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Physicochemical characterization and identification of pharmaceutical compounds present in pharmaceutical industry wastewater of Telangana State

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ABSTRACT

The chemical contamination of water supplies is one of the greatest problems facing humanity in the twenty-first century. The bioactivity and high solubility of pharmaceuticals and personal care items set them apart from other growing chemical contaminants in the environment. They might also have negative effects on people's and other living things' health. Drugs are released into the environment, primarily through wastewater, and eventually end up in surface and ground water. Despite this, compared to other chemical pollutants, medications got less attention as environmental contaminants (e.g. heavy metals and pesticides). Investigating the presence of some of the most often prescribed medications from a contaminated Lake Hussain Sagar in Hyderabad at locations connected to industrial discharges was the goal of this work. In order to achieve this, wastewater samples from the location were taken twice a week for four months, during which time the substances were identified using tandem LC-MS. In the influents and effluents of the contaminated Hussain Sagar Lake, a total of five (5) medicines have been discovered in amounts over the limit of detection. The investigated medicines' low amounts in the wastewater were found to be consistent with expectations. Ibuprofen (98.5 ng/mL) had the highest concentration, followed by diclofenac (31.4 ng/mL), levofloxacin (18.5 ng/mL), metrinidazole (11.4 ng/mL), and paracetamol (4.03 ng/mL). With a concentration range of 4.03-98.5 ng/mL, it is interesting to note that the levels of these medicines in the PIW did not significantly differ from those discovered in the untreated wastewater (influents). The findings of this study, which are corroborated by numerous other investigations, show that existing conventional wastewater treatment techniques are ineffective at removing such a large group of active and potentially dangerous contaminants from wastewater.

Key words: PIW, Hyderabad, Diclofenac, Levoflaxacin, Ibuprofen, Paracetamol.

INTRODUCTION

Pharmaceutical compounds (PCs) are a collection of various chemicals used in the analysis, prophylaxis, and treatment of diseases. In Nowadays, pharmaceutical chemicals of various therapeutic classes are employed excessively and widely around the world (Li et al. 2014). These substances include a wide variety of active substances with complex molecules that have many types of structures, functions, behaviours, physicochemical properties, and biological properties.

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They often include active ingredients, excipients, additives, inorganic salts, and other substances in the form of pills or liquid. They are created and employed because to their more or less specialised biological activity, and their ionic nature stands out as their most distinguishing feature (Kümmerer 2009). Pharmaceutical substances are typically divided into two categories: over-the-counter medicines and prescription-only drugs.

These developing pollutants have been known to persist in the environment for decades due to their varied and complicated structural makeup. Since pharmaceutical substances have been found in soil, sediments, surface water, and groundwater, their occurrence in the ecosystem is turning into a serious problem (Santos et al. 2010). In wastewater treatment plant effluent, surface waters like river streams, and less frequently in drinking water and groundwater, medications have mostly been found (Rivas et al. 2012). As a result of their operations, numerous pharmaceutical manufacturing enterprises are accountable for producing toxic and dangerous effluent. These businesses generate wastewater, which includes solids, liquids, biodegradable and non-biodegradable substances, etc. They have high levels of total suspended solids (TSS), biological oxygen demand (BOD), and chemical oxygen demand (COD) (Osuolale and Okoh 2015).

Due to the different ways that medicines are produced during different processes, pharmaceutical firms often do not produce consistent types of waste streams (Kavitha et al. 2012; Vuppala et al. 2012). Since medications can directly interact with humans and other species, their lipophilic, non-biodegradable nature, and a variety of biological activities make them a major problem (Ebele et al. 2017). Researchers have found drug residues in the terrestrial environment as well, with some pointing to the application of animal waste and bio-solids from wastewater treatment plants as manure to agricultural land (Ying et al. 2002). As a result of their hydrophobic character and low volatility, several medications are easily absorbed in sediments and soil. Consequently, the terrestrial ecosystem sees an increase in their concentration (Hernando 2006). Therefore, it is crucial to look into the dispersion and presence of pharmaceuticals in environmental matrices released by pharmaceutical enterprises. In order to accomplish this, the current study was designed to examine the physicochemical aspects of wastewater produced by the pharmaceutical industry (PIW) and to look for residues of regularly made drugs in both the PIW and the sludge.

Materials and Methods

Collection and preservation of samples

At locations connected to industrial discharges, samples of pharmaceutical industry wastewater and sludge were taken from a contaminated Lake Hussain Sagar in Hyderabad (Figure-1). The Hussainsagar to Musi river nala will cause greater stink, health risks, groundwater pollution, and, in the worst case scenario, inundation for residents of nearby communities. Gandhinagar, Ashoknagar, Himayatnagar, Chikkadpally, Barkatpura, and Nallakunta are all along the canal's path. The cause is that wastewater and highly toxic industrial waste will be routed through Hussainsagar and directly into the nala from the Kukatpally Nala.

Sampling points at several Hussain Sagar Lake locations show the location of the locals' primary places of worship. Due to the disposal of decorative items, plastics,

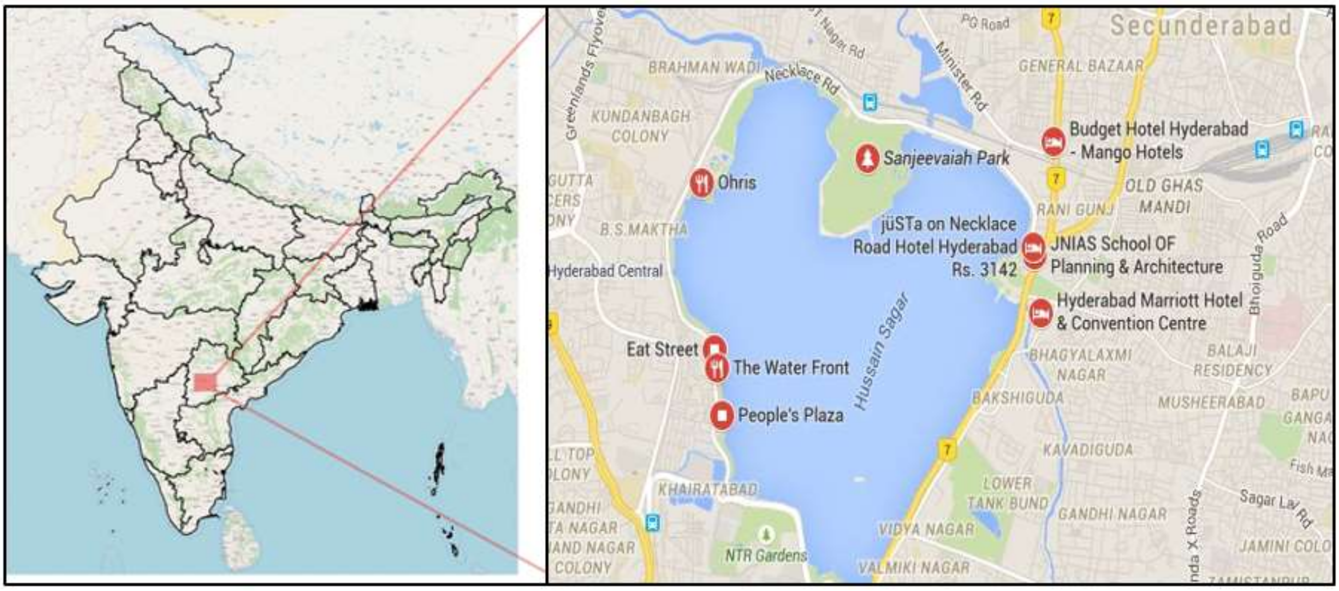

Figure-1. Sample locations of Hussain Sagar Lake, Hyderabad

clothing, flowers, coconut coir, piths, jute, and other religiously worn-out items, the physical look of this location appears to be unappealing.

The wastewater from scrubbers, washing and mixing processes, purification steps, and runoff from the pharmaceutical manufacturing facilities were all included in the pharmaceutical industry's effluent. At the point where wastewater was released into the open environment, samples were collected in amber-colored bottles, filtered using Whatmann filter paper, and stored at 4°C until use. The preservation process is shown in Table-1.

Table-1. Preservation procedure of PIW sample for analysis of various physicochemical parameters

Parameter	Preservation technique	Maximum storage duration
Colour	4 °C	24 h
Odour	4 °C	24 h
pH	Measured on sampling site	No storage
Alkalinity	4 °C	24 h
Sulfate	4 °C	7 h
Nitrate	40 mg Hgcl2 L-1 at 40 °C	-
COD	40 mg Hgcl2 L-1 at 40 °C	7 days

Analysis of physicochemical parameters of PIW

It was necessary to analyse PIW in order to assess the water's quality. It included the procedure for analysing the physicochemical pollutants found in a sample of wastewater. Merck India and Sigma Aldrich Private Limited provided the chemicals and reagents used in the study. By using the manual of the standard procedure for the study of water and wastewater, the physicochemical parameters of PIWW were evaluated (APHA 2011). pH, conductivity, colour, turbidity, TS, TDS, TSS, alkalinity, hardness, COD, chloride, sulphate, nitrate, sodium, and other parameters were examined.

Analysis of physicochemical properties of sludge

Sludge samples were obtained from a nearby contaminated site, and standard analytical techniques were used to determine their physical and chemical features (Jackson 1973).

Detection of pharmaceutical compounds present in pharmaceutical industry wastewater

Drugs found in wastewater were identified using the orthogonal Zelectrospray interface of a quadrupole-time of flight (Q-TOF) mass spectrometer (Q-TOF Xevo G2) made by Waters Micromass, Manchester, UK, and capable of both positive and negative ion operation. The Q-TOF mass spectrometer's greatest resolution indicated up to m/z 100000 with a full-width half-maximum (FWHM) >22500 (Boix et al. 2016). Data from mass spectrometry was collected with a time scan of 0.3 seconds and a m/z range of 50–1900. Between the sprayer and capillary, a potential difference of 3 to 3.5 kV was used for effective electroscopy. The source temperature was 120°C, and a 30 V cone voltage was supplied. Aqueous sample was used in the current study, and it was combined with methanol as a solvent before being placed in a glass vial. The vial was inserted into the evacuated ion source with the tip of the direct probe attached to the heating cable. The sample was ionised in a brief burst, which effectively caused the generated ions to "fly" into an evacuated tube of a certain length. These ions moved steadily in a straight line toward the detector, where the plot of % abundance was acquired. The operating system MassLynx version 4.1 (Waters) was used for data analysis.

Results and Discussion

Detection of pharmaceutical compounds present in PIW

In India, the pharmaceutical industry is expanding as a result of rising populations and increasing production rates. Although these industries directly dump into the water stream without using suitable treatment procedures, they do not adhere to national or international environmental regulations. Using QTOF mass spectrophotometry, pharmaceutical substances were detected in the current investigation. Ibuprofen, paracetamol, ciprofloxacin, and ofloxacin have all been found in the wastewater from pharmaceutical firms, according to Rosal et al (2010) study. The list of identified medicines in pharmaceutical industry water is provided in Table-2 below, and Figures 2-6 depict mass spectra along with their chemical structures.

Table-2: Drugs identified in pharmaceutical industry wastewater

Identified drugs	Molecular weight (g/mol)	Concentration
Ibuprofen	206.29	98.5 ng mL−1
Diclofenac	362.15	31.4 ng mL−1
Levofloxacin	361.36	18.5 ng mL−1
Metronidazole	171.16	11.4 ng mL−1
Paracetamol	151.16	4.03 ng mL−1

The detected drugs have been found in most of the samples as shown in Table-2. As expected, the concentrations of individual pharmaceuticals in the PIW

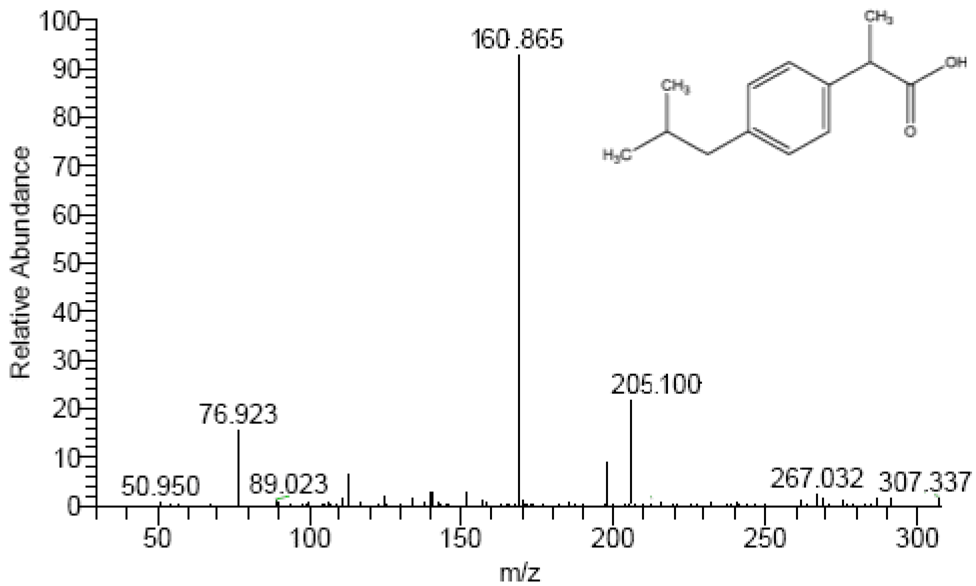

Figure-2. Full scan mass spectra for Ibuprofen precursor (205.100 m/z) and major fragment (160.86 5 m/z)

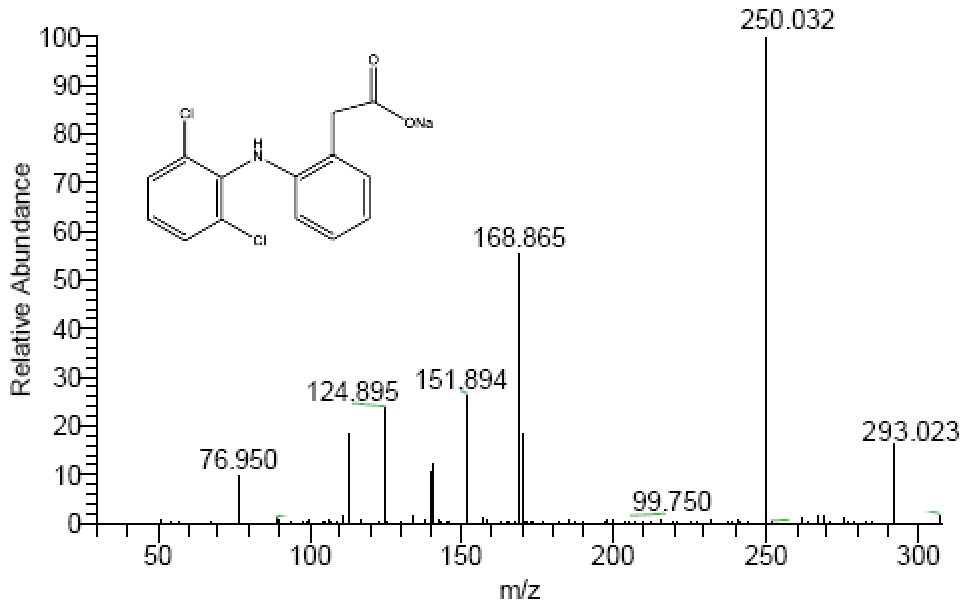

Figure-3. Full scan mass spectra for Diclofenac precursor (293.023m/z) and major fragment (250.032m/z).

were found to be low with an average concentration of 4.03–98.5 ng/mL. The highest detected concentration was for ibuprofen (98.5 ng/mL), followed by diclofenac (31.4 ng/mL), levofloxacin (18.5 ng/mL), Metrinidazole (11.4 ng/mL), and paracetamol (4.03 ng/mL) . Interestingly, the amounts of these pharmaceuticals in the PIW did not differ much from those found in the raw wastewater (influents), with a concentration range .03–98.5 ng/mL.

Mass spectra analysis

The positive ion mode is used to operate the equipment. The analytes that eluted according to the mass spectral analysis were Ibuprofen, Levofloxacin, Metronidazole, Paracetamol, and Diclofenac. Figures 2–6 display the extracted chromatogram, mass spectrum, and product ion spectrum for each analyte that has been found in the PIW at levels higher than the LOD. In PIW, a total of 5 medicines were discovered. Table-2 displays the concentrations of various medications. Some medications have lesser solubility and stay insoluble as the solid component in wastewater, despite the fact that the majority of pharmaceuticals have high solubility in water and hence remain soluble in the aqueous phase. The concentrations that were reported in this experiment only include the water-soluble fraction of the analytes because the samples were filtered before extraction.

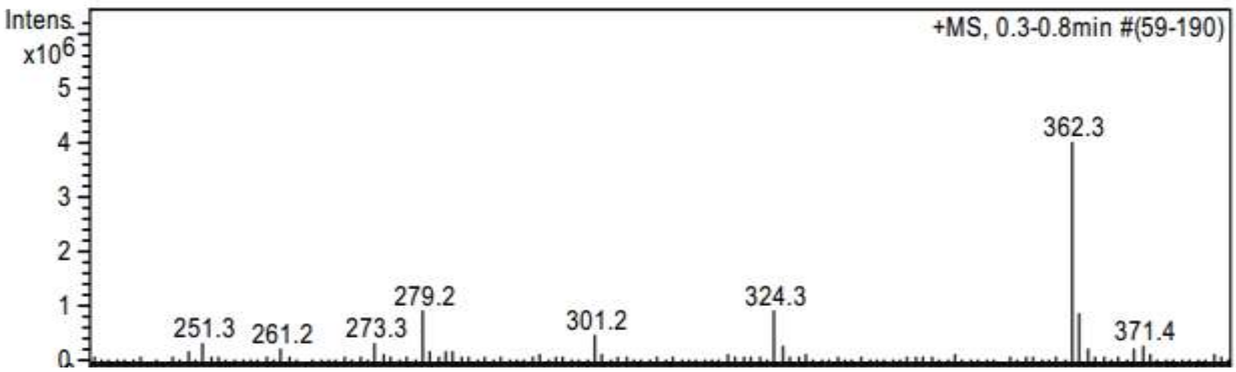

Figure-4. Full scan mass spectra of levofloxacin (279.2 m/z) and major fragment (362.3 m/z)

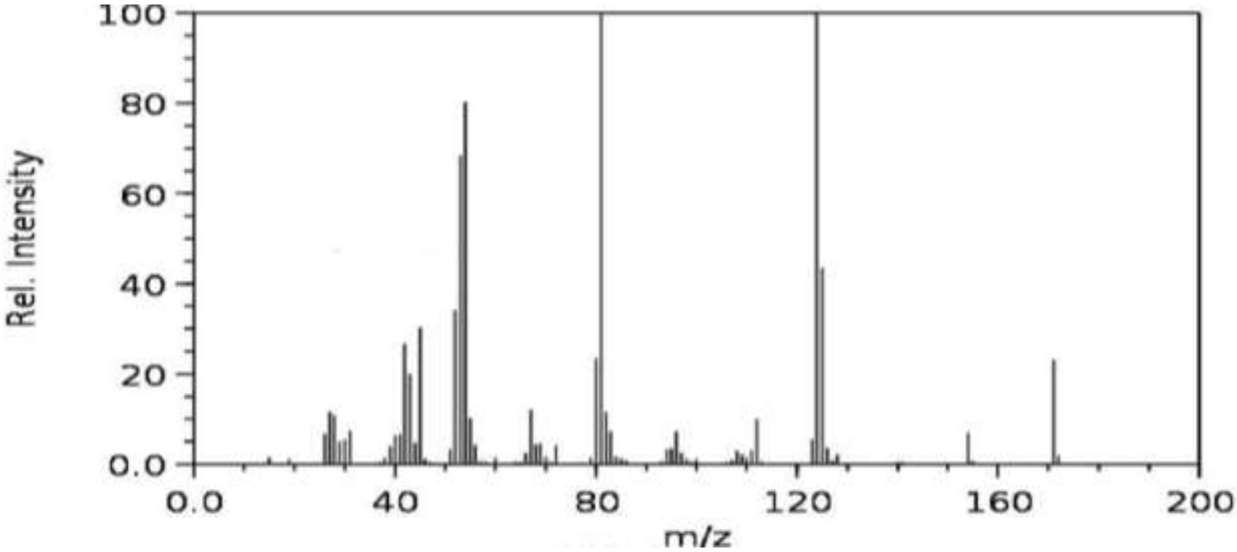

Figure-5. Full scan mass spectra for Metronidazole (80.024 m/z) and major fragment (122.4 m/z)

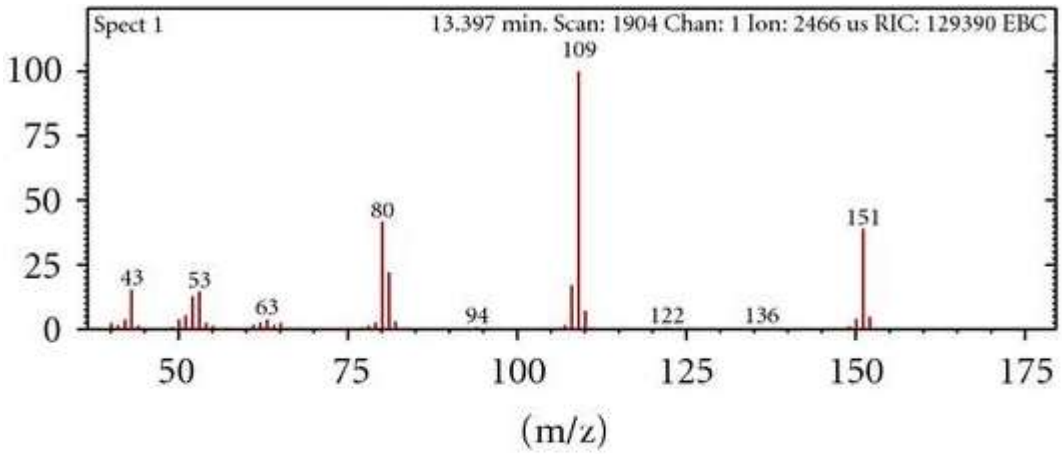

Figure-6. Mass spectrum of the chromatographic peak corresponding to the retention time of 13.4 min (109 m/z and 151 m/z)

The initial quadrupole selects the precursor ions for ibuprofen and diclofenac at 205.100 m/z and 293.023 m/z, respectively (Q1). After collision-induced fragmentation in Q2, the product ions of ibuprofen and diclofenac are measured at 160.865 m/z and 250.032 m/z, respectively. For both Q1 and Q3, a resolution of one unit (at half peak height) is applied. Figures 2 and 3 display the full scan mass spectra for ibuprofen and diclofenac, respectively.

The study's findings are in line with numerous reports in the literature that reported negligible levels of pharmaceuticals in municipal wastewater (Bartelt-Hunt et al., 2009, Gracia-Lor et al., 2010, Rosal et al., 2010). For instance, Rosal et al. (2010) observed the presence of almost 70 pharmaceuticals in the influents of municipal wastewater, with some of the chemicals (such as paraxanthine, caffeine, and acetaminophen) in the ng/mL concentration range and the others in the ng/mL range (Rosal et al., 2010). In a subsequent study by Gracia-Lor et al. (2010), influents of urban wastewater samples had traces of 13 out of the 20 medications they had examined, with salicylic acid having the highest quantity (276.7 ng/mL) (Gracia-Lor et al., 2010).

On the other hand, it was discovered that various medicines were present in low concentrations in the effluents of urban wastewater and receiving waters (Joss et al., 2008; Gracia-Lor et al., 2010; Bartelt-Hunt et al., 2009). This clearly shows that the majority of present wastewater treatment methods fall short of totally eliminating such pollutants. For instance, among all wastewater and receiving surface water samples in England, 5 medications (including propranolol, sulfamethoxazole, carbamazepine, indomethacine, and diclofenac) were discovered, with carbamazepine having the highest amounts (2.336 ng/mL). These chemicals' reported removal efficiency from wastewater ranged from 43% to 92% (Zhou et al., 2009). Another investigation found that both influent and effluent samples from 4 STPs in Seville, Spain, had traces of 5 out of 6 medicines (diclofenac, ibuprofen, ketoprofen, naproxen, carbamazepine, and caffeine) in the ng mL-1 concentration range. Between 6% and 98% of these medications were removed, according to reports (Santos et al., 2007).

The physico-chemical nature of most pharmaceuticals, which is the acidity and high solubility in water, is reported to be the main factor influencing the removal efficiency of pharmaceuticals from wastewater. Other factors that affect this efficiency include the climatic conditions, the type of wastewater treatment and its operational conditions (e.g., temperature, redox conditions, solids and hydraulic retention time), as well as the age of the activated sludge used in the plant. These conditions, particularly the final one, cause these chemicals to extremely poorly sorb to sludge, leaving them soluble in the aqueous phase (Gracia-Lor et al., 2012). It is also important to point out that some of the drugs found in the wastewater were also found in the sludge produced by the wastewater treatment systems. This is because these medications have a low solubility, which causes them to remain insoluble and show up in the sludge (Gao et al., 2012).

When a single medication is taken into account at low quantities, as those described in this study and other research, it may be considered that there aren't many health hazards connected to long-term exposure to such a medicine. However, even at low concentrations, there are health concerns connected to exposure to numerous medicines, their metabolites, and transformation products.

Conclusion

The results of the current investigation indicate that the majority of the physicochemical characteristics were outside of the predetermined ranges. The findings of this study, which are corroborated by related research in the literature, show that many medicines, together with their metabolites and byproducts of transformation, are not effectively removed during wastewater treatment operations (sometimes tertiary treatment, as in this study). This may imply that current methods of wastewater treatment are ineffective in entirely eliminating these substances, opening the door for them to enter the aquatic environment, contaminate water supplies, and endanger the health of people and other living things. Despite the fact that the observed levels of pharmaceuticals in the treated water are fairly low, it is important to consider the health concerns of prolonged exposure to a variety of medicines. As contaminants enter the soil and groundwater from wastewater discharge, parameters that are over the limits frequently result in poor water quality and soil danger. High levels of pollutants and persistent pharmaceutical residues remain stable over time, causing ongoing pollution and endangering the survival of living things. Improved treatment approaches should be suggested to address these issues and lower the concentrations of these parameters.

Conflicts of Interest

Authors declare that there is no conflict of interests regarding the publication of this paper.

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