Research article

Assessment of removal efficiency of pharmaceutical products from wastewater in sewage treatment plants: A case of the sewerage systems Ghana limited, Accra

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ABSTRACT

Pharmaceuticals put the environment at high risk when found in products of wastewater treatment plants, hence need to be removed efficiently. This study quantified selected pharmaceutically active compounds (PhACs) (diclofenac, aspirin, paracetamol, and ibuprofen) in wastewater and evaluated its removal efficiency from wastewater treatment plant (WWTP). Samples were taken from the WWTP of the Sewerage Systems Ghana Limited (SSGL) for 18 consecutive days. Both effluents and influents were tested in the laboratory to determine the concentrations of the various pharmaceutical products. The results reveal diclofenac as the PhAC with the highest concentration in the influent with an average of 121.31 µg/ml. Paracetamol recorded an average of 65.54 µg/ml, then ibuprofen with an average of 19.54 µg/ml. Aspirin was the PhAC with the lowest concentration in the influent with an average of 0.27 µg/ml. Further assessment was also done on the trickling filter (biological filter) which is part of the process plant at the secondary stage to assess how the trickling filter aids in the removal of these selected pharmaceuticals.

The average removal efficiency found were; diclofenac 74%, aspirin 93%, paracetamol 98%, and ibuprofen 99%. The technologies suggested for improvement, particularly for diclofenac, based on comprehensive literature were phototransformation and sorption of diclofenac onto sludge which occurs via absorption and adsorption, that can be adopted by the management of the WWTP at SSGL to help increase the removal efficiency of the selected PhACs. It was also identified that the trickling filter is the stage that substantially aids in the removal of the selected pharmaceuticals due to its special features.

1. Introduction

1.1. Background

Water pollution is an emanating issue in most areas across the globe especially in developing countries. Most water bodies and treatment plants have linkages with sewerage systems and other effluents from hospitals, mining companies, and chemical industries thereby posing a great threat to them (Zameerulla et al., 2018). Water bodies can be polluted in diverse ways. Amongst that, Xenobiotic organic compounds (XOCs) include pharmaceutically active compounds (PhACs), endocrine disruptors (EDs), and chemicals employed in industry and agriculture forms a greater proportion with varying levels of effects.

PhACs include an extensive range of compounds in diverse forms, purposes, activities, and performances and are used in the medical field to enhance human health. Several approaches for the removal of pharmaceuticals from wastewater have been presented in the literature and continue to draw much attention as a result of its toxic nature (Kanakaraju et al., 2014; Renita, 2017).

Wastewater treatment was fixated on protecting the environment from the negative impacts of wastewater discharges. Hence, suitable WWTPs were built to counter these kinds of pollutants. Different treatment technologies and procedures have since been adopted to advance the removal efficiency of such compounds which are unknown to nature and are termed xenobiotics. In the long term, the manufacturing of chemicals and some pharmaceuticals, its application, and its utilisation

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has been heavily linked with the high pollution of the environment and grave health consequence (Godheja et al., 2016).

Most of these chemicals are used excessively as personal care products, health care products, hygiene, and PhACs. Others such as mycotoxins, aflatoxins, some hormones are considered xenobiotics since they are foreign even though they are produced naturally. Xenobiotics mostly from domestic and industrial sectors spread in the water cycle and their detection is very difficult. Portugal could not detect any form of xenobiotics in the wastewater until 2005 where they detected some xenobiotics in their wastewater. Some of these were drugs, environmental pollutants, naturally occurring poisons, and industrial chemicals (Godheja et al., 2016).

Their presence in the environment poses a very hectic threat to environmental sustainability. Regions that do not have water reuse systems get their groundwater being contaminated by the wastewater. This can be a possible contamination source of drinking water supply aquifers.

Most of these xenobiotics are also a source of worry in urban water management since urban drainage, water supply, and wastewater treatment systems were formerly designed only to tackle issues such as water supply issues, sanitation issues, and flooding issues. Considering all these there is a need to get an understanding of how they are integrated, their source, their path, their fate, and their effects on both ecosystems and humans. Most of these xenobiotics are freed into the environment rendering the way they are used for instance the pharmaceuticals and the personal care product. These types of xenobiotics come into the environment day in day out as a result of surge in population, urbanization, industrialization, and agricultural malpractices and their effects have not yet been examined (Kumar and Pal, 2018).

Pharmaceuticals are intended to control the endocrine and immune systems and cellular signal transduction and have the likelihood to hinder the existence of some organisms in the environment. That notwithstanding some illegal drugs form new classes of chemicals with a potential of unknown effects and psychoactive properties to the aquatic environment (Deo and Halden, 2013; Kapelewska et al., 2018). The incidence of these drugs and other xenobiotics in water resources in several countries such as the Italy, U.S.A, and others of which Ghana is not an exception is the reason that necessitates the study of removal of pharmaceuticals from sewage treatment plants (Zuccato et al., 2006).

There are several methods of treating pharmaceutical wastewater as a feature of water management. In particular, a new approach graphene applications in water treatment have been reported in detail (Kumar et al., 2018). Kumar et al. (2019) further used Functionalized Nanosize Graphene and Its Derivatives for Removal of Contaminants in waste water. Moreover (Tatarchuk et al., 2019), employed green and environmental friendly substances for the treatment of Inorganic and organic pollutants in water. Also (Bourdón, 2019), characterized graphene and assessed its usage in reducing Trihalomethanes. Anku et al. (2019) assessed Photocatalytic degradation of pharmaceuticals making use of graphene-based substances. Siddiqui et al. (2019) employed Graphene Oxide Nano-hybrids in removing arsenic from water. Nujić and Habuda-Stanić (2019) utilized Graphene Oxide Nanocomposite in removing harmful metal ions in potable Water and was very Effective. Bao (2019) employed catalytic ozonation of aromatics in aqueous solutions over graphene and their derivatives. However, this study focuses on the removal efficiency of pharmaceutical products from wastewater in the Mudor Sewage Treatment Plant.

2. Materials and methods

2.1. Sewerage systems Ghana limited treatment plant

The WWTP of the SSGL is located in Accra, Ghana. The Taysec Construction built and inaugurated the plant in the year 2000 and after a couple of years of operations, it was shut down as a result of lack of financial pressures and maintenance issues but was then overhauled and put into operation in the year 2017 (Ahmed et al., 2018). The WWTP collects wastewater from Osu, Labone, High Street, Ministries, some areas Dansoman, Korle Bu, and Accra Central in Greater Accra Region of Ghana. Pump stations can be found in most of these areas that pump wastewater into the plant which generates a discharge flowrate of 16,000 to 18,000 m^3 per day (Ahmed et al., 2018).

2.1.1. The Mudor plant layout

The Mudor plant layout is as shown in Figure 1. The plant encompasses a course screen, grit chamber, fine screen before the UASB tank. Next is to this unit is the distribution boxes, the biological filter is also known as the trickling filter and finally the sedimentation tank. The screened wastewater is released into a receptacle and then deposited to the finer screen compartment, to trap objects of smaller sizes. The grit and screened materials find their way in waste chute that is deposited into a bin for disposal. The product from the grit chamber is channelled to primary distribution boxes. These boxes ensure an even distribution of flow to the biological reactors (UASB and trickling filters). The products from the primary distribution boxes feed the secondary and tertiary distribution boxes. The tertiary distribution boxes are connected to the downpipes and sends wastewater to the bottom of the reactors in the plant. Anaerobic by-products like methane, carbon dioxide, and hydrogen sulphide are formed. The produced gas from the reactors is then collected via gas collector hoods to avoid the release of biogas into the surroundings. Effluent from the UASB reactor flows to the trickling filter by gravity which then flows to the sedimentation tanks for fine solids to settle. Further organic removal is achieved before effluent goes to the final sampling chamber and is discharged into the receiving waterbody. Figure 1 shows the flow chart of the Mudor wastewater treatment plant of SSGL.

2.2. Selected pharmaceutically active compounds

The aim of this study is to evaluate the efficiency of the WWTP in removing pharmaceutical products from wastewater. However, four PhACs including paracetamol, aspirin, ibuprofen, and diclofenac were selected. The selection of these PHACs was influenced by the fact that they are the ones commonly used in the health sector in Ghana and elsewhere in Africa.

2.2.1. Paracetamol

Paracetamol is known to cause a potential risk in the environment when found in wastewater. This makes it one of the most important PhACs in hospital wastewater. Paracetamol is a common analgesic and antipyretic drug and has widespread usage as the raw material of many drugs (Al-Itawi, 2020). Several researchers have studied the treatment of paracetamol using physio/chemical methods, such as adsorption. In general, membrane separation technologies and adsorption are the most common methods in paracetamol removal from wastewater (Ayyash et al., 2015; Al-Itawi, 2020).

2.2.2. Aspirin

This PhAC marketed as aspirin in 1899 and used as symptomatic relief of fever, pain, and inflammation is an acetylsalicylic acid that was first used in an industrial environment in 1897 (Patrono, 2019). Aspirin is fast absorbed in the upper intestine and the stomach with plasma levels peaking at 30–40 min after ingestion (Patrono, 2019). It is used in lessening stroke, heart attacks, and anticancer effects. The removal of this acetylsalicylate is important because it has a 2–3 h half-life time and cannot be metabolized completely (Chegeni et al., 2019).

2.2.3. Ibuprofen

Ibuprofen is a PhAC which when found in the environment, can pose a threat to algae, fish, and macroinvertebrates. It is broadly used nonsteroidal and anti-inflammatory drug that exhibits anti-inflammatory and analgesic actions and it is the first approved drug of propionic acid derivatives (Logu et al., 2019). It relieves numerous forms of pains and
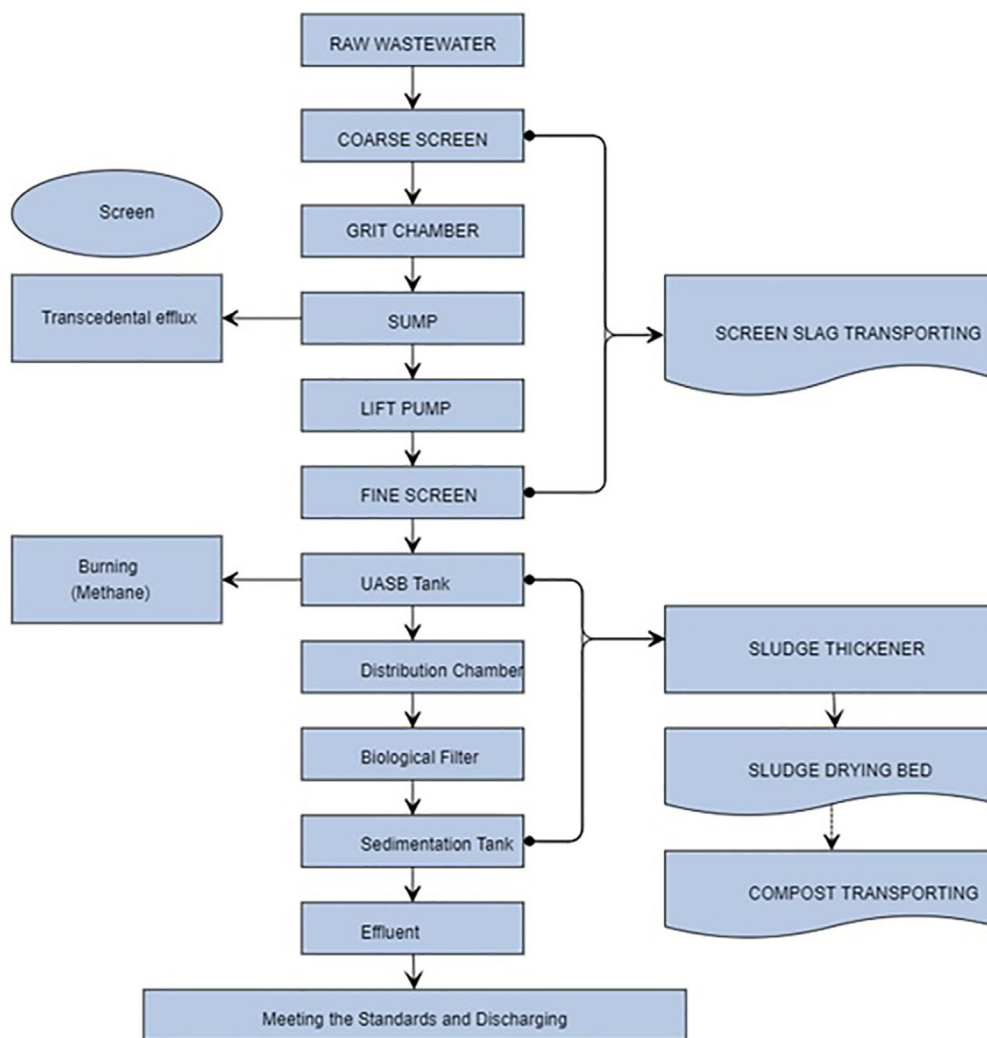
Figure 1. Process flow chart of the Mudor wastewater treatment plant (Ahmed et al., 2018).

discomfort such as dysmenorrhea, muscular pain, headache, toothache, and backache as well as inflammation (Logu et al., 2019). Ibuprofen when found in the body, almost completely metabolizes when it comes into contact with the carboxy-ibuprofen, inactive metabolites, and 2-hydroxy-ibuprofen (both eliminated in urine) through oxidative reaction (Logu et al., 2019).

2.2.4. Diclofenac

Diclofenac is a known anti-inflammatory product, often found in surface waters, wastewaters, and effluents. It is also known to adversely affect numerous environmental species already at concentrations of ≤1 µg/l (Vieno and Sillanpää, 2014). It is a non-steroidal anti-inflammatory drug used either as a topical gel or as an oral tablet. Diclofenac is administered orally or topically. It undergoes almost total biotransformation in the human body with topical gel adsorption of 6–7% (Vieno and Sillanpää, 2014). Between 20–30% of the orally administered dose is released in faeces and 65 and 70% in urine as metabolites or the parent drug (Vieno and Sillanpää, 2014). The majority of diclofenac is metabolized in the human system and only 1% of the dose consumed is excreted as un-metabolized.

2.3. Wastewater sampling

Two grab samples of the wastewater were taken each day continuously for sixteen (16) days, one from the influent point of the Mudor Wastewater Treatment Plant-SSGL and the other from the effluent point. The grab samples were taken between 12 noon and 1 pm each day where the air temperature is expected to be highest. This is based on the observation that maximum loads are received by the WWTP at that time. Amber high-density polyethylene (HDPE) bottle, rinsed previously with ultrapure water at the laboratory, and subsequently with the water to be sampled before sample collection was used for the collection of the wastewater.

Each grab sample was transported to the laboratory in a cool box at 4 °C temperature where it was tested and analyzed for concentrations of PhACs present.

Two other grab samples were collected on the seventeenth (17th) day and another two on the eighteenth (18th) day from the trickling filter (biological filter) which is the secondary treatment stage of the process plant. One grab sample of the wastewater entering the trickling filter and one grab sample taken from the wastewater leaving the trickling filter on each day. This was done to assess how the trickling filter aids in the removal of these selected pharmaceuticals.

2.3.1. Sample preparation, pharmaceuticals extraction and clean-up

Before Solid-Phase Extraction (SPE) was used, samples were filtered with Whatman filter paper (No. 10). 4mL MeOH and 6mL distil water was used to precondition Water Oasis hydrophilic-lipophilic balance (HLB) cartridge before use following the protocols used by Azanu et al. (2018). 1 litre of the sample was filtered using a 0.45 µm millipore filter to get rid

of impurities. A litre of the filtered sample was passed through the cartridge at a flow rate of 5–8 mL/min utilising a vacuum extraction manifold. Subsequently, the cartridge was washed using 10 mL of ultra-pure water and was later dried in air for 5 min. Acidified methanol (10mL of MeOH, 3mL of 0.5 N HCL) was used to elute the analyte into a glass test tube. The extracts were decreased to a volume of 100 μL under a flow of nitrogen gently, and the volume was extended to 250 μL using water/methanol (9:1) mix (Mahmood et al., 2019). The product was then filtered in 0.45 μm filters and further sent to autosampler vials and 20μl injected into the HPLC.

2.4. Determination of analgesics

2.4.1. Standard preparation

2.4.1.1. Diclofenac and aspirin. Standards of diclofenac and aspirin were obtained from Merck, Germany with >99% purity. For diclofenac and aspirin, 1mg of each was weighed into a beaker and dissolved with 5ml of the mobile phase, acetonitrile (1% acetic acid in water (80:20 v/v)). The solution was then transferred quantitatively into a 100ml flask and topped up to the mark. Serial dilution in concentrations ranging from 0 -10 ug/ml was prepared as the calibration standards.

2.4.1.2. Paracetamol and ibuprofen. Standards of paracetamol and ibuprofen were obtained from Merck, Germany with >99% purity. A stock solution was prepared with 1mg of paracetamol and 10mg of ibuprofen into a beaker and dissolved with 5ml of the mobile phase, acetonitrile (1% acetic acid in water (65:35 v/v)). The solution was then transferred quantitatively into a 100ml flask and topped up to the mark. Using serial dilution, the following calibration solution concentrations were prepared, paracetamol (ranging from 0 - 10 ug/ml) and ibuprofen (ranging from 0 - 16 ug/ml).

2.4.2. HPLC analysis
To detect the pharmaceuticals, present in the wastewater, a Cecil Adept Binary Pump HPLC with Wave Quest DAD Detector (Cambridge, UK) was used for all the analysis. The conditions used in detecting these pharmaceuticals (analgesics or group of analgesics) were as follows:

2.4.2.1. Diclofenac and aspirin. For diclofenac and aspirin, the mobile phase was acetonitrile (1% acetic acid in water (80:20 v/v)) pumped at a flow rate of 1 ml/min. The detection wavelength was set at 250nm. Agilent Zorbax C18, 4.6 mm × 250 mm, 5μm was used as a column with a temperature of 30 °C (Mahmood et al., 2019). 0.07 μg/ml was the Limit of Detection (LOD) for diclofenac and aspirin were 0.15 μg/ml 0.20 μg/ml respectively. Limit of Quantification (LOQ) for both chemicals was 0.50 μg/ml.

2.4.2.2. Paracetamol and ibuprofen. For paracetamol and ibuprofen, the mobile phase was acetonitrile (1% acetic acid in water (65:35 v/v)) and pumped at a flow rate of 1 ml/min. The detection wavelength was set at 230nm. SunFire C18, 4.6 mm × 150 mm, 5μm was used as a column with a column temperature of 30 °C (Mahmood et al., 2019). Limit of Detection (LOD) for paracetamol and ibuprofen were 0.06 μg/ml and 0.90 μg/ml respectively. was the Limit of Quantification (LOQ) for paracetamol and that of ibuprofen were 0.20 μg/ml and 2.00 μg/ml respectively.

2.4.3. Quality assurance for analytical method
Precision and trueness studies were carried out using recovery studies by spiking five (5) blank samples with the target analgesics at 2ppm and 10ppm respectively. Recoveries % were 93 ± 1.05, 91 ± 0.74, 95 ± 1.46, 93 ± 0.87 for diclofenac, aspirin, paracetamol and ibuprofen respectively. The calibration curve for target analgesics exhibited good linearity with a coefficient of determination (R^2) of 0.998. There were no detectable amounts of m-dopa for the blank samples run periodically.

The coefficient of variation was less than 15% for replicates and also for intra and inter-day precision.

2.5. Removal efficiency of the PhAC's selected

In evaluating the removal efficiency of the WWTP for the selected PhACs, the following equation was adopted as was used by Gaffney et al. (2017).

The removal efficiency of the WWTP was determined using Eq. (1);

$$\text{Efficiency}(\%) = \frac{C_{inf} - C_{eff}}{C_{inf}} \times 100 \tag{1}$$

C_{inf} = *the* average influent concentration of the measured PhAC
C_{eff} = the average effluent concentration of the measured PhAC

Computation was done to determine the removal efficiency of the WWTP for the selected PhACs based on the results obtained from the analysis.

2.6. Technologies to reduce PhACs

Further technologies that could be used to decrease the concentrations of the selected PhACs in the wastewater mainly diclofenac were suggested based on its effectiveness as was reported in related literature.

According to (Zhang et al., 2008), phototransformation was recognised as the main destructive process for, particularly diclofenac in lake Greifensee in Switzerland. It was presented by (Buser et al., 1998; Poiger et al., 2001; Tixier et al., 2003) that out of the total diclofenac concentration entering the lake, 90% was removed and is attributed to photolytic degradation. In the research by (Buser et al., 1998), diclofenac underwent rapid photodegradation when the water was subjected to sunlight. Other literature (Andreozzi et al., 2003; Pérez-Estrada et al., 2005) reported the direct photolysis of diclofenac and other PhACs found in the aquatic environment.

According to (Vieno and Sillanpää, 2014) sorption to membrane bioreactor sludge is slightly higher than activated sludge. An STP in Sweden showed that diclofenac concentration reduced by 50% during the pre-treatment process of sewage by removal of grit and primary sedimentation (Zorita et al., 2009). This could mean that diclofenac interacts with the sludge through adsorption. It has been reported that sorption of diclofenac to sludge could be a way of removing diclofenac by WWTPs (Martín et al., 2012; Suárez et al., 2012; Verlicchi et al., 2012).

However (Joss et al., 2005), reported that even when extreme solids retention time (SRT) was applied, no acceleration of elimination rates of diclofenac was noted. Similarly (Suárez et al., 2012), noted no association between SRT and the elimination of diclofenac. An increase in the elimination of certain pharmaceuticals such as ibuprofen has been associated with hydraulic retention time (Vieno and Sillanpää, 2014).

2.6.1. Physical and chemical parameters of the WWTP

2.6.1.1. pH. Table 1 presents the physical and chemical properties of the WWTP. The mean pH values of the final product, Plant reactor effluent, Tricking filter effluent and final effluent were 8.96, 6.7, 7.51, 7.5 and 7.45 respectively. The pH of the influent is alkaline which may be attributed to the use of Sodium Hydroxide in washing fermenters which could be the main source of high pH in the alkaline range. The pH values for the UASB reactor effluent was close to a neutral range due to the fact that the reactor serves as a buffer zone. The mean value for the Final settling tank and final effluent was in the alkaline level and this favours bacteria reaction serving as after-treatment of the UASB reactors.

2.6.1.2. Dissolved oxygen (DO). The mean DO values were 0.46 mg/l, 0.58 mg/l, 5.26 mg/l, 4.24 mg/l and 4.24 mg/l for the final influent,

Table 1. Characteristics of sewage at the different phases and comparison of effluent with EPA Ghana 2000, guidelines (Awuah and Abrokwa, 2008).

Parameter	Final influent mean values	UASB reactor effluent	Trickling filter effluent	Final settling tank effluent	Final effluent mean values	Total efficiency of the plant (%)	EPA Ghana guidelines 2000
pH	8.96 ± 0.98	6.7 ± 0.19	7.51 ± 0.13	7.5 ± 0.14	7.45 ± 0.14	-	6–9
Dissolved oxygen (mg/l)	0.46 ± 0.26	0.58 ± 0.21	5.26 ± 0.32	4.24 ± 1.08	4.24 ± 1.08	-	-
Turbidity (NTU)	1923 ± 646	265 ± 44	207 ± 62	125 ± 50	$122 \pm 5e0.27$	-	75
Total solids (mg/l)	3200 ± 2571	1011 ± 130	1038 ± 135	966 ± 94	958 ± 93.78	68.8	–
COD (mg/l)	3173 ± 1528	340 ± 74	310 ± 69	145 ± 21	146 ± 20.62	94.4	250
BOD (mg/l)	1206 ± 397	73 ± 16.2	42 ± 114	23 ± 5.7	23 ± 5.74	98.1 50	
Ammonia-nitrogen (mg/l)	4.3 ± 1.73	19.6 ± 2.4	7.9 ± 1.4	2.6 ± 0.7	2.6 ± 0.68	39.5	1.5
Nitrate-nitrogen (mg/l)	29 ± 2.82	6.0 ± 1.6	16.6 ± 2.5	22.1 ± 0.83	22.1 ± 0.83	23.8 0.1	
Phosphate-phosphorus	2.31 ± 0.14	1.03 ± 0.17	1.47 ± 0.53	0.5 ± 0.14	0.5 ± 0.14	78.3	2
Faecal coliform (No./100ml)	$9.2 \times 10^5 \pm 1.1 \times 10^5$	$2.0 \times 10^5 \pm 4.9 \times 10^4$	$1.2 \times 10^5 \pm 1.8 \times 10^4$	$2.15 \times 10^2 \pm 16.31$	$2.16 \times 10^2 \pm 16.31$	99.9	10–100

UASB reactor effluent, Tricking filter effluent and final effluent respectively. There was a low concentration of DO in the final influent. This may be due to the flow being close to sewer lines. Moreover, the reactor plant record high concentrations of dissolved oxygen indicating the product from flows via open channels and a point in the treatment process where it is released from high to low levels i.e. absorbing oxygen from the atmosphere. Mean value of the trickling filter effluent was high and this could be as a result of the wastewater trickling through the bed i.e. takes oxygen from the air. The existence of algae in the final settling tank influenced the DO levels through photosynthesis, leading to the final effluent being released into natural aquatic bodies without causing any environmental and health impact.

2.6.1.3. Turbidity. The mean values for turbidity for the WWTP were 1923 mg/l, 265 mg/l, 207 mg/l, 125 mg/l, and 122 mg/l for the final influent, UASB reactor effluent, Tricking filter effluent and final effluent respectively. The results show that the mean values were extensively alleviated through the different processes, however, they did not meet the 2000 guidelines of Ghana EPA. On the other hand, the Total solids had a mean value of 3200 mg/l at the final influent and 958 at the final effluent. The overall removal efficiency depicted by the final effluent was 68.8%. The reduced performance in the removal efficiencies of all the treatment phases is because of their limited retention times.

2.6.1.4. Chemical oxygen demand (COD). The mean COD for the final influent and final effluent was 3173 mg/l and 146 mg/l respectively. This variance indicates the features of the sewage were greatly varied because the UASB reactor was effective in getting rid of organic substances from wastewater. The removal efficiencies of the UASB reactors was 94.4% (Awuah and Abrokwa, 2008). This is higher than the removal efficiency attained by (Ahmed et al., 2018).

2.6.1.5. Biochemical oxygen demand (BOD). The results show that the average values of BOD were 1206 mg/l, 73 mg/l, 42 mg/l, 23 mg/l and 23 mg/l for the final influent, UASB reactor effluent, Trickling filter effluent and final effluent respectively. The wide variation of the sewage indicate the flow of various features. The low value of the product from the final settling tanks is due to the UASB reactor significantly lowering the average BOD values in the range of 73 mg/l to 1206 mg/l. The removal efficiency of the WWTP was 98.1% (Awuah and Abrokwa, 2008).

2.6.1.6. Ammonia–Nitrogen (NH_3–N) and Nitrate–Nitrogen (NO_3–N). The final influent recorded a mean value of 4.3 mg/l, but amplified to 19.6 mg/l, in the reactor. This increase can be attributed to the de-nitrification. However, the average value decreased to 2.6 mg/l in the

subsequent treatment units. The Nitrate-Nitrogen concentrations in the reactor were anticipated to be 0. However, the mean value recorded was 6 mg/l which is probably due to the dilution before the analyses. The Nitrification at the other areas increased the nitrate concentrations of the final effluent to an average of 22.1 mg/l. The attained concentrations however, exceeds EPA highest standard guideline for release of 1.5 mg/l (EPA, 2000). The effluent could be suitable for irrigation to enhance the soil fertility.

2.6.1.7. Phosphate-phosphorus. The mean phosphate values obtained were 2.31 mg/l, 1.03 mg/l, 1.47 mg/l and 0.50 mg/l for the final influent, reactors effluent, trickling filters effluent and final settling tanks effluent respectively. The final effluent concentrations however met the EPA Ghana, 2000 standards of 2 mg/l.

2.6.1.8. Faecal coliform. The faecal coliform recorded mean values 9.2×10^5, 2.0×10^5, 1.2×10^5, 2.15×10^2, and 2.16×10^2 for the final influent, reactors effluent, trickling filters effluent and final settling tanks effluent respectively. The lower removal efficiency of the UASB was due to the shorter retention time. However, the post-treatment of the UASB reactor effluent by rest of the treatment units achieved a high removal efficiency. The total removal efficiency achieved by the WWTP was 99.9% (Awuah and Abrokwa, 2008).

3. Results and discussion

3.1. Quantification of PhAC in influent and effluent

Figure 2 shows a graph of sampling days against concentration for the selected pharmaceutically active compounds. The graph shows that diclofenac is predominant and has the highest concentration in wastewater. Diclofenac had the highest concentration recorded in 11 out of the 16 samples taken for the sixteen days as could be seen from Figure 2. High concentration these days can be linked with the release of pharmaceutical waste from the Korle-Bu Teaching Hospital which is nearby. This Hospital is the main source of the release of pharmaceutical waste into the influent point of the WWTP because it is the biggest health facility nearby and this is the basis of associating it to the high concentration of diclofenac of those days. Since the Korle-Bu Teaching Hospital is the main source of the pharmaceutical waste that gets into the WWTP, it can be said that the hospital releases high amounts of diclofenac into the WWTP as compared to the other three PhACs (aspirin, paracetamol, and ibuprofen), which finds its way to the influent point. The average diclofenac concentration recorded for the 16 samples (one sample per day for the sixteen days) was 121.16 μg/ml.
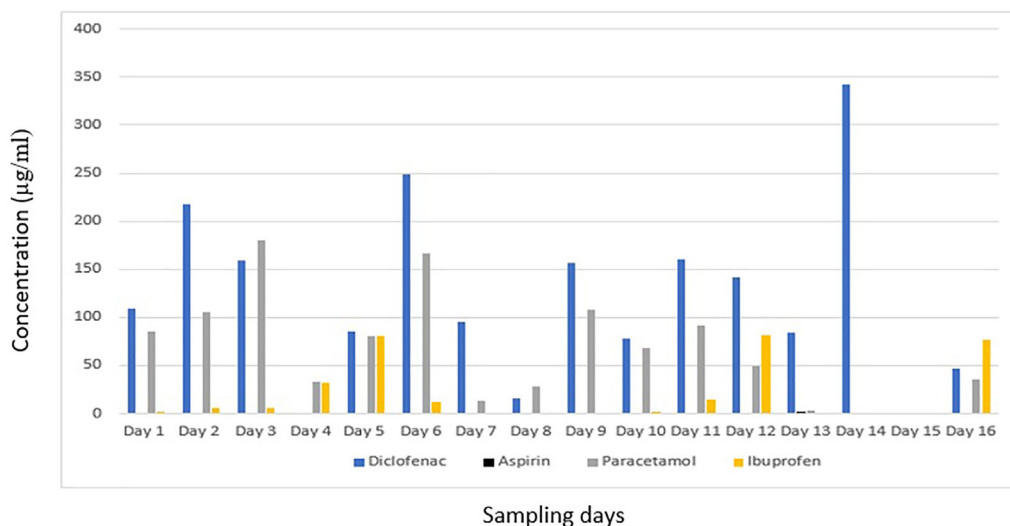
Figure 2. Daily influent concentration of selected pharmaceutically active compounds.

Aspirin on the other hand was found to have the lowest concentration in all the sampling days except the sample taken on day 13, which recorded ibuprofen to have the lowest concentration. It can be inferred from the above that the Korle-Bu Teaching Hospital releases low amounts of aspirin into the WWTP. This also goes to show that aspirin is not used frequently by the Ghanaian community as compared to the other three PhACs. The average aspirin concentration recorded for the 16 days sampling was 0.27 μg/ml. However, the average paracetamol and ibuprofen concentrations recorded for the 16 samplings were 66.44 μg/ml and 19.38 μg/ml respectively. From Figure 3, diclofenac concentration for the effluent was 0 μg/ml from the wastewater sampled on days 1, 4, 6, 8, 15, and 16 i. e complete removal. The results showed that concentrations of diclofenac received by the WWTP that exceeded 78.47 μg/ml were difficult to remove completely.

For aspirin, the concentration of the effluent was 0 μg/ml from the sampled wastewater on days 1, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 14, 15, and 16 except two particular sampling days (2 and 13). From the results of the test, the influent wastewater sampled on days 1, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 14, 15, and 16 had concentrations ranging from 0 to 0.49 μg/ml. This shows that for aspirin, the WWTP was able to completely remove concentrations within that range. The wastewater sampled on days 2 and 13

still had traces of aspirin in the effluent because the influent concentration was 0.69 μg/ml and above, which the WWTP wasn't able to completely remove.

Paracetamol concentration of the effluent was 0 μg/ml for sampled wastewater on days 1, 3, 6, 8, 10, 12, 13, 14, and 15. The results showed that concentrations of paracetamol received by the WWTP that exceeded 80 μg/ml were difficult to remove completely. The wastewater sampled on days 2, 4, 5, 7, 9, 11, and 16 still had levels of paracetamol concentration in the effluent because the influent concentrations exceeded 80 μg/ml.

On ibuprofen, the concentration of the effluent was 0 μg/ml from the wastewater sampled on days 1, 2, 3, 4, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15. This is mainly due to the reason that relatively lower concentrations of the ibuprofen were received by the WWTP on these days of complete removal as shown in the graphs. From the results of the test, the influent sampled on days 1, 2, 3, 4, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15 had concentrations ranging from 0 to 31.87 μg/ml. This shows that for ibuprofen, the WWTP was able to completely remove concentrations within that range. The wastewater sampled on days 5 and 16 still had traces of ibuprofen in the effluent because the influent concentration was 76.39 μg/ml and above, which the WWTP wasn't able to completely remove.
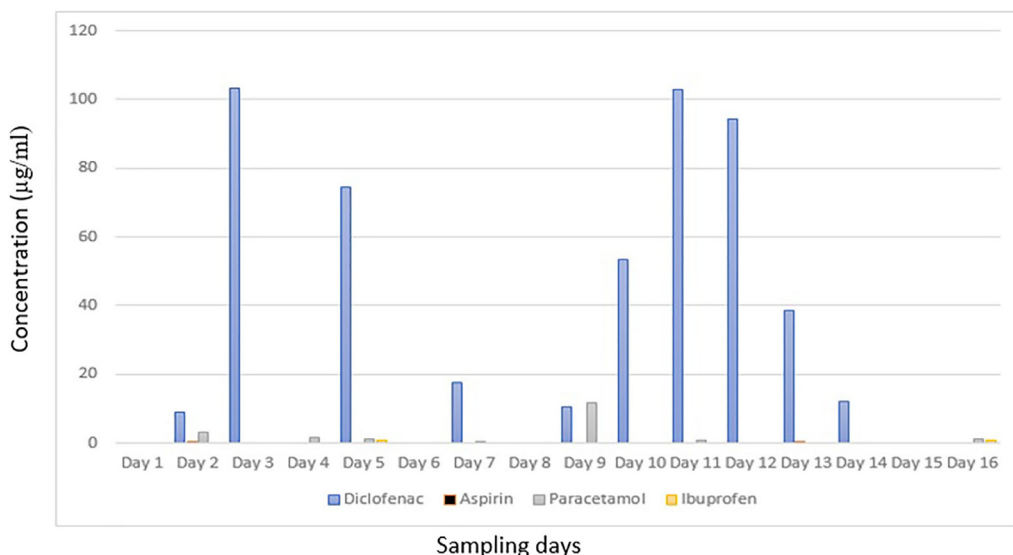

Figure 3. Daily effluent concentration of selected pharmaceutically active compounds.
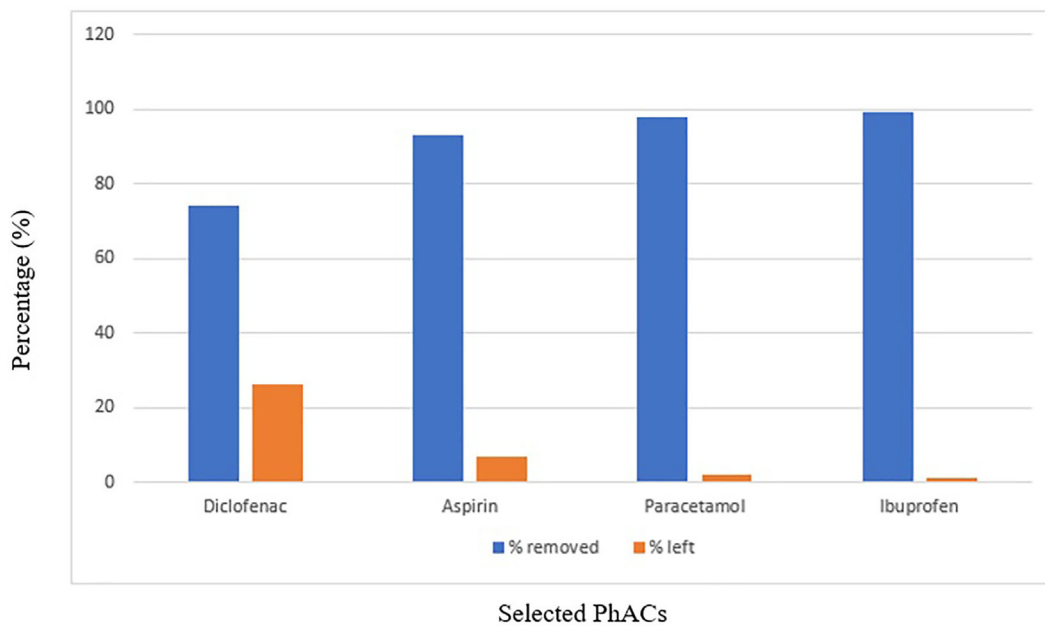
Figure 4. The average removal efficiency of the WWTP for the selected PhACs.

3.2. The removal efficiency of the WWTP for the selected PhACs

It can be deduced from Figure 4 that the removal efficiency of diclofenac is not as high as the other PhACs with a removal efficiency of 74%. This could be the presence of a chemical toxin inhibiting the microorganisms in the sewage that act on diclofenac. The WWTP could be upgraded or adjusted to increase the removal efficiency of diclofenac as a very significant percentage gets released into the environment.

The WWTP is efficient in the removal of aspirin (93%), paracetamol (98%) and ibuprofen (99%) with very low percentages of these pharmaceuticals released into the environment Figure 4. Hence, little or no upgrade or adjustment may be needed to enhance the removal efficiency of aspirin, paracetamol, and ibuprofen. Of the stages in the WWTP, the aerobic and biological treatment nature of the trickling filter is the stage that majorly removes biological and chemical compounds or

contaminants from wastewater. Hence, an assessment was done subsequently on the trickling filter to assess its removal efficiency of the selected PhACs.

3.3. The removal efficiency of the trickling filter

Comparing the trickling filter's average removal efficiency (74%) of diclofenac to that of the overall WWTP's average removal efficiency of diclofenac, it can be deduced and concluded that the trickling filter is the stage that removes an average of 74% diclofenac that the WWTP removed.

Figure 5 also shows a 95% removal efficiency of aspirin by the trickling filter. This is the representation of the two days of sampling from the trickling filter. However, the initial sixteen days of sampling from the whole WWTP showed an average 93% removal efficiency of aspirin with +2 variation in comparison to that of the last two days. This
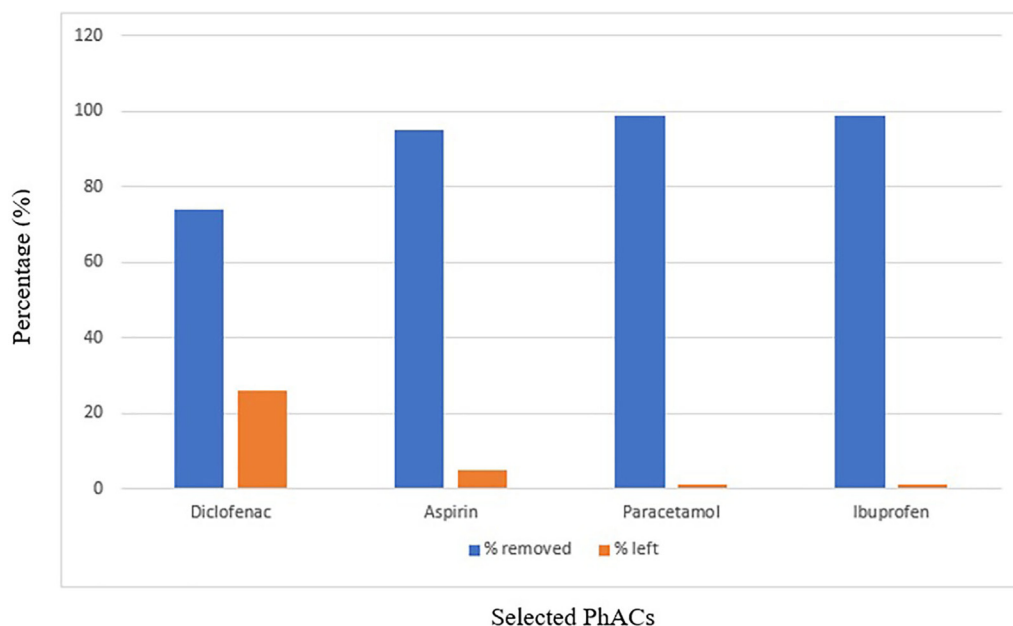

Figure 5. The average removal efficiency of the trickling filter for the selected PhACs.

Table 2. Comparison of previous and current removal efficiencies of WWTP.

Parameter	Performance (%)		
	Current Study	Ahmed et al. (2018)	Awuah and Abrokwa (2008)
PhACs			
Diclofenac	74		
Aspirin	95		
Paracetamol	99		
Ibuprofen	99		
Physical, Chemical and Biological			
BOD	98.8	98.1	
COD	91.2	94.4	
TSS	62.8	68.8	
Nitrate-Nitrogen	28.6		
Phosphate-Phosphorus	81.7	78.3	
Ammonia-nitrogen	43.6		
Sulphate	82.5		
faecal coliform	99.6	99.9	

shows that the trickling filter bed has a culture of microorganisms that acts effectively on the treatment of aspirin from the wastewater. The assessment on the trickling filter confirmed that it is the stage that majorly aids in the removal of aspirin.

A 99 per cent removal efficiency of paracetamol by the trickling filter for the samples taken for the last two days can be seen from Figure 5 confirming the biological treatment stage majorly aiding in the removal. The removal efficiency of the whole WWTP for the initial sixteen days of sampling was 98 per cent.

Figure 5 also shows a 99 per cent removal efficiency of ibuprofen by the trickling filter for the two days of sampling. The removal efficiency of the whole WWTP for the initial sixteen days was 99 per cent, the same as that of the trickling filter. This confirmed the trickling filter treatment stage aids in the treatment of ibuprofen from the wastewater. The results for this study agree with the study of (Ahmed et al., 2018) and (Awuah and Abrokwa, 2008) that revealed the total removal efficiencies of the WWTP for different parameters (see Table 1). However, comparing the findings, the removal efficiencies attained in the removal of PhACs in this study supersedes the former. Thus, the performance of the WWTP was better in removing the selected PhACs from the other parameters such as physical, chemical and biological parameters (Table 2).

4. Conclusion

In the quantification of the selected PhACs present in the wastewater which were diclofenac, aspirin, paracetamol, and ibuprofen, sampling from the WWTP recorded diclofenac as the PhAC with the highest concentration in the influent with an average of 121.31 μg/ml. Paracetamol recorded an average of 65.54 μg/ml, then ibuprofen with an average of 19.54 μg/ml. Aspirin was the PhAC with the lowest concentration in the influent with an average of 0.27 μg/ml. For the effluent samples, diclofenac was the PhAC with a high concentration in the effluent with an average of 32.28 μg/ml. Paracetamol recorded an average of 1.24 μg/ml, then ibuprofen with an average of 0.09 μg/ml. Aspirin was the PhAC with the lowest amount in the effluent with an average of 0.02 μg/ml.

The average removal efficiency of the selected PhACs was; diclofenac 74%, aspirin 93%, paracetamol 98%, and ibuprofen 99%. The assessment done on the trickling filter for the two days showed that the trickling filter is the stage in the WWTP that majorly aids in the high removal efficiency for particularly aspirin, paracetamol, and

ibuprofen. The research also suggested phototransformation and sorption onto sludge as the techniques to further reduce the PhACs concentration in the wastewater based on a comprehensive and concise review of the literature.

Declarations

Author contribution statement

Kwadwo Kodom: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Francis Attiogbe: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Francis Atta Kuranchi: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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