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Analytical Study of Types and Quantity of Some Pharmaceutical Compounds in Treated Water from Khirbet Al-Samra Wastewater Treatment Plant in Jordan

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Abstract

This study was conducted to detect some organic compounds used in the pharmaceutical industry in the treated wastewater generated from the Khirbet Al-Samra wastewater plant in Jordan, this water is mixed with fresh water at King Talal dam and then used in irrigation in Jordan Valley. To estimate the number of organic compounds present in treated wastewater and study the seasonal variation (winter vs summer), a group of reference chemicals were used, including commonly used pain relievers: Ketoprofen, Naproxen, Diclofenac, Ibuprofen, and two antibiotics, including Sulfamethoxazole, Erythromycin, in addition to Carbamazepine. Liquid chromatography-mass spectrometry is used for the analysis of some pharmaceutical compounds. Results of the study showed that the concentration of Diclofenac was 6.4µg/L in winter samples compared with 4.2µg/L in summer samples. Naproxen was also present in the samples at relatively high concentrations of 5.2µg/L in winter and 3.5 µg/L in summer. Ibuprofen concentrations ranged between 3.7 and 1.1µg/L in winter and summer samples. Carbamazepine was present in the winter and summer samples at 1.3µg/L. Other compounds, including Ketoprofen, Sulfamethoxazole, and Erythromycin were not detected in both winter and summer samples. It can be seen that the concentration of detected pharmaceutical compounds in summer samples for Diclofenac, Naproxen and Ibuprofen was less than that in winter samples. The presence of some pharmaceutical compounds in treated water is not considered a major health problem. However, it is still important to monitor and evaluate the content of pharmaceuticals in treated water that is used to irrigate crops.

Paper type: Short Communication

Keywords: Treated wastewater, pharmaceutical compounds, Liquid Chromatography-Mass (LC-Mass), seasonal variation.

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Introduction

Water scarcity is a serious challenge affecting the future of all Jordanians. The Ministry of Water and Irrigation in Jordan works according to health and quality specifications related to treated water and works to ensure the availability of water that meets the specifications for use in irrigating crops (Cotruvo and Bell, 2014). The water quality is regularly tested and monitored to verify its conformity with Jordanian and international specifications and standards for the reuse of treated water in agriculture. Despite severe challenges, Jordan is one of the few countries in the world that has managed its limited water resources well as approximately 91% of treated wastewater is reused in agriculture (Ministry of Water and Irrigation, 2006). The quality of treated water may differ from one region to another in Jordan, as it may be affected by factors such as the source of raw water and the treatment processes used in each region (Abunaser and Abdelhay, 2020). Studies indicate the presence of a variety of different compounds in the treated water (Abdelhay and Abunaser, 2020).

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There are also various sources of volatile organic pollutants, such as industrial and agricultural pollutants. These pollutants include compounds such as volatile hydrocarbons and volatile organic solvents (Sun *et al.,* 2020; Lin *et al.,* 2020). There are also many interactive organic pollutants: such as organic compounds used in various water treatment processes, disinfectants and detergents. The frequent use of organic waste in agricultural production, such as the use of pesticides and fertilizers, leads to part of it being leaked into the water (Yang *et al.,* 2022; Bechmann, and Stålnacke, 2019). Wastewater treatment usually aims to remove organic and mineral pollutants in general, and some compounds are usually left in small quantities such as pharmaceutical compounds, some metals and other compounds (Kiemle and Fuchs, 2022). Some organic and pharmaceutical compounds remain after the wastewater treatment process (Jones *et al.,* 2001). Toxic dissolved and organic compounds were present in wastewater that came from agricultural fields irrigated with treated wastewater (Pedersen *et al.,* 2003). Although the toxicity of many of these compounds is poorly characterized, some may be harmful to human health (Guibal *et al.,* 2017). Water treatment processes aim to remove and reduce these organic compounds when possible, through the use of appropriate filtration, sedimentation and sterilization processes. Periodic testing and monitoring is also implemented to monitor the water quality and ensure that no harmful organic pollutants are present at elevated levels (Saravanan *et al.,* 2021). The concentration and type of organic compounds in treated water can vary depending on several factors, including the raw water source, the treatment processes used, and environmental conditions (Bavumiragira *et al.,* 2022). Wastewater is one of the main sources of environmental pollution that includes many compounds including pharmaceuticals. So, the different treatment processes must be evaluated to know if conventional and natural treatment technologies are efficient in the removal of these compounds (Guedes-Alonso *et al.,* 2020). Drug-derived organic compounds are usually detected in wastewater due to drug elimination by individuals via urine or faeces. The expected percentages of these compounds depend on several factors such as the amount of drug used, the quality of water used in the concerned area, and the sewage treatment methods used (Madikizela *et al.,* 2020). Reported that About 11 pharmaceuticals were detected in treated wastewater in Spain, the treated wastewater is generated from conventional purification technologies plants (Long *et al.,* 2022). In general, studies indicate that the expected levels of these drugs in wastewater are low in the range of nanograms to micrograms per litre of water enough to not affect the environment or human health (Yueh and Tukey, 2016) However, the presence of these drugs in wastewater must be monitored periodically to ensure water safety and to assess their impact on the aquatic environment. To encourage the use of treated wastewater in irrigation as an adaptation strategy to climate, change it is necessary to monitor their quality, therefore, the study aimed to detect some pharmaceutical compounds in the treated water generated from the Khirbet al-Samra plant in Jordan.

1 Materials and Methods:

1.1 Source of treated wastewater:

All samples were collected from treated water coming out of Khirbet al Samra wastewater treatment plant as shown in the image below. This plant receives wastewater from highly-populated areas of Amman the capital and Zarqa governorate This wastewater plant is the largest wastewater treatment plant in Jordan, with a peak flow of 840,000m³ each day, the facility treats an average flow of 267,000m³ of wastewater, serving a population of 2.2 million living in the Greater Amman and Zarqa areas (SIGMA JO, 2024), and uses advanced technologies to remove organic matter and other impurities from the wastewater. Multiple processes are carried out in the plant, including preliminary screening, aeration, sedimentation, coagulation, filtration and disinfection, intending to remove harmful substances and achieve the required quality standards.

1.2 Time of sampling

To estimate the amount of organic compounds present in treated wastewater and study the seasonal variation between winter and summer seasons, about 15 treated wastewater samples were collected in January. Samples were taken day after day during the month, starting from January, first. The 15 treated water samples were collected in June, day after day during the month, starting from June, first.

1.3 Treated wastewater samples

Treated wastewater samples were collected in brown glass bottles, immediately transferred to the laboratory, filtered through 0.6-mm glass fibre filters to remove fine particulates that could block the solid phase extraction (SPE) cartridges, and stored at 4°C until extraction within 24 hours of sampling. A gentle stream of nitrogen was used to evaporate the pooled extracts to dryness. The residues were reconstituted in 1mL of 50:50v/v water/acetonitrile with 0.1% formic acid and transferred into 2mL amber auto-sampler vials. Samples were collected from bottles of 1L, filtered stored at 4^0C storage conditions (Smyth 2006; Omotola and Olatunji, 2020).

1.4 Selection of the reference chemicals

The standard solutions of reference chemicals were used to determine the concentration of organic pharmaceutical compounds in treated wastewater samples. The selected eight human drugs (Ketoprofen, Naproxen, Diclofenac, Ibuprofen, and two antibiotics, including Sulfamethoxazole and Erythromycin, in addition to Carbamazepine) with a purity of > 98% were purchased from Sigma-Aldrich (Omotola and Olatunji, 2020). The pharmaceutical analysis was performed in the Zarqa University College laboratories.

1.5 Structures of reference chemicals

The reference chemicals include some commonly used pain relievers: Ketoprofen, Naproxen, Diclofenac, Ibuprofen, and two antibiotics, including Sulfamethoxazole and Erythromycin, in addition to Carbamazepine.

1.6 LC-Mass analysis

Agilent 1200 Rapid Resolution LC-Mass system (Agilent Technologies Inc., Santa Clara, CA) equipped with a Gemini C-18 column (150×2 mm, 3-µm particle size; Phenomenex, Torrance, CA, USA), coupled to an Agilent 6410 triple quadruple mass spectrometer with ESI ion source (Agilent). A binary gradient of 1.5% acetic acid in deionized water and 0.05% acetic acid in acetonitrile was used for chemical separation (Smyth, 2006; Omotola and Olatunji, 2020).

2 Results and Discussion

Treated water samples were analyzed using the standard method of water analysis (Jiang *et al.*, 2013). To detect some pharmaceutical compounds in two seasons (winter vs summer). The tested compounds include Ketoprofen, Naproxen, Diclofenac, Ibuprofen, and two antibiotics, including Sulfamethoxazole, Erythromycin, in addition to Carbamazepine. The first step of compound detection was the injection of standards into LC-Mass, then winter and summer samples were injected into LC-Mass to determine the concentration of pharmaceutical compound in all samples.

2.1 Injection of standards into LC-Mass.

The standards of Ketoprofen, Naproxen, Diclofenac, Ibuprofen, and two antibiotics, including: Sulfamethoxazole, Erythromycin, in addition to Carbamazepine were injected into LC mass. These solutions are used as a reference with previously known concentrations of the chemical compound. The LC-Mass reading for some of standard solutions is seen in **Figure 1**. The concentrations of chemical compounds in the treated water sample were compared with the readings of these standard solutions.

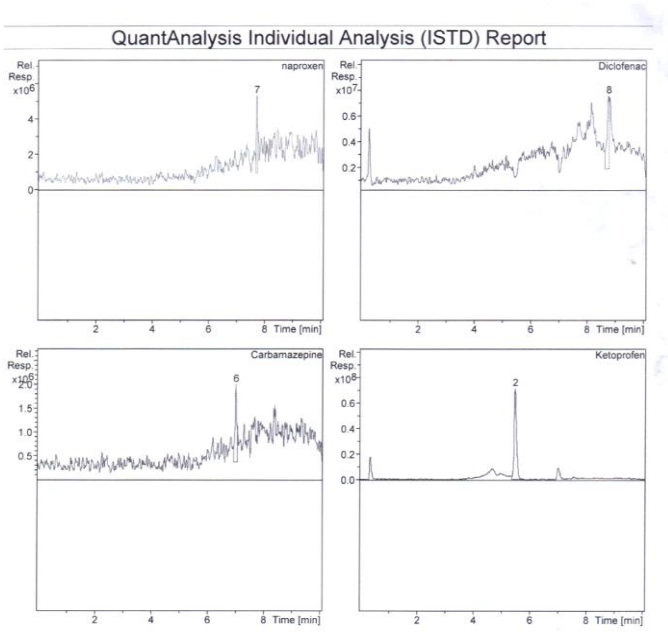

Fig. 1 LC-Mass reading for some of standard solutions**.**

2.2 Detection of pharmaceutical compound in treated water samples

Pharmaceutical compounds were detected in the treated water samples collected from the Khirbet Al-Samra wastewater treatment plant in Jordan. Although there were difference in the concentrations of the compounds between the summer and winter seasons, these concentrations were present in low percentages that do not affect the use of this water in agriculture (WHO, 2012). Pharmaceutical compound concentrations that were detected in water samples (winter and summer) are listed in **Table 1**. The

major detected pharmaceuticals in treated water samples were: Naproxen, Diclofenac, and Ibuprofen, while other compounds were found at very low concentrations.

2.2.1 Pharmaceuticals compounds in winter and summer samples

The maximum average concentration of Diclofenac was 6.4µg/L in winter samples compared with 4.2µg/L. Naproxen was also present in the samples at relatively high concentrations of 5.2µg/L in winter and 3.5µg/L in summer. Ibuprofen concentrations ranged between 3.7 and 1.1µg/L in winter and summer samples. Carbamazepine was present in the winter and summer samples at 1.3µg/L. Ketoprofen Lamotrigine Trimethoprim Sulfamethoxazole Erythromycin were not detected in either winter or summer samples. It can be seen that the concentration of pharmaceutical compounds in summer samples for Diclofenac, Naproxen and Ibuprofen was less than that in winter samples. The presence of pharmaceutical compounds in the treated water may be due to the drug being ingested by individuals and excreted from the body through the urine (Jones *et al.*, 2001). Given that the amount of water consumed during the summer is much greater than that consumed in the winter, it is expected that the concentration of pharmaceutical compounds will be less than that in the winter.

Table 1 Mean concentrations of pharmaceutical compounds in water samples.

No	Compound	Mean concentration (µg/L) in Winter	Mean concentration (µg/L) in Summer
1	Ketoprofen	0.05a*	0.00a
2	Sulfamethoxazole	0.06 a	0.28b
3	Erthromycine	0.05a	0.07a
4	Carbamazepine	1.34a	1.30 a
5	Naproxen	5.20 a	3.55b
6	Diclofenac	6.43a	4.23a
7	Ibuprofen	3.72 a	1.16b

*Mean followed by the same letter within the same row doesn't differ significantly according to Duncan Multiple Range Test (DMRT).

Conclusions

Some pharmaceutical compounds have been detected in treated water generated from Khirbit Al-Samra wastewater treatment its concentrations range in low levels and are not harmful to general health (WHO, 2012) in both winter and summer, with a difference in the concentration of compounds between summer and winter. The presence of some pharmaceutical compounds in treated water is not considered a major health problem. However, it is still important to monitor and evaluate the content of pharmaceuticals in treated water. It's important to monitor its impact on the environment and public health. In case of concentrations present, actions can be taken to improve water treatment or use additional techniques to remove the dangerous compounds.

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