absorption Technology. A calibration curve of the elements investigated was done using standard solutions (1000 ppm, Merck). The same result was obtained on the water samples using blank samples containing reagents alone to provide analytical accuracy and to correct, any background contamination [17].

2.4. Mathematical Laws and Calculations

The performance and risks that were associated with the plant were estimated using the following equations:

1) **Removal Efficiency (R %)**: The calculation of the capability of the Al-Shirqat WTP in the removal of pollutants was done as follows:

$$R\ \% = C_{raw} - C_{treated} \ / C_{raw} \times 100 \ \ldots\ldots\ldots\ldots\ldots 1$$

Where C{raw} and C{treated} represent the concentrations in raw and treated water, respectively[9].

2) **Water Quality Index (WQI)**: The weighted arithmetic index was used to find out the overall suitability of the water to be used as a drinking medium.
3) **Health Risk Assessment**: Due to the necessity to calculate non-carcinogenic health risks, the Chronic Daily Intake (CDI), Hazard Quotient (HQ) and Hazard Index (HI) were computed[18].

$$\mathbf{HQ} = CDI \ / R\textstyle\int D$$

Hazard Index

$$\mathbf{HI} = \Sigma\ \mathbf{HQ} = \mathbf{HQ_{Cu}} + \mathbf{HQ_{Fe}} + \mathbf{HQ_{Pb}}$$

Where R ʃ D is oral reference dose of both metals. HI<1, the water is claimed to be safe to be taken by human beings.

2.5. Statistical Analysis

The data and the standard deviations (SD) were compared using the SPSS software to find the mean values of the data [19]. Precision of Analysis: Relative Standard Deviation (RSD%) was calculated in order to determine the reliability of measurement. Operation Stability: The coefficient of determining (R2) of the raw and treated water concentration was also determined using the linear regression analysis to determine the stability of the plants [20]. The decision was made that the level of statistical significance must be p<0.01 in order to demonstrate the efficiency of the treatment process[21].

3. Results and Discussion

3.1. Raw and Treated Water Quality

The experimental values of the physicochemical parameters under investigation in raw and treated water (influent and effluent water respectively) are indicated in Table 2. It is possible to note that all parameters showed the significant reduction after treatment.

Table 2. Descriptive mineral parameters, raw water and treated water.

No.	Parameter	Raw Water Influent 1	Raw Water Influent 2	Raw Water Influent 3	Treated Water Effuent 1	Treated Water Effuent 2	Treated Water Effuent 3	Unit
1	Tds	300	312	291	205	198	202	ppm
2	Total hardness	288	283	286	175	170	173	ppm
3	Potassium	3.94	3.91	3.91	1.10	0.95	1.00	ppm
4	Magnesium	31.1	31.3	31.0	8.10	7.80	7.50	ppm
5	Sodium	20.1	20.1	20.3	11.2	10.8	10.5	ppm
6	Calcium	73	70	69	32	29	31	ppm
7	Silica	2.73	2.76	2.71	1.05	0.98	1.02	ppm
8	Iron	0.04	0.03	0.06	0.015	0.012	0.014	ppm
9	Copper	0.14	0.11	0.16	0.020	0.018	0.017	ppm
10	Lead	0.01	0.021	0.011	0.006	0.007	0.005	ppm
11	Cadmium	0.003	0.005	0.001	0.0015	0.0012	0.0010	ppm
12	Manganese	0.07	0.05	0.07	0.025	0.020	0.022	ppm

3.2. Descriptive Statistics and Treatment Efficiency

The analysis of descriptive statistics was used (n=3) to demonstrate the significance of the positive changes in all the measured physicochemical parameters after the treatment process. The results were given in the table as in Table 2.

Table 3. Descriptive statistics, removal efficiency, and statistical significance of water quality parameters.

No.	Parameter	Before (SD ± Mean)	After (SD ± Mean)	Removal %	p-value
	TDS (ppm)	10.6 ± 301.0	3.5 ± 201.7	33.0%	0.01>
	Total hardness (ppm)	2.5 ± 285.7	2.5 ± 172.7	39.5%	0.01>
	Potassium (ppm)	0.02 ±3.92	0.08 ± 1.02	74%	0.01>
	Magnesium(ppm)	0.15 ± 31.13	0.30 ± 7.80	75%	0.01>
	Sodium(ppm)	0.12 ± 20.17	0.35 ± 10.83	46%	0.01>
	Calcium(ppm)	2.08 ± 70.67	1.53 ± 30.67	57%	0.01>
	Silica (ppm)	0.03 ± 2.73	0.04 ± 1.02	63%	0.01>
	Iron(ppm)	0.015 ± 0.043	0.0015 ± 0.0137	68%	0.01>

Copper(ppm)	0.025 ± 0.137	0.0015 ± 0.0183	87%	0.01>
Lead(ppm)	0.006 ± 0.014	0.001 ± 0.006	57%	0.01>
Cadmium(ppm)	0.0020 ± 0.003	0.00025± 0.000123	59%	0.01>
Manganese(ppm)	0.012 ± 0.063	0.0025 ± 0.0223	65%	0.01>

The Total Dissolved Solids (TDS) decreased significantly ($p < 0.01$) between 301.0 ± 10.6mg/L and 201.7±/3.5mg/L with a removal efficiency of 33.0% as indicated in Table 1. This decrease is not as big as done by other parameters; however, it could be attributed to the fact that certain suspended solids and other relevant ions have been eliminated to some degree during the course of coagulation and flocculation process [24].

The remaining part of TDS is a highly soluble salt as the plant has not yet acquired the modern desalination technologies such as reverse osmosis and pass through the normal treatment [9,22].

The overall loss of hardness was also noted to be large (39.5%) which is also a testimony to the good removal of the hardness forming ions. Magnesium (75 %) and Calcium (57 %) were the best ion. It is very probable that such huge reduction is due to co-precipitation, or retention on the surface of the so-formed flocs of aluminum or iron hydroxide in the process of coagulation, but not the actual chemical precipitation [22].

The trace metals were also lowered ($p < 0.01$) with majority of the trace metals being copper (87%), iron (68%). Such extensive copper and lead removal rate can be attributed to the fact that they are highly adsorbed on the resulted flocs and they were eventually removed during the sedimentation and filtration stages [9,22]. The lead concentration was decreased to from 0.014 ± 0.006 mg/L to 0.006 ± 0.001 mg/L that was fully acceptable to the drinking water standards which was recommended by World Health Organization[23].

The explanation of such differences in removal efficiencies with the metals under study is given by the difference in the chemical speciation and solubility behavior of the metals within the operation pH of the plant. Finally, the low percentage Relative Standard Deviation of all the measurements is (RSD< 5%) which means that there is a high level of analytical accuracy and reliability of the used Flame Atomic Absorption method [20].

3.3. Graphical Comparison of Raw and Treated Water

Further illustrate the performance of the treatment, a graphical variation of the untreated and the treated concentration is illustrated in Figure 1.

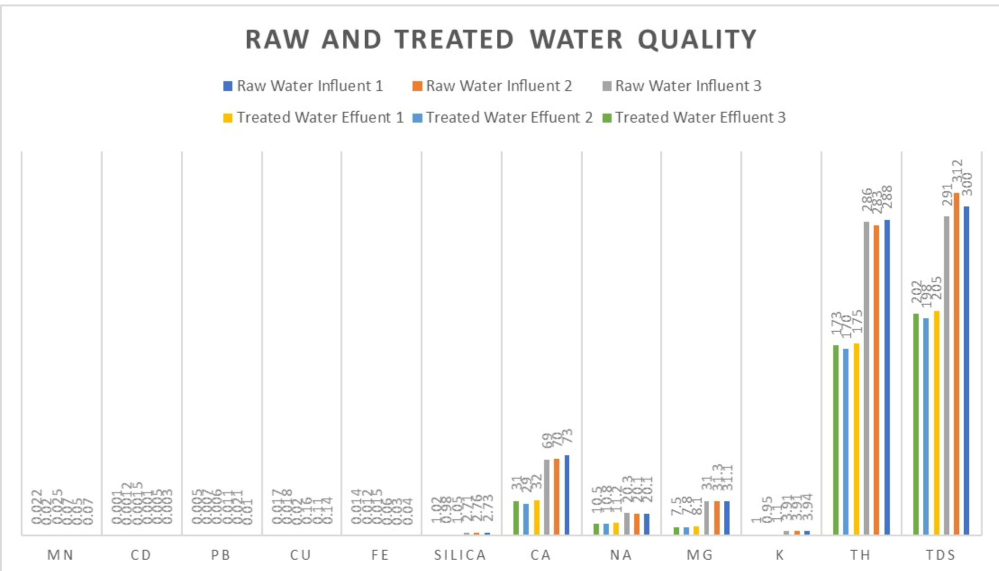

Figure 1. Raw and treated water concentration comparison.

Figure 1 is a graphic representation of the negative trend in all parameters, but magnesium, calcium and copper have reduced sharply.

3.4. Removal Efficiency Analysis

The calculated removal efficiencies are graphically summarized in Figure 2. The removal efficiency of the parameters measured was also very different as shown in Figure 2. The highest removal rate of 87% and 75% recorded by the copper and the Magnesium respectively means that it is effective in the removal of heavy metals as well as reducing divalent cations. On the other hand, the TDS also had a lesser capacity of removing, i.e. 33 %. This is equivalent to the constraints of the traditional treatment procedures, which are mainly aimed at the elimination of suspended solids, turbidity against highly soluble salts [9,22,24].

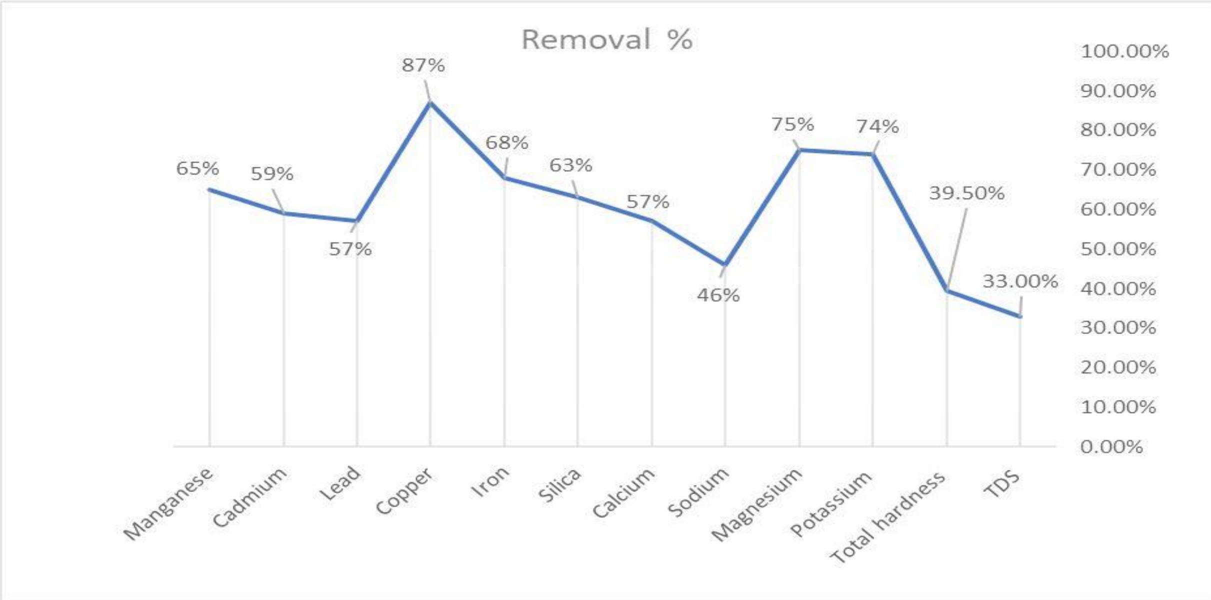

Figure 2. Removal efficiencies of Heavy metal in water.

3.5. Regression Analysis

Linear regression analysis was performed between raw and treated concentrations to evaluate operational consistency. As shown in Table 3. The treatment consistency and stable operation of the plants are indicated by the coefficient of determination ($R^2 = 0.94$).

Table 4. Linear regression analysis between influent and effluent concentrations.

Parameter	Regression Equation (y =ax + b)	R2	Interpretation
All Parameter	y = 0.58 – 2.31	0.94	Strong treatment consistency

3.6. Water Quality Index and Health Risk Assessment

Treatment of water was observed to positively affect the Water Quality Index (WQI) of the raw water being 50.9, and the treated water being 34.2 showing that there was much change in the general classification of the water as being good or poor. Table 4 contains the results of health risk assessment. The Hazard Index (HI) was reduced to 0.08 after the treatment compared to 0.17. The HI values were also not too close to the one mark (HI > 1), so the treated water should not be associated with excessive non-carcinogenic health effects on the consumers.

Table 5. Hazard Quotient (HQ) and Hazard Index (HI) for heavy metals.

Metal	Mean Before (ppm)	Mean After (ppm)	HQ Before	HQ Aftwr
Lead (Pd)	0.014	0.0060	0.11	0.05
Cadmium (Cd)	0.0030	0.0012	0.06	0.03
Hazard Index (HI)	----	----	0.17	0.08

3.7. Comparative Analysis and Compliance with International Standards

A stringent analysis of the analytical results of the treated water samples (effluent) against the World Health Organization (WHO) guideline as well as the Iraqi Drinking Water Standards (No. 417) was conducted. The findings indicated complete adherence to all the considered parameters. With regard to heavy metals, the mean Lead (Pb) decreased to 0.006 ± 0.001 mg/L which is very low as compared to the maximum acceptable level of 0.01mg/L. In the same tone, Cadmium (Cd) was observed to contain trace levels of 0.00012mg/L which is far less than the top limit of 0.003mg/L which means that there is indeed high effectiveness of the sedimentation and filtration units in the plant in removing the fine pollutants [23]. On the important constituents, Copper (Cu) was stabilized at 0.0183mg/L, which is relatively very low as compared to WHO, 2.0mg/L. Total Dissolved Solids (TDS) removal efficiency was 33 yet the ultimate outcome of 201.7 ± 3.5mg/L is still in the range of palatability of drinking water that is excellent. The Water Quality Index (WQI) in its turn shifted to a better level, i.e., the marginally polluted (50.9) to the Good (34.2) level of the raw water and in the treated effluent, respectively [17]. When such results are compared to the previous environmental analysis of Iraq, the Copper removal efficiency of the Al-Shirqat plant (87%) is more than the result of the regional evaluation of the tap water implying that the coagulation processes are effective [7]. Further, the concentrations of the heavy metals in this study were lower than that in the Khabur River which can be attributed by the fact that industrial discharging in the current study area was low [25]. Finally, the reduction of Hazard Index (HI) to 0.08 that is significantly lower than the unity level (HI<1) is in line with the findings of determining that the treated water does not harbor any severe non-carcinogenic health hazard to the long-term human use [22].

4. Conclusion

The present study examined how the treatment process can be effective and used to enhance the quality of water and reduce potential health hazards. The results showed that the system of treatment was highly successful in enhancing all the physicochemical parameters ($p < 0.01$), with a removal efficiency of a range of 33 to 87%. The best result came with copper (87%) and magnesium (75%) thus demonstrating that the divalent cations and trace metal were removed effectively during the coagulation and filtration processes. Moreover, the heavy metal concentration particularly of lead and iron were minimized to a level of satisfying the world health organization drinking water standards to the latter.

On health risk mitigation, Water Quality Index (WQI) took a reduction of more than fifty percent with the water quality of 50.9 in the raw water declining to 34.2 in the effluent and therefore shifted in to a "good" water quality category. The fact that, the final HI < 1 is the assurance that the treatment of influent water to effluent has no any significant non-carcinogenic health risk in the long-run, and that the coefficients of influent and effluent in the equation are very close to 1 (R2 = 0.94) indicates that the plant is highly consistent and stable throughout the course of its operations. Overall, the integrated management of the Al-Shirqat plant was a highly effective and feasible answer to ensure the safety of drinking water, as well as to safeguard the human health.

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