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# Research Article
# Sustainable Approach for Pharmaceutical Wastewater Treatment and Reuse: Case Study

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## Abstract

**Background and Objective:** Pharmaceuticals and personal care products (PCP) are used to cure humans and animals. This industry consumes a huge amount of water during their manufacturing process. The wastewater discharged from it is contaminated by organic and inorganic matters which can be toxic to the ecosystem. The main goal of this study was the treatment of hazardous pharmaceutical wastewater containing low phenol content using activated sludge process (ASP) in combination with UV-free surface reactor process (UV-FSR) as a post treatment for disinfection. **Materials and Methods:** Environmental screening for the raw materials used in the manufacturing process at the pharmaceutical industry was investigated. Also, extensive physcio-chemical characterization for real pharmaceutical wastewater was carried out before and after each treatment step. Moreover, respiration activity test was done to investigate the toxicity of the raw pharmaceutical wastewater as well as the treated effluent using respiration activity method. Determination of the optimum operating conditions for the ASP and UV-FSR were achieved. **Results:** The wastewater collected from the end-off-pipe were characterized by high organic loads represented by chemical and biological oxygen demands (COD, $BOD_5$) and high content of total suspended solids (TSS). Their average values were 3200 $mgO_2\ L^{-1}$, 1690 $mgO_2\ L^{-1}$ and 296 mg $L^{-1}$, respectively; the main source of pollution comes from the syrup department. The wastewater contains three β-lactams antibiotics one belongs to cephalosporin (cephalexin and cefuroxime) while the other two belong to penicillin's (ampicillin and amoxicillin) and other ingredients. However, operation of the ASP at a detention time of 6 h was capable for the degradation of the wastewater through sorption processes and hydroxylation. The average removal values of COD, BOD and TSS were 98.57, 98.99 and 98.31% with a residual value of 45.6, 17 and 5 mg O $L^{-1}$, respectively. Furthermore, using UV-FSR for the elimination of *Escherichia coli* (*E. coli*), intestinal nematodes with the optimum UV-dose of 1.8 m Ws $cm^{-2}$ was carried out. **Conclusion:** This treatment approach produces a good quality of treated effluent complying with the Egyptian code of practice (ECP 501/2015) for reuse in agricultural purposes.

Key words: Hazardous pharmaceutical wastewater, toxicity test, treatment, activated sludge process, ultra violet free surface reactor

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Data Availability: All relevant data are within the paper and its supporting information files.

## INTRODUCTION

Egypt is considered as one of the countries facing water scarcity due to the high rates of population growth, shortage of fresh water resources and industrialization. The Egyptian Government currently is trying to explore neoteric water resources[1]. The treatment of industrial wastewater and reuse of the treated effluents plays a momentous role in water sustainability[2]. Pharmaceutical industries consumes a huge amount of water during the manufacturing process. These industries have a diversity of products, processes, plant sizes, as well as wastewater quantity and quality which depend on the market needs. They offer many kinds of products such as biological products, medicinal chemicals, PCP and botanical products for medications of humans and animals. The consumption of pharmaceuticals per capita and per year is estimated to be about 15 g in developing countries while in industrialized countries the value ranged between 50 and 150 g. They are considered as one of the emerging containments which may be found in traces and can pose a significant risk on the ecosystem and human health[3,4]. The wastewater produced mainly goes to the wastewater treatment plants (WWTP) without any proper treatment. Elimination pathways of pharmaceuticals wastewater are varied, it include sorption, biodegradation, photo-transformation, advanced oxidation and other processes[5]. Biological treatment of pharmaceutical wastewater is one of the most common and long-term cost effective treatment methods still applied[6]. The selection of the biological treatment method depends on the chemical structure, initial concentration as well as the physico-chemical characteristics of the wastewater. However, the removal efficiency in the biological methods depend on the hydraulic retention time (HRT), sludge retention time (SRT), suspended/attached growth[7,8] redox conditions[9,10] and pH[11]. Gonzalez-Gil *et al*.[12] stated that aerobic treatment has faster degradation kinetics for the majority of PCPs and some pharmaceuticals, as compared to anaerobic ones. The main removal mechanisms involved in the aerobic treatment such as conventional activated sludge process are biodegradation and sorption (adsorption and absorption). Activated sludge process can break down certain pharmaceutical compounds to less hazard degree and produce a good quality of effluents. However, in some conditions biological methods aren't sufficient for the removal of all potentially hazardous constituents of the wastewater for reuse[13,14]. The reuse purposes including: irrigation (restricted or unrestricted) discharging on aquifers, surface water discharging, industrial applications, toilet flushing and other urban uses.

Recently, membrane bioreactor (MBR) technology[15], ozonation[16] and advanced oxidation processes (AOPs)[17] were used incorporation with conventional treatment methods for the treatment of hazardous wastewater. Emerging contaminants in wastewater including the pharmaceuticals and some resistant bacteria can be treated via AOPs, including the UV-disinfection for reuse purposes[18]. The UV irradiation represents one of the most common disinfection methods in addition to membrane processes and to a certain extent electro-chemical procedures. These processes avoid the addition of disinfectant chemicals such as chlorine. The use of conventional disinfection process leads to the increase in the total dissolved solids (TDS) and the formation of carcinogenic compounds which have known effects towards human being due to the formation of chlorinated hydrocarbons. Furthermore, the use of chlorine is not sufficient for killing of many types of pathogens[19]. However, the utilization of electrochemical disinfectants could have hazardous effects due to the formation of halogenated organics (AOX)[18].

In this study, UV-FSR is used due to many advantages: (1) The wastewater is directly irradiated, (2) There is no need for the quartz protection tube since UV radiation power suffers no losses, (3) There is no direct contact between the radiators and the wastewater avoiding the scaling problems and formation of bio-films on quartz tube, (4) A highly polished aluminum reflector allows the reflection of the backwards-directed radiations, (5) Turbulent mixing of the wastewater, the accessible wastewater surface is constantly renewed and (6) There are no laminar boundary problems[17].

The aim of this paper was the treatment of hazardous pharmaceutical wastewater containing low phenol content using activated sludge process (ASP) in combination with UV-free surface reactor process (UV-FSR) as a post treatment for disinfection. Furthermore, reaching zero liquid discharge (ZLD) and the possibility of reuse of the treated effluent in agricultural purposes according to the Egyptian code of practice for the use of treated wastewater in agricultural purposes (ECP, 501/2015)[20] will be considered.

## MATERIALS AND METHODS

**Site description:** A company located at 6th of October industrial city, Egypt, was selected for this study. The company was divided into four main departments namely; Production Department, Management and Engineering Department, Workshop Department and Packing and Storage Department. Figure 1 showed the water distribution in the company. During the manufacturing processes the company produces

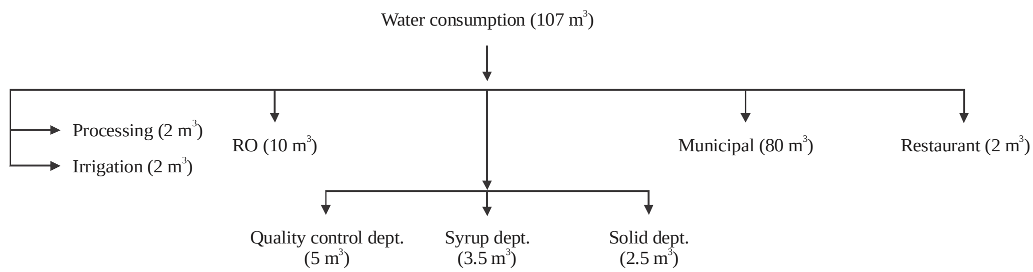


Fig. 1: Water distribution in the company

Table 1: Pharmaceutical classification

| Pharmaceutical class | Pharmaceutical |
|---|---|
| Antibiotics | Cephalosporin |
| | Amoxicillin } Beta-lactam antibiotics |
| | Ampicillin |
| Nitrates | Isosorbide nitrate, nitro glycerin |
| Angiotensin- receptor blocker (ARB) | Candesartan |
| Analgesic- anti-inflammatory | Diclofenac potassium , paracetamol, bumadizone |
| Muscle relaxant | Methocarbamol |
| Metabolites | Salicylic acid |
| Anti-exudative, antirheumatic | Lysozyme hydrochloride, calcium semihydrate, dequalinium chloride |
| Others | Caffeine, manganese sulphate, L-biopterin, calcium phospholactate, calcium carbonate, lactic acid, nitrate acid amide, flavors, vitamins (A, B1, B2, B6, C, D, G), folic acid, biotin, copper sulphate, ethyl alcohol 95%, methyl ester, propyl ester, glucose and starch |

several products such as tablets, capsules, powder, syrup, drops, solutions, spray, soft gelatine capsules, ampoules, vials and creams. The products are categorized into: antibiotics, multivitamins, cardiovascular, urology, dermatology, central nervous system (CNS), chest and cold medicines.

**Screening of pharmaceuticals in the company:** The environmental screening for the raw materials used in the manufacturing process and the products indicated that the company produces a variety of pharmaceuticals as shown in Table 1. They can be classified as antibiotics, anti-inflammatory, analgesics, antirheumatic, anti-depressant and PCPs.

**Sampling location and collection:** Composite samples were collected from the main sources of wastewater discharge as follows: solid department, liquid department, quality control and lab department, boiler and reverse osmosis (RO) department as well as from the end-off-pipe. Composite samples were collected during the working shifts. After collection, the samples were kept in glass bottles and preserved into an icebox then transferred to the lab for physico-chemical characterizations and treatment.

**Treatability study**

**Primary treatment:** Collecting or equalization tank has been used as a primary treatment to receive the industrial wastewater from the end-off-pipe during the working shifts. This was followed by pH adjustment (~7.0) using 0.1 N NaOH/10% $H_2SO_4$ before the biological treatment process.

**Activated sludge process:** Batch laboratory experiment was carried out using activated sludge process as a secondary treatment for the end-off-pipe after equalization. The experiments were conducted using 2.5 L Plexiglas laboratory columns. The columns was seeded with aerated sludge collected from Zenin WWTP with an initial concentration of mixed liquor suspended solids (MLSS) of 3-4 g $L^{-1}$, containing almost 75% of volatile matters. Air supply using air pump was adjusted to produce 2-3 mg $L^{-1}$ dissolved oxygen. Growth rate experiment was carried out at the first 8 h and then after 24 h "Extended aeration" to determine the optimum detention time needed for biodegradation. This was carried out by hourly measurements for the residual concentration of turbidity and COD. Nutrients concentrations were adjusted to insure that there is no nutrients deficiency. Ammonium dihydrogen phosphate ($NH_4H_2PO_4$) was added when required to compensate any nutrients deficiency and the COD:N:P ratio is 300:5:1 (based on COD concentration) was adjusted according to Metcalf and Eddy[21]. Acclimatization was carried out using real sewage mixed with pharmaceutical wastewater out to adapt the sludge to this type of wastewater. At the beginning of the experiment the ratio of industrial wastewater to sewage water was 25:75 for 1 week, then this ratio was

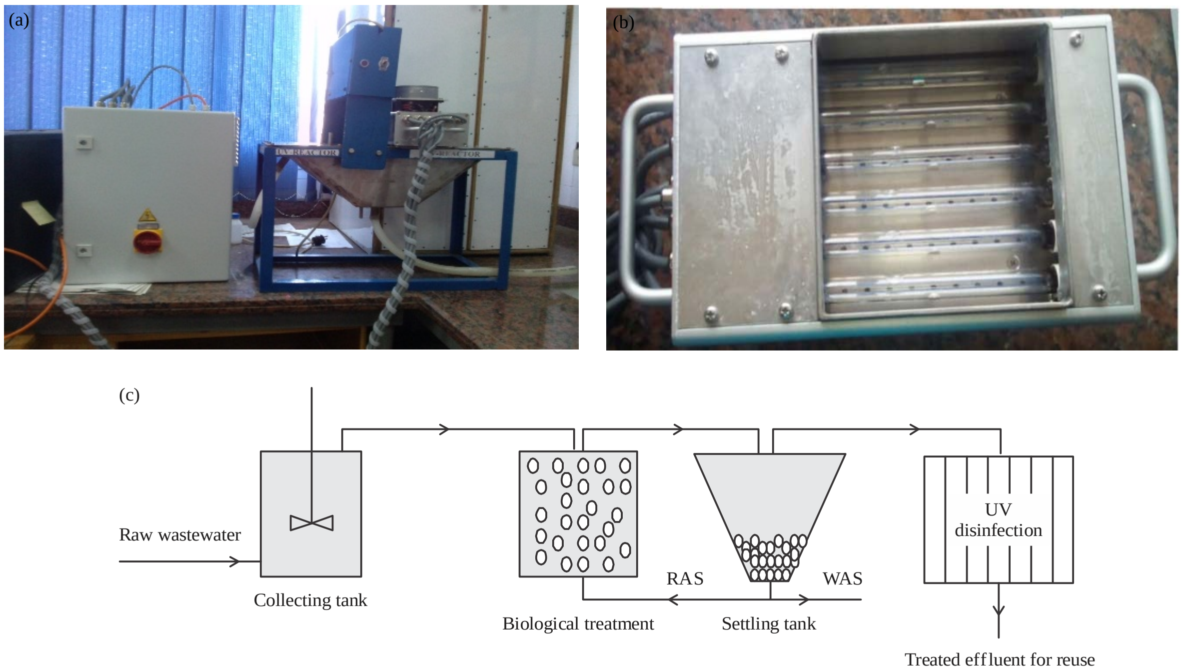


Fig. 2(a-c): (a) UV-FSR system, (b) UV-Radiators and (c) Block diagram for the overall treatment process

increased to 50:50 for further 1 week days and finally full feeding (100%) of pharmaceutical wastewater was done for a week until the steady state is reached as indicated by almost constant values of COD and turbidity. Also, microscopic examinations for the detection of the viability of microorganisms have been examined as well as sludge tests were carried out during the study.

**Post treatment using UV-FSR:** The biologically treated effluent was subjected to disinfection using 10 L UV-FSR as shown in Fig. 2a and b[22]. This was carried out to obtain ZLD discharging limits for *E. coli* and intestinal nematodes for the safe disposal and reuse of the treated effluent in agricultural purposes. The radiators used consists of 6-low pressure mercuric lamps (LPML) with total power of 210 W, the emission spectrum at UV-C region about 254 nm. Figure 2c showed a block diagram for the overall treatment process.

**Analyses:** All the analyses, unless specified had been carried out according to the Standard Methods for the Examination of Water and Wastewater[23]. The analyses included; pH, turbidity, soluble COD ($COD_S$) , total COD ($COD_t$), Biochemical oxygen demand ($BOD_5$), Settable solids (SS) , TSS, Total dissolved solids (TDS), Total kjeldahl nitrogen (TKN), Ammonia ($NH_3$), Nitrates ($NO_3$), Nitrites ($NO_2$), Total phosphorous (TP), Oil and grease and all extractable matters by chloroform (O and G), Total sulfides ($H_2S$) and Phenol. Total heavy metals including Cu, Cd, Zn, Pb, Ni and Fe were measured using inductively coupled plasma optical emission (ICP-OES), Agilent 5100 Synchronous Vertical, Dual View (SVDV) with Agilent Vapor Generation Accessory VGA 77P. Sludge analysis include total sludge weight, volatile sludge weight, sludge volume and sludge volume index (SVI). Microscopic examination of sludge was investigated using microscope model number B-180, Optika for the detection of the different microorganisms. Bacteriological analysis including *E. coli* while parasitological analyses including nematodes were carried out according to Engelbrecht and Lalchandani[24] and Al-Herrawy[25].

**Respiration activity test:** Respiration activity test had been carried out to investigate the toxicity of the pharmaceutical wastewater before and after treatment using activated sludge process[26,27].

**Statistical analysis:** Descriptive statistical functions namely; minimum, maximum and average were calculated using Microsoft Excel 2013 version.

## RESULTS AND DISCUSSION

**Physico-chemical characteristics of wastewater:** The data in Table 2 showed the physico-chemical characterization of

Table 2: Physico-chemical characterization of raw pharmaceutical wastewater

| | Solid department | | | Liquid department | | | Quality control and lab department | | | End-off-pipe | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Parameters | Min. | Max. | Average | Min. | Max. | Average | Min. | Max. | Average | Min. | Max. | Average |
| pH | 6.70 | 7.60 | 7.285 | 5.30 | 7.40 | 6.62 | 5.10 | 7.60 | 6.87 | 6.70 | 7.2 | 7.10 |
| $COD_t$ (mg $O_2$ $L^{-1}$) | 243.00 | 1250.00 | 654.67 | 240.00 | 9400.00 | 4581.67 | 970.00 | 8125.00 | 3158.67 | 2062.00 | 4750.0 | 3200.00 |
| $COD_s$ (mg $O_2$ $L^{-1}$) | 169.00 | 990.00 | 526.83 | 200.00 | 8750.00 | 4229.33 | 748.00 | 6304.00 | 2284.33 | 1230.00 | 3900.0 | 2567.00 |
| $BOD_5$ (mg $O_2$ $L^{-1}$) | 98.00 | 380.00 | 224.00 | 150.00 | 4620.00 | 2493.33 | 250.00 | 4800.00 | 1695.00 | 1008.00 | 2440.0 | 1690.00 |
| TSS (mg $L^{-1}$) | 24.00 | 218.00 | 77.50 | 11.00 | 580.00 | 174.50 | 22.00 | 470.00 | 176.83 | 198.00 | 354.0 | 296.00 |
| TKN (mgN $L^{-1}$) | 7.20 | 64.96 | 19.58 | 5.00 | 45.00 | 18.22 | 11.20 | 80.46 | 47.99 | 24.60 | 82.7 | 30.80 |
| $NH_3$ (mgN $L^{-1}$) | N.D** | 18.50 | 3.42 | N.D | 12.00 | 3.88 | N.D | 17.90 | 10.37 | N.D | 22.5 | 8.00 |
| TP (mgP $L^{-1}$) | 0.10 | 4.64 | 0.94 | N.D | 2.00 | 0.81 | 0.10 | 2.70 | 0.97 | 3.00 | 2.8 | 0.60 |
| O and G (mg $L^{-1}$) | 4.00 | 40.00 | 23.83 | 5.00 | 84.00 | 21.00 | 2.00 | 222.00 | 45.83 | 98.00 | 157.0 | 24.00 |
| $H_2S$ (mg $L^{-1}$) | N.D | N.D | N.D | N.D | N.D | N.D | N.D | N.D | N.D | 0.40 | 1.8 | 1.00 |
| Phenol (mg $L^{-1}$) | 0.01 | 1.00 | 0.39 | 0.01 | 0.80 | 0.28 | 0.00 | 0.20 | 0.09 | 0.05 | 0.4 | 0.20 |
| Cyanide (mg $L^{-1}$) | N.D | N.D | N.D | N.D | N.D | N.D | N.D | N.D | N.D | N.D | N.D | N.D |
| Total heavy metals (mg $L^{-1}$)*** | <5.00 | <5.00 | <5.00 | <5.00 | <5.00 | <5.00 | <5.00 | <5.00 | <5.00 | <5.00 | <5.0 | <5.00 |

*Average of 10 samples for each department, ** N.D: Not detected, ***Total heavy metals (Cu, Cd, Zn, Pb, Ni and Fe)

pharmaceutical wastewater obtained from the different wastewater streams from the production departments in the company as well as the end-off-pipe before discharge into the public sewerage network. The results revealed that all the departments except the RO department were violating and are contaminated with different organic and inorganic pollutants over the discharging limits. The highest values were obtained from the liquid (syrup) department which was the main source of pollution. It is characterized by high organic content, TSS, oil and grease. This was due to the cleaning and washing of equipment's used after each batch. The total and soluble COD ranged between 240-9400 and 200-8750 mg $O_2$ $L^{-1}$ with an average value 4581 and 4229 mg $O_2$ $L^{-1}$, respectively. It was obvious that the total COD was near to the soluble COD which indicates that the organic matter is mainly soluble. Oil and grease reached 84 mg $L^{-1}$ and total phenol concentration ranged between 0.01-0.8 mg $L^{-1}$ with an average value of 0.28 mg $L^{-1}$. Also, the end-off-pipe was contaminated by high loads of organic matters represented by COD and $BOD_5$, TSS, oil and grease and phenol. The maximum concentrations reached 4750 and 3900 mg $O_2$ $L^{-1}$; 354, 157 and 0.4 mg $L^{-1}$. The end-off-pipe was free from cyanide and the heavy metals (Cu, Cd, Zn, Pb, Ni and Fe) were less than the detection limit. However, the RO department has the lowest value for COD (10 mg$O_2$ $L^{-1}$).

The results showed that the pharmaceutical wastewater was fluctuated and can't be easily characterized like other types of wastewater. This was due to the variety of the manufacturing processes which were mainly batch processes, diversity of products, size of production plant, chemicals and other active ingredients used for the production of different types of pharmaceuticals. The manufacturing process included fermentation, chemical synthetization, recovery, isolation or formulation or may be include all of these mixed processes. It also depends on the biochemical activities for the micro-organism used in the fermentation process to extract the active ingredient for synthetization of different pharmaceutical products (Antibiotics, vitamins and PCP). The physcio-chemical characterization obtained during the study period indicated that pharmaceutical wastewater was classified as high strength wastewater and can be degraded biologically. The ratio of COD/BOD $\geq$0.5 according to Metcalf and Eddy[21].

**Treatability study:** Due to the wide production of different pharmaceuticals produced during the manufacturing processes which depend mainly on the market needs. The wastewater discharged was fluctuated with variable organic and inorganic matters with a non-constant flow rate. It was obvious that an equalization tank was recommended as a primary treatment process to provide homogenous and constant flow rate of wastewater streams during the daily discharge[1]. Nutrients addition was carried out after equalization to promote the microbial metabolism needed for cell growth before the biological treatment process.

### Secondary treatment

**Start-up and operation of ASP:** The acclimatization period for activated sludge process takes about 21 days at a detention time of 24 h. It was assured by constant COD removal rates (Extended aeration). It ranged between 87-92.8% with residual concentration of 110 and 58 mg $O_2$ $L^{-1}$, respectively. The MLSS, equivalent to dry cell weight, in the ASP was 3.8 g $L^{-1}$ and MLVSS was 2.7 g $L^{-1}$. This indicates that the sludge has a good quality. The food to micro-organism ratio (F/M) was 0.11 kg BOD $kg^{-1}$ VSS.d which was similar to that stated in the literature for extended aeration process[28]. Also, microscopic examinations as shown in Fig. 3 revealed the

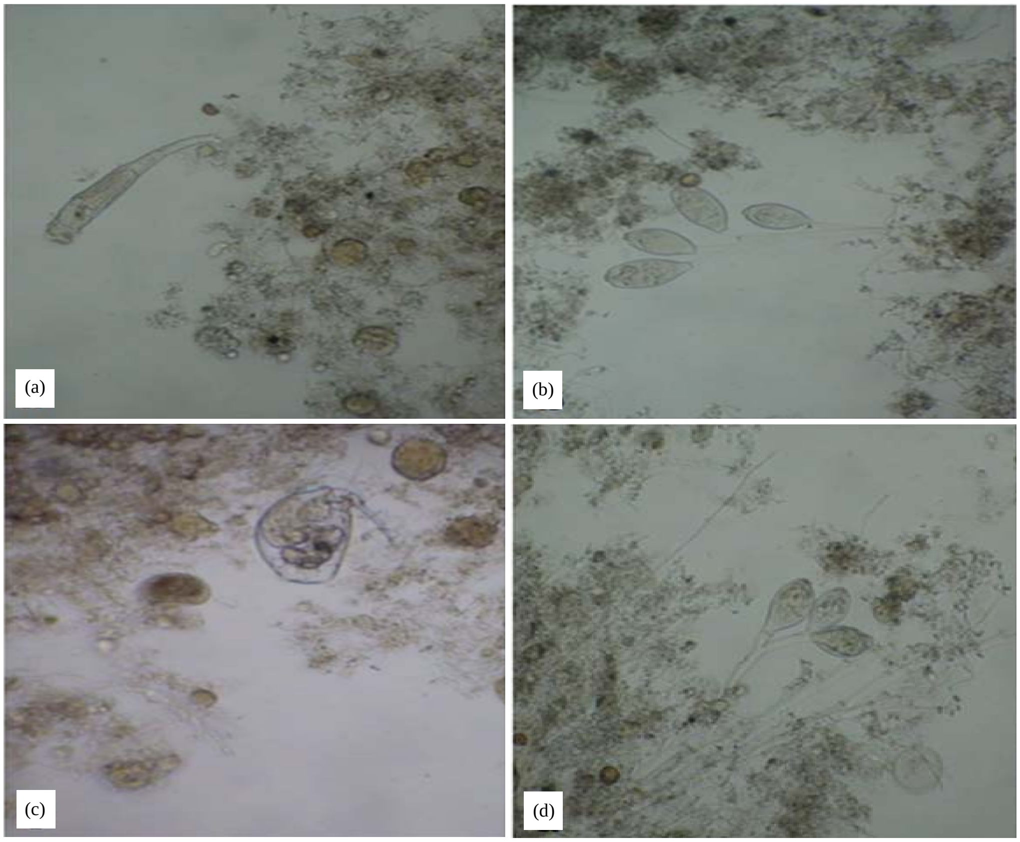


Fig. 3(a-d): Types of active micro-organisms found in the activated sludge column, (a) Rotifers, (b) Ciliates, (c) Crustaceans, (d) Non-motile green Algae and Amoeba

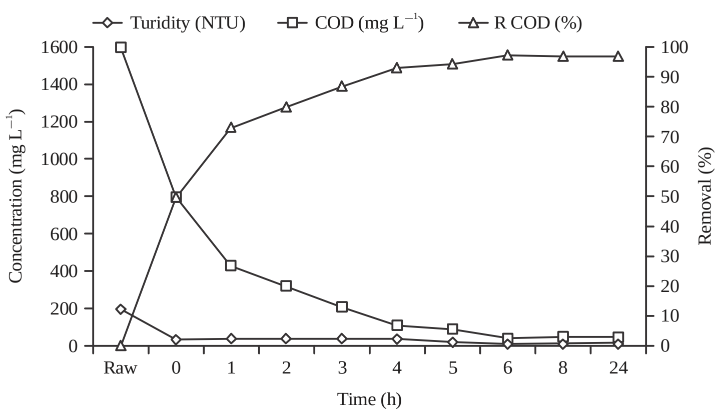


Fig. 4: Growth curve for the determination of the optimum detention time

presence of different viable cultures in the wastewater. Aerobic bacteria which are mainly responsible for the removal of organic nutrients from wastewater, utilize carbon as a food source and oxidize it to carbon dioxide and water. Protozoa like free-swimming ciliates, amoeba, vorticella, flagellates and paramecium; they adsorb the suspended solids on their cell wall and clear the water.

**Determination of the optimum operating conditions for ASP**

**Growth rate experiment:** Growth rate experiment for the end-of-pipe was carried out to determine the optimum detention time needed for biological degradation. Figure 4 showed that the best removal rates for COD and turbidity were achieved after 6 h detention time during the steady state conditions. Their corresponding residual values were

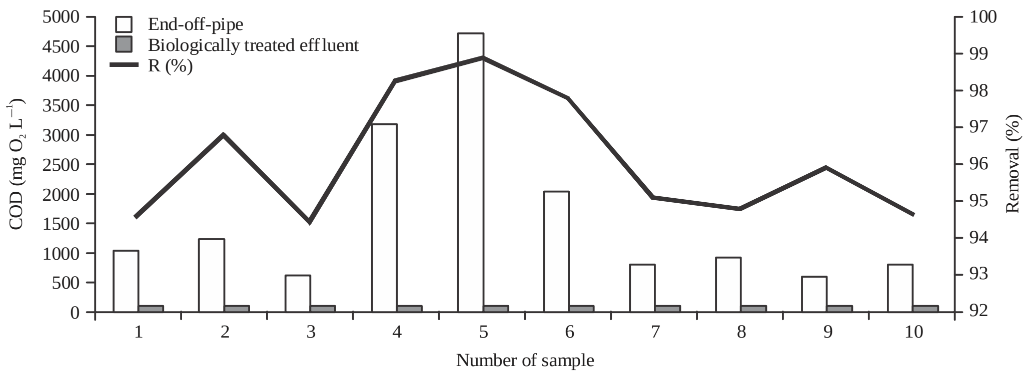


Fig. 5: Variations of COD concentration and its of removal (%) in ASP

40 mg $O_2$ $L^{-1}$ and 10 NTU. Their corresponding removal rates were 97.5 and 94.95%, respectively. Increasing the aeration time up to 8 h does not affect the removal rates of COD and turbidity. The quality of sludge was assured by SVI measurements, it ranged between 63-68 which indicate that sludge has rapid settling properties and dense.

**Removal pathways of pharmaceuticals in ASP:** During the ASP, the aerobic biomass (activated sludge) was responsible for the mineralization of organic pollutants to water and $CO_2$ or to break them to a less toxic form. Biotransformation of pharmaceutical compounds can vary from partial transformation to complete mineralization. This depends on the logarithm of $K_{OW}$ (octanol/water partition coefficient), this value describes the water solubility of chemicals and its ability to partition to an aqueous phase or an organic phase (soil and biota). In this study, acid diclofenac log $K_{OW}$ value was 4.06 which are considered as hydrophobic and thus have high water solubility[29] and can undergo hydrolysis easily under aerobic conditions. Jewell *et al.*[30] suggested that cascade of reactions in ASP occur including-hydroxylation, decarboxylation, oxidation, amide formation, ring-opening and reductive de-chlorination which leads to the formation of unknown non-toxic transmission products (TPs). β-lactams such as ampicillin, cephalosporin and amoxicillin are acidic drugs that can be degraded in neutral or basic media[31]. Morse and Jackson[32] also investigated that amoxicillin has affinity for microbial degradation in ASP. The degradation opens the β-lactam ring resulting in inactivation and breakdown of the antibiotic. Andreozzi *et al.*[33] reported that 90% of COD was removed successfully using batch experiments activated sludge process through biodegradation and adsorption at HRT of 5 h for wastewater containing amoxicillin. The hydrolysis of the antibiotic amoxicillin at neutral pH led to the formation of carboxylic acid fractions, lactam ring formation and decarboxylation[34]. Also, cephalosporins structure has on the side chain at C-7 and the substituent on C-3 atom. The presence of a good leaving group at C-3 facilitates spontaneous expulsion of the 3'-substituent by concerted event due to hydrolysis of C–N bond of β-lactam nucleus by any general nucleophile or β-lactamase[35]. The results depicted in Fig. 5 showed the variations of COD concentration and its percentage of removal in ASP for the biologically treated effluent at a HRT of 6 h. The residual concentration of COD ranged from 25–53 mg $O_2$ $L^{-1}$ with removal efficiency of 95.94 and 98.88%, respectively.

These results were in agreement with Abou-Elela and El-Khateeb[36], they use activated sludge process for β-lactam degradation and they reached up to 98% for COD removal. The mechanism of removal of pharmaceutical compounds in activated sludge process is complicated and difficult to assess, it is attributed to their absorption onto the fat fraction and the bacterial lipid structure of sludge through hydrophobic interactions of the aliphatic and aromatic groups of the compounds. They are also adsorbed into the sludge due to their high log $K_{OW}$ value positive charged whereas sludge surface is negatively charged and/or they can bind chemically to bacterial proteins and nucleic acids which leads to the adsorption of the pharmaceutical compounds to sludge via cation exchange process. Moreover, the removal mechanism other than hydrophobic partitioning, such as hydrogen bonding, ionic interactions and surface complexation play a potential role in the sorption of pharmaceuticals in/on sludge. Snyder *et al.*[37] stated that pharmaceutical removal mechanisms according to therapeutic class can be through degradation (biodegradation, activated sludge process, photo degradation). Current results were in agreement with Chang *et al.*[38], Khan and Mostafa[39] and Abdel-Shafy and Mansour[40]. They use activated sludge process with other technologies for the degradation of pharmaceutical and hospital wastewater and the removal rates for COD ranged between 75-99%.

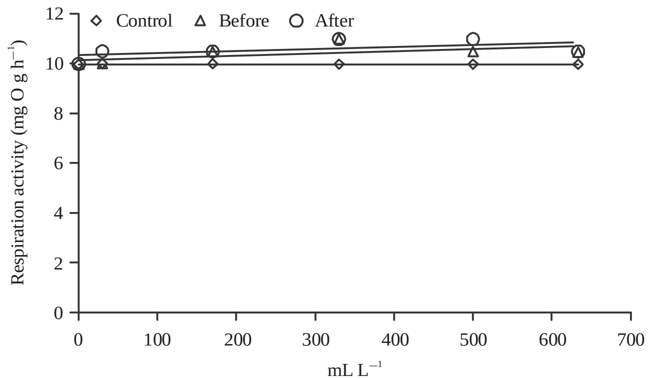


Fig. 6: Respiration activity test for the pharmaceutical wastewater before and after treatment

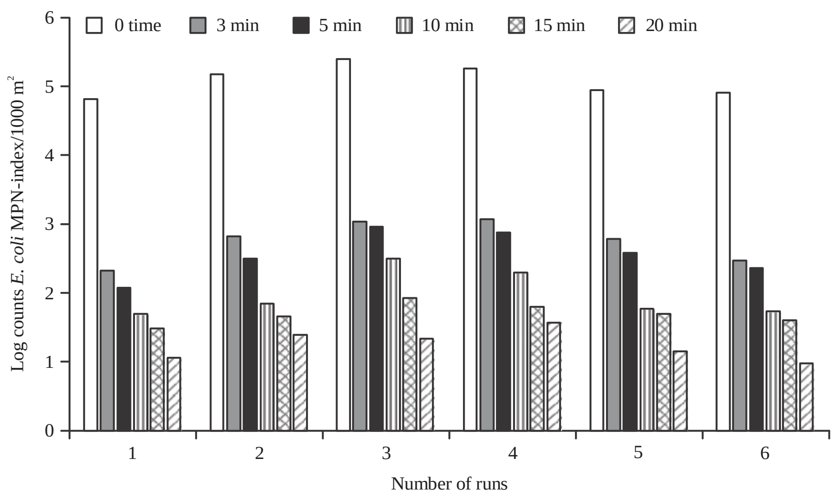


Fig. 7: Residual concentration of *E. coli* before and after using UV-FSR

As Table 3 showed the overall efficiency of ASP for the degradation of pharmaceutical wastewater. The analysis of the treated effluent indicated that great removal of organic matter and suspended solids were achieved successfully at a detention time of 6 h. The average removal values of COD, BOD and TSS were 98.57, 98.99 and 98.31% with a residual value of 45.6, 17 and 5 mg$O_2$ L$^{-1}$, respectively. Also, it was noticed that slight increase in the pH value to the alkaline range took place and this may be due to opening of β-lactams ring during hydrolysis[34].

**Respiration activity test:** The respiration activity test for pharmaceutical wastewater before and after treatment reveals that there are no noxious effects towards the activated sludge in relation to the control test. The wastewater showed no harm effect to word the activated sludge before and after treatment as shown in Fig. 6.

**Efficiency of post treatment using UV-FSR:** The treated effluent obtained from the ASP process was subjected to disinfection as a post treatment by UV-FSR. The elimination of *E. coli* was achieved for the safe disposal and reuse of the treated effluent for agricultural purposes as shown in Fig. 7. The results revealed that the optimum UV-dose of 1.8 mWs/cm$^2$ to reach the safe discharging limits. The concentration of *E. coli* in the raw wastewater ranged between $6.6\times10^4$-$2.5\times10^5$ MPN-index/100 mL, while the residual values ranged between 10-38 MPN-index/100 mL in the final treated effluent. This complies with the ECP (501/2015) grade (B) for the reuse of treated effluent for irrigation. However, intestinal nematodes were not detected in the raw and consequently in the final treated effluent.

Table 3: Efficiency of ASP for degradation of pharmaceutical wastewater

| Parameters | Raw wastewater Min. | Max. | Average | Biologically treated effluent Min. | Max. | Average | Min (%) R | Max (%) R | Average (%) R | MD | City regulations* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | 6.7 | 7.2 | 7.1 | 7.1 | 7.8 | 7.6 | -- | -- | -- | 6 - 9.5 | 6 - 9.5 |
| COD (mgO $_2$ L$^{-1}$) | 616 | 4750 | 3200 | 25 | 53 | 45.6 | 95.94 | 98.88 | 98.57 | < 1100 | < 1100 |
| BOD (mg $O_2$ L$^{-1}$) | 322 | 2440 | 1690 | 14 | 20 | 17 | 95.65 | 99.18 | 98.99 | < 600 | < 244 |
| TSS (mg L$^{-1}$) | 120 | 354 | 296 | 2 | 8 | 5 | 98.33 | 97.74 | 98.31 | < 800 | < 339 |
| TKN (mg N L$^{-1}$) | 24.6 | 82.7 | 30.8 | 12.3 | 20.4 | 14 | 50 | 75.33 | 54.54 | < 100 | < 100 |
| TP (mg P L$^{-1}$) | 1.2 | 3.4 | 3 | 0.6 | 2.8 | 1.4 | 50 | 17.64 | 53.33 | < 25 | < 25 |
| O and G (mg L$^{-1}$) | 24 | 157 | 98 | 2 | 1.5 | 2.5 | 91.66 | 99 | 97.44 | < 100 | < 100 |
| Phenol (mg L$^{-1}$) | 0.05 | 0.4 | 0.2 | ND** | ND | ND | 100 | 100 | 100 | < 0.05 | < 0.05 |
| **Sludge analysis** | | | | | | | | | | | |
| Total sludge weight at 105°C (g L$^{-1}$) | | | | 3.1 | 3.8 | 3.6 | | | | | |
| Volatile sludge weight 550°C (g L$^{-1}$) | | | | 1.9 | 2.7 | 2.5 | | | | | |
| SVI, (mL g$^{-1}$) | | | | 63 | 68 | 65 | | | | | |

*Average of 10 samples, MD: Ministerial decree 44/2000 for wastewater discharge into public sewer network[41], City regulations: Discharge limits to the sewerage network of 6th October for BOD should be <244 and TSS <339, **ND: Not detected, HRT: 6 h

## CONCLUSION

Pharmaceutical wastewater is one of the emerging micropollutants which threaten the water quality and the ecosystem. Selection of the treatment process mainly depends on the chemical structure and solubility of the pollutant. However, no single technology can be used; in this study activated sludge process (ASP) was carried out incorporation with UV-free surface reactor process (UV-FSR) for the treatment of pharmaceutical wastewater. It contains three β-lactams antibiotics one belongs to cephalosporin (cephalexin and cefuroxime) while the other two belong to penicillin's (ampicillin and amoxicillin) and other ingredients. The overall efficiency of the biologically treated effluent at detention time of 6 h. were ranged between 95.65-98.99% for BOD and 98.33-98.31% for TSS. Moreover, the use of UV-dose (1.8 mWs cm$^{-2}$) improve the quality of final effluent for the removal of *E. coli*. The residual concentration ranged between 10-38 MPN-index/100 mL and intestinal nematodes were not detected in either raw or treated effluent. Toxicity test utilizing the respiration activity method had been carried out for the raw wastewater as well as the treated effluent. A non-toxic raw wastewater and treated effluent were proved by the toxicity test. The treated effluent complies with the ECP (501/2015) grade (B) for the re-use of wastewater in dry grains, citrus fruits and medicinal plants.

## SIGNIFICANCE STATEMENT

According to 2030 Egyptian strategic plan for treated wastewater reuse in agriculture, re-use of treated wastewater is an alternative water source. This will help the Egyptian Governorate to achieve water sustainability to cope water shortage. Sustainable approach for pharmaceutical wastewater was successfully implemented using ASP in combination with UV-FSR as a post treatment for re-use in irrigation. This will help the Egyptian industry stakeholders to implement such approach for wastewater treatment and reuse.

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