Chapter

# Secondary Sludge Biodegradation and Electricity Generation in Biocathode Microbial Fuel Cells

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## Abstract

The looking for sustainable sewage sludge management technology in the wastewater treatment plants, has brought to light the biocathode microbial fuel cells (bMFCs) which allow simultaneous biological stabilization and direct energy generation, avoiding the production of biogas. In the present study, the performance of bMFCs for the treatment of secondary sludge as anodic substrate was evaluated by analyzing the removal of organic matter, destruction of volatile solids and the generation of electrical energy under different operating conditions and applying two types of cathode chambers. The results indicated that VSS and tCOD removals up to 92% and 87% respectively can be achieved in the anodic chamber generating simultaneously energy. Current and power densities of 1.80 ± 0.09 $A{\cdot}m^{-3}$ and 0.43 ± 0.02 $W{\cdot}m^{-3}$ respectively were reached, showing that bMFCs are a reliable alternative to generate electricity during the sewage sludge stabilization process. It was revealed that the pH value and the type of cathodic zone are statistically significant factors that influenced the performance of the bMFCs. The obtained results demonstrated that the electrochemical performance of the bMFCs was better at pH value of 6 in the anodic chamber and when aerobic cathode zone was used.

**Keywords:** Biocathode, electricity, microbial fuel cell, sludge stabilization

## 1. Introduction

The wastewater treatment plants generate a lot of sludge and numerous approaches have been proposed for their management, such as anaerobic digestion, dewatering, composting, and landfill treatment [1]. The main processes for organic matter removal (accounting for about 55–60% of total $BOD_5$, COD, or TOC removal) during wastewater treatment are biodegradation, biotransformation, and sorption to activated sludge in the biological steps (like activated sludge and clarification, anoxic/aerobic/aerobic, aerobic/anoxic/oxic, sequencing batch reactors, and membrane bioreactors) [2, 3]. If considering the initial content of volatile solids in sludge of 100%, about 40–60% of $BOD_5$, COD, or TOC can be degraded during the anaerobic digestion process if mechanical, thermal, chemical, and biological pretreatments are applied [1, 4]. As it is known, the hydrolysis of complex organic matter (particularly the insoluble organic matter) of sludge into dissolved organic matter is the first and the rate-limiting step of anaerobic sludge digestion [5]. Subsequently, the biodegradable dissolved organic matter fraction can be fermented to volatile fatty acids (VFAs), and they are subsequently converted to biogas by methanogens, while the refractory fraction remains in both, the liquid and solid phase of the anaerobic digestate. The looking for more sustainable sewage sludge management technology in the wastewater treatment plants, has brought to light the biocathode microbial fuel cells (bMFCs) which allow simultaneous biological stabilization and direct energy generation, avoiding the production of biogas. The Microbial Fuel Cell (MFC) is a biochemically catalyzed electrochemical system that converts chemical energy to electrical energy by oxidizing the biodegradable organic matter by means of microorganisms via catalytic reactions [6]. The use of biocathodes can enhance the energy generation, and bMFCs can be applied to convert the organic matter in sewage sludge to electricity under ambient temperature, normal pressure, and neutral pH.

Society is facing an increasing demand for energy and has noticed the urgency of changing the energy structure, which today still relies heavily on fossil fuels. The bioenergy is a renewable resource which provides an efficient way of reducing the global warming impact [7]. MFCs are bioenergy source devices that belong to the field of bio-electrochemical systems, and they are considered a sustainable technology since they allow combining the treatment of low value wastes streams, like the wastewater or the sewage sludge, with a direct conversion of the chemical energy into electrical one through bio-electrochemical reactions using microorganism catalysis [8]. MFCs consist of anode and cathode chambers, which are separated by the proton exchange membranes. The power can be generated through the organic matter anaerobic oxidation, performed by electrogenic bacteria in the anode chamber, and reduction of final electron acceptors in the cathodic one [9]. The electrons are transferred to the anode, and they flow to the cathode via a conductive material having an external resistance; the protons migrate through the membrane, and they are reduced by accepting these electrons through the cathode.

Scaling this technology has been difficult and one of the main limitations has been the cost of the cathode materials incorporating precious metals such as Pt and the unsustainable use of ferricyanide as a catalyst independent of the cathode electrolyte [10]. One of the explorations to eliminate these limitations and improve the cathodic stabilization and power generation, enhancing the economic viability and environmentally sustainability of MFC systems, has been the microbial cathode, which uses electro-trophic bacteria as biocatalysts to accept electrons in the cathode substrate [11]. Moreover, this so-called biocathodes enable the use of alternate electron acceptors that can broaden the utility of MFCs and present potential opportunities for the microbially catalyzed conversion of electrical current into various value-added products [10]. Therefore, bMFCs have attracted a lot of attention and they have been considered as a sustainable way to improve the performance of MFC systems.

For the proper MFC performance, a substrate is required in the anode chamber that provides a source of biodegradable carbon and electrons. Generally, any substrate can be used [12], from simple molecules, such as carbohydrates and proteins, to complex mixtures of organic matter, such as those which can be found in the secondary sludge. For a wastewater treatment plant (WWTP), the main source of energy for the equipment is the electricity and this item represents more than 60% of the plant operating costs [13]. The most widely used wastewater treatment process in Mexico is the conventional activated sludge and their electrical energy consumption is 0.10–1.18 $kWh \cdot m^{-3}$ [14]. One of the disadvantages of this process is the generation of large amounts of secondary sludge with high content of organic matter that must be properly treated before their disposal; however, due to the complex sludge composition, their treatment is difficult and expensive [15]. That is why the developing of alternative technologies that simultaneously degrade organic pollutants and generate energy directly has been one of the main topics in this research. The studies related to the use of sewage sludge as substrates in bMFCs are still very scarce [13, 16]. The main objective of the presented study was to evaluate the performance of a bMFCs for electricity generation using secondary sludge as anodic substrate, applying different operating conditions, and testing two types of cathodic chamber, aerobic and anaerobic. They were measured and analyzed the power generation, current densities, and coulombic efficiencies, as well as the organic matter removals and the volatile solid destructions.

## 2. Methodology

### 2.1 Experimental setup

Ten cylindrical dual chamber bMFCs, 12 cm in diameter and 13 cm in height, were made of plexiglass. Each reactor was divided into two compartments by a Nafion® proton exchange membrane (Nafion 117#, Sigma-Aldrich, London, UK) with a cross-sectional area of 156 $cm^2$. In order to increase the porosity of the membrane and improve the electrical efficiency of the cell, a pretreatment was performed following the recommendations presented in the reference [17].

The effective volume of each chamber was 0.679 L. All the reactors had anaerobic chambers, 5 of them had aerobic cathodic chambers and 5 had aerobic ones. In the superior part of each chamber there are two holes, one is for the electrode and the other one is for feeding or for reference electrode introduction, or for pH and temperature monitoring. The second hole is sealed in the anaerobic camaras to prevent oxygen diffusion to the anodic chamber, and it is opened in the aerobic ones. To provide homogenization in the anaerobic chambers, recirculation was introduced using peristaltic pumps (Masterflex). For the recirculation two openings were considered on the side of the anaerobic compartments. The mixing in the anaerobic and abiotic cathodic zones were also performed hydraulically using peristaltic pumps. The aeration of the aerobic chambers was performed by air injection and diffusion in the bottom using porous stone diffusers.

Millrose® carbon fiber brushes with twisted titanium wire were used both as anode and cathode, 5.1 cm in diameter and 7.6 cm long, having a projected surface area of 1.46 $m^2$.

Electrode and PEM pretreatments were performed according to [17, 18]. Both electrodes were connected using a titanium wire (0.5 mm, purity >99.98%, Alfa Aesar, Heysham, UK).

### 2.2 Experimental design

The experimental design consisted of a full factorial design ($2^3$), which is a powerful tool that is used to identify the effect of the independent variables on the responses at different levels. The eight experiments were performed twice, and four additional experiments were added with abiotic cathodes, 2 with aerobic cathodic zone and another 2 with aerobic ones.

The independent variables were kind of the cathodic zone (aerobic and anaerobic), VSS concentration of the treated sludge (8 and 16 g/L), and pH in the anodic zone (5 and 6). The experiments were performed twice, in two phases (10 runs in each one). To evaluate the effects caused by the independent variables, the following parameters were determined as response variables: maximum volumetric power density ($PD_{vol\ max}$), maximum volumetric current density ($CD_{vol\ max}$),

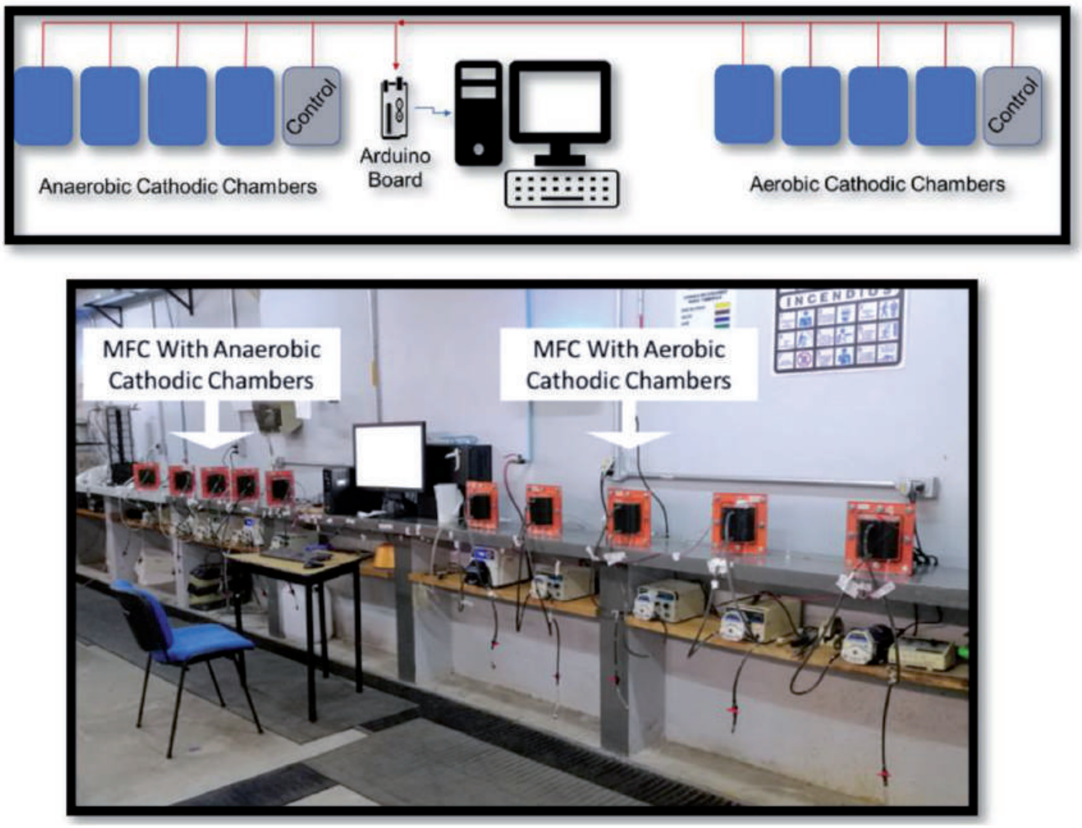


**Figure 1.**
*Schematic diagram of the experimental system.*

coulombic efficiency (CE), organic matter removal ($R_{COD}$), and volatile suspended solids removal ($R_{SSV}$). The obtained data were analyzed using STHATGRAPHICS Centurion XV ® software. The comparisons of the results were also based on statistical analysis of variance.

The **Figure 1** shows the deployment of the complete experimental system. The left side of the computer shows the anaerobic cathodic zone bMFCs, while the right side of the computer shows the aerobic cathodic zone bMFCs. The purpose of this is to evenly distribute the distance between the computer and the reactors, and to reduce the probability of voltage drops due to the additional resistance that could be caused by the distance of the wiring.

### 2.3 Inoculation and operating conditions

The experimental bMFCs were operated as sequential batch reactors, allowing the system to adapt to the operating conditions of each cycle (83 days of total operation).

The volume of the catholyte and anolyte were 680 mL each one. The sludge used as substrate for the anode chambers was collected from the secondary settlers of the conventional activated sludge treatment system in one of the wastewater treatment plants located in Mexico City. The sludge was characterized and stored at 4°C until their use as anodic substrate. Two thickened sludge samples were prepared, one with 8 $gVSS \cdot L^{-1}$ and another one with 16 $gVSS \cdot L^{-1}$. The pH of the sludge was adjusted to 5 and to 6 before the reactor feeding. Milled granular anaerobic sludge from real scale USBR reactor was used as inoculum in the anodic chambers with TS of 155.67 $g \cdot L^{-1}$. Almost 5 $gTS \cdot L^{-1}$ of inoculum was added to each anodic chamber.

Both catholytes, the aerobic and the anaerobic ones, were formed from a combination of two solutions, so that microorganisms can carry out their metabolic functions: A solution of macronutrients (including the substrate) and a solution of micronutrients (also referred to in this work as a solution of trace elements). The conformations of the first and second solutions are shown in **Tables 1** and **2** [18]. The proportion between both solutions was 8 mL of trace element for each liter of macronutrient solution [19].

The four aerobic cathodic chambers (Aer. C.) were filled with 543 ml of the catholyte and 136 ml of inoculum. Thickened activated sludge from real scale reactor was used as inoculum (SSV of 23231 mg/L, TS of 36875 mg/L). The aerobic cathodic chambers were continuously aerated using porous stone diffusers and aeration system.

A concentration of 733 $mg{\cdot}L^{-1}$ of sodium nitrite was added to the anaerobic cathodic chambers as final electron acceptor [20]. The four anaerobic cathodic chambers (An.C.) were filled with 648 ml of the catholyte and 32 ml anaerobic inoculum.

The MFC's were operated for three cycles, where each cycle ended when the energy generation dropped below 50 mV. At each cycle change, both the anolyte and the catholyte were exchanged for fresh, new substances. All experiments were performed in duplicate.

The bMFCs were operated at a temperature of 26.9 ± 2.7°C. To start with the experiments, the bMFC's were left operating at open circuit for 165 hours, this allowed the exoelectrogenic microorganisms to adapt to their environment. Subsequently, the electrical circuit was closed by imposing an electrical resistance

| Compound | Quantity |
|---|---|
| $NH_4Cl$ | 1.000 |
| $K_2HPO_4$ | 1.200 |
| $MgSO_4$ | 0.500 |
| KCl | 0.500 |
| $KH_2PO_4$ | 0.140 |
| $Fe_2(SO_4)_3{\cdot}H_2O$ | 0.010 |
| Yeast extract | 0.020 |

**Table 1.**
*Macronutrientes (in g/L).*

| Compound | Quantity |
|---|---|
| $FeSO_4{\cdot}7H_2O$ | 1000.0 |
| $ZnCl_2$ | 70.0 |
| $MnCl_2{\cdot}4H_2O$ | 100.0 |
| $H_3BO_3$ | 6.00 |
| $CaCl_2{\cdot}6H_2O$ | 130.0 |
| $CuCl_2{\cdot}2H_2O$ | 2.0 |
| $NiCl_2{\cdot}6H_2O$ | 24.0 |
| $Na_2Mo_4{\cdot}2H_2O$ | 36.0 |
| $CoCl_2{\cdot}6H_2O$ | 238.0 |

**Table 2.**
*Trace elements (in mg/L).*

of 100 ohms to all the bMFC's and based on the voltage reading under this condition, we proceeded to calculate the response parameters.

### 2.4 Analytical methods

The organic matter removals and the volatile solid degradations were calculated based on the obtained results. The sludge stabilization was followed determining the total chemical oxygen demand (TCOD) and volatile suspended solids (VSS). For the determination of TCOD and VSS content, analytical techniques were used according to standard methods [21].

For all the bMFC's, simultaneously the voltage (V) generation was recorded every hour during the whole operation time of each of the 3 cycles, for this basic data acquisition system was designed, programmed, and implemented. Its assembly consisted of a development board based on the ATmega2560 microcontroller, better known as "Arduino Mega 2560" and electronic accessories such as the prototyping board, 22-gauge parallel cable of two soft copper conductors with individual thermoplastic polyvinyl chloride insulation and joined by a track of the same material (commonly known as duplex cable), alligators, digital temperature sensor and jumper wires with male–male terminals. To avoid data loss in the event of a power outage to the laboratory, the computer was connected to a backup power supply capable of supplying power for two hours without interruption.

The current (I) was calculated using Ohm's law and the electrical power (P) with the formula P = V I. The maximum current density (CDmax) and the maximum power density (PDmax) were normalized with the electrode area.

The CE was calculated according to Eq. (1) where Ui is the recorded voltage in volts (V) of the bMFC at time i, in seconds (s), R is the external resistance, in ohms (Ω), F is the Faraday constant (96485. 3365 C $\cdot mol^{-1}$ $e^-$), b is the number of moles of electrons exchanged per mole of oxygen used in the degradation of organic matter (4 mol $e^-$ $\cdot$ $mol^{-1}$ $O_2$), ΔS is the removed concentration of COD (mg $O_2 \cdot L^{-1}$), V is the volume of the anolyte, in liters (L), and M is the molecular weight of oxygen (32,000 mg $O_2 . mol^{-1}$) [18, 22, 23].

$$CE(\%) = \frac{\sum_{i=1}^{n} U_i t_i}{RFb\Delta SV_{anol}} M \times 100 \tag{1}$$

| Instrument | Manufacturer | Model |
|---|---|---|
| Portable multimeter | HACH | HQ40d |
| Laboratory Low Maintenance Gel Filled pH Electrode | HACH | IntelliCAL PHC101 |
| Laboratory 4-Poles Graphite Conductivity Cell | HACH | IntelliCAL CDC401 |
| Laboratory Spectrophotometer for water analysis | HACH | VIS DR2800 |
| Peristaltic pump | MASTERFLEX L/S economy drive | HV-77916-10 |
| Potentiostat | GAMRY INSTRUMENTS | Interface 1010E |

**Table 3.**
*Instruments used in this study.*

Cycic Voltammetry analysis was done during the last batch cycle of each bMFC in the voltage range of −0.8 V to +0.8 V at the scan rate of 1 $mV \cdot s^{-1}$. This technique was conducted using a potentiostat with the cathode as the working electrode, the anode as counter electrode and an Ag/AgCl reference electrode, and it was used to evaluate the oxygen reduction reaction catalytic activity of the bMFC with aerobic and anaerobic cathodic zone. The instruments used for analyses, operation and measurements are presented in **Table 3**.

## 3. Results and discussion

### 3.1 Performance of the biocathode microbial fuel cells at open circuit

The startup of all the bMFCs was performed at open circuit conditions, with a cycle duration of 165 h. The voltages increased over the time in the bMFCs with aerobic cathodic chambers (Ae.C.Ch.), while a contrary tendency was observed in the bMFCs with anaerobic cathodic chambers (An.C.Ch.). The maximum voltages obtained at different experimental conditions are presented in **Figure 2**. Higher maximum voltages were obtained with aerobic cathodic chambers. For pH of 5, higher voltages were obtained with the lower VSS concentrations, but at pH of 6, the higher VSS concentration allowed obtaining of higher voltages.

The maximum voltages in the bMFCs were lower than those obtained in the MFCs with abiotic cathodic chamber; higher voltage was obtained only in the bMFCs with aerobic cathodic chamber, operated with a VSS concentration of 15 $g \cdot L^{-1}$ and pH 5. The analysis of the average voltages indicated that there was not statistically significant difference between the values obtained in the MFCs with biocathodes and in MFCs with abiotic cathodes.

### 3.2 Performance of the biocathode microbial fuel cells at closed circuit

The next operating cycles were performed at closed circuit with resistances of 100 Ohms and the obtained results are presented at **Figure 3** and the maximum voltages obtained at each operational condition are illustrated in **Figure 4**.

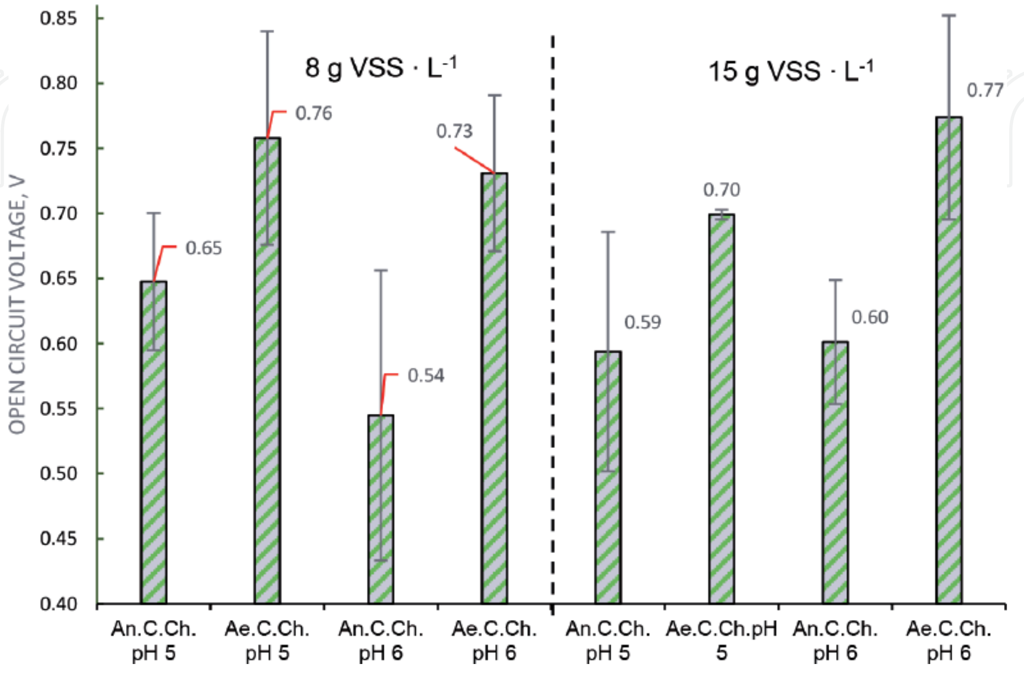


**Figure 2.**
*Maximum voltages reached at open circuit during the first operational cycle.*

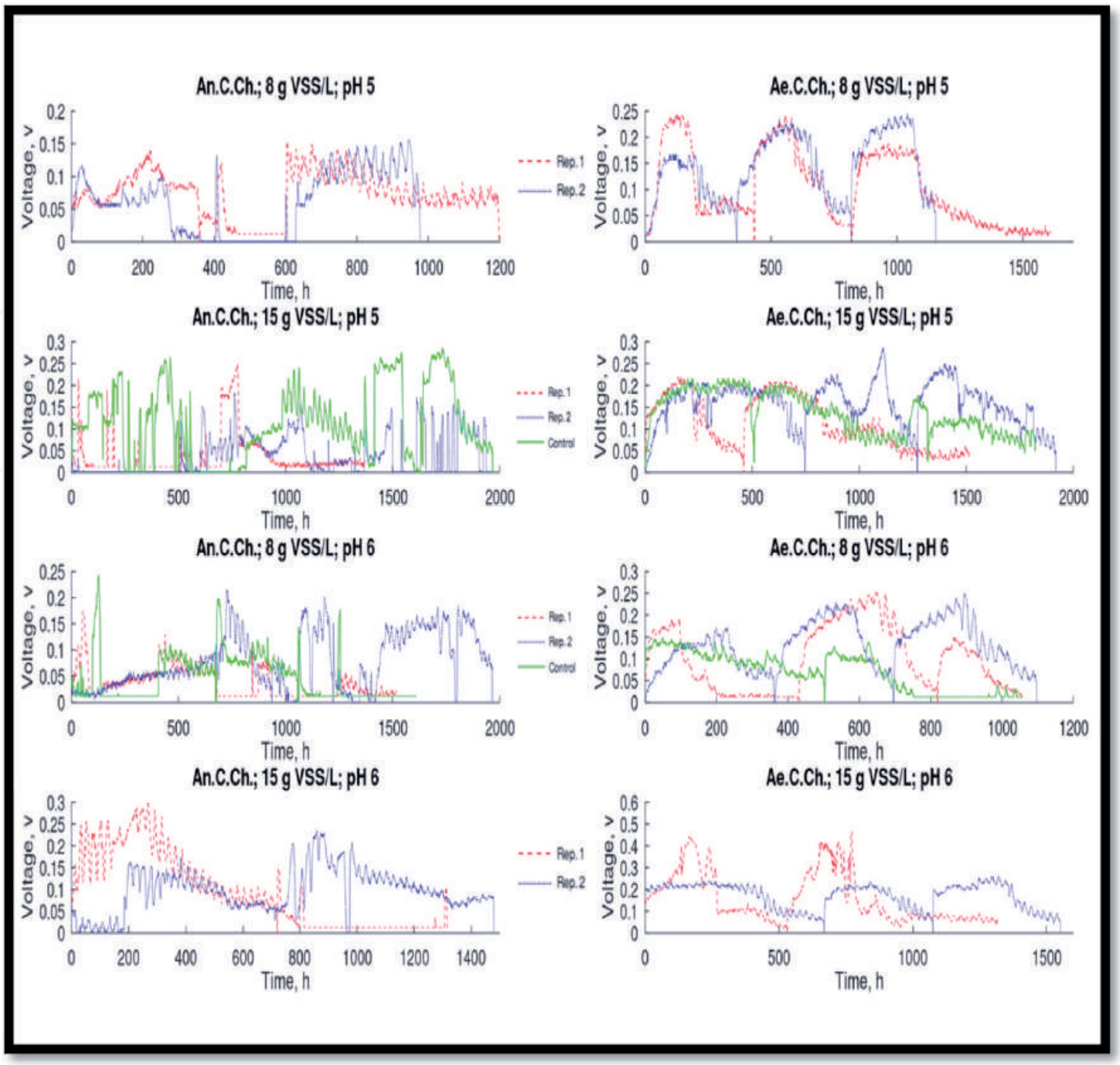


**Figure 3.**
*Obtained voltages in the experimental reactors during the closed-circuit operating cycles.*

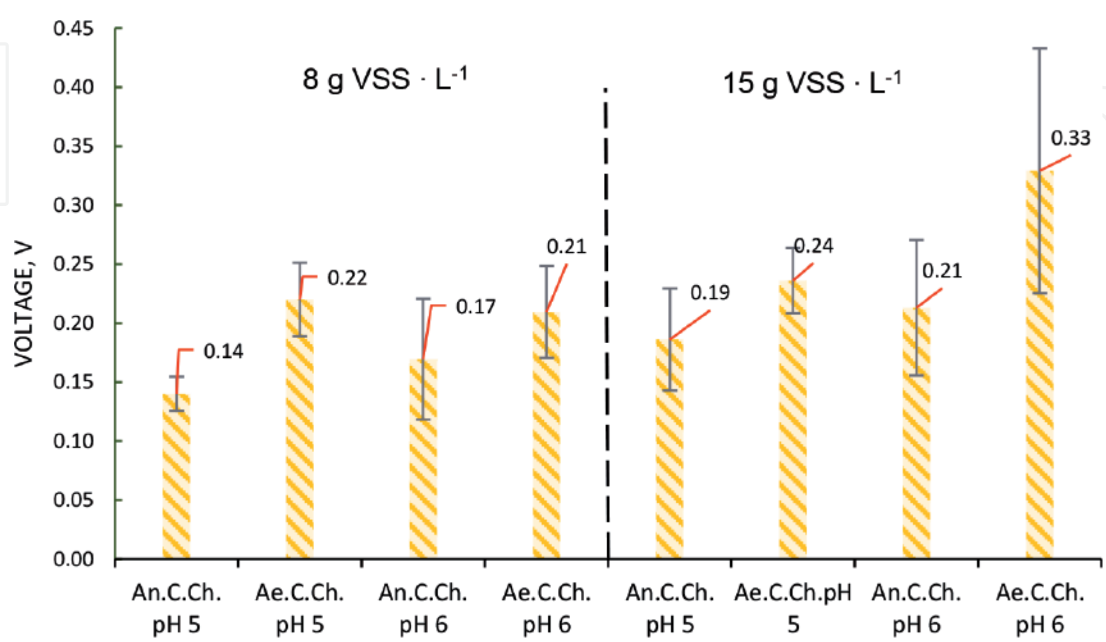


**Figure 4.**
*Maximum voltages obtained during the closed-circuit operating cycles.*

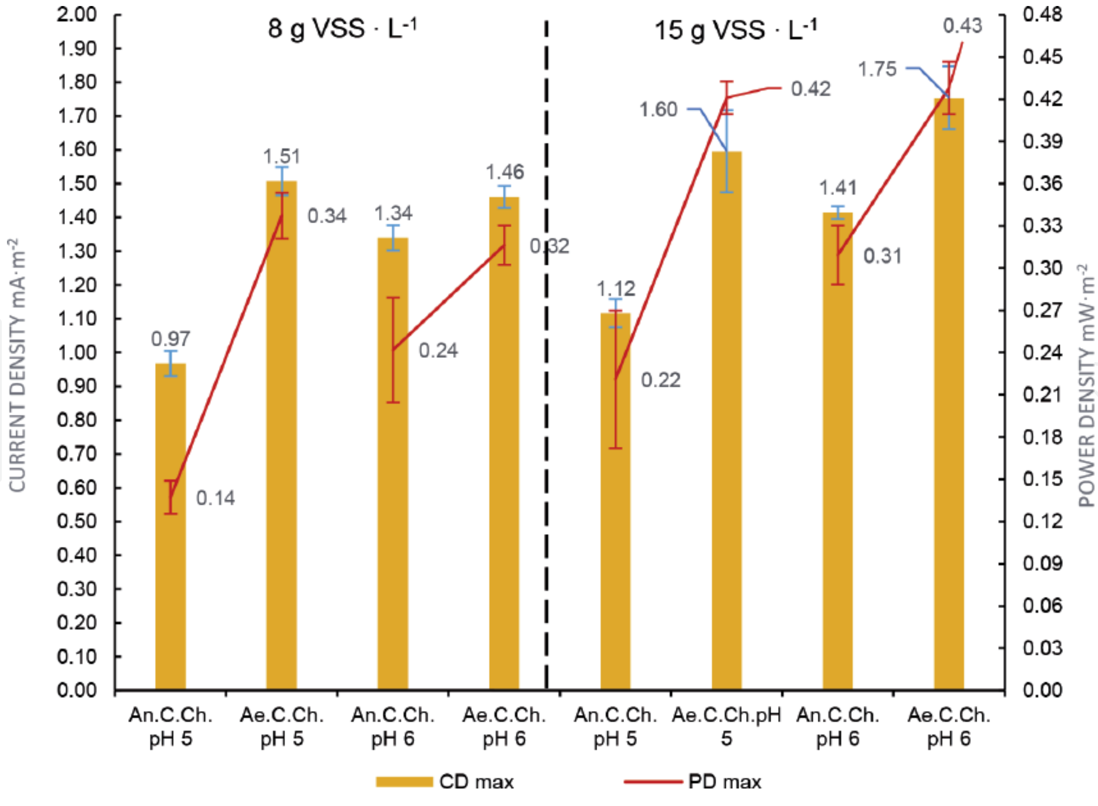


**Figure 5.**
*Maximum volumetric current and power densities achieved during the experiments.*

As it can be seen higher voltage were obtained when the oxygen was the final electron acceptor in the cathodic chamber. With respect to the initial concentration of the substrate, the highest VSS concentrations allowed increasing of the obtained voltages. The highest voltages of 0.33 ± 0.03 V were reached with the bMFCs operated with a sludge initial concentration of 15 g VSS·$L^{-1}$ and pH of 6.

To corroborate the statistical difference between the effects of each of the factors on the response variables, volumetric power density (PD) and volumetric current density (CD), regression analysis and ANOVA were carried out. The analyzed data regarding volumetric power density and current density are shown in **Figure 5**. Second order polynomic models were used with determination coefficients ($R^2$) of 0.925 for PD and 0.922 for CD and adjusted determination coefficient (adj-$R^2$) of 0.876 for DC and 0.87 for DC, which indicated a good capability of the models to predict the responses within the proposed experimental ranges. There is statistically significant difference between the results obtained with different type of cathodic zones, being the aerobic one that allowed obtaining of higher values for both, PDmax and CDmax, compared with the determined in the reactors with anaerobic cathodic zone (**Figure 6**). The effects of the VSS concentrations and pH values were much lower, but statistically significant, greater results were obtained using sludge with higher VSS concentration (of 15 g·$L^{-1}$) and higher pH (pH of 6). The lowest effect on PD was the one of pH and on CD was the one of VSS concentration.

A comparison of the electrical power generation in bMFCs and in MFCs with abiotic cathode is presented in **Figure 7**. As it can be observed, higher DCmax and PDmax were obtained in bMFCs with aerobic cathodic chambers operated with 8 g VSS·$L^{-1}$ and pH of 6. However, based on the average values, it was obtained that the difference is not statistically significant for PD (p-value = 0.116059), but it is significant (p-value of 0.0874862) for CD, in favor of the system that used biocathode, applying alpha value of 0.1. Statistical t-tests performed for the case of bMFCs

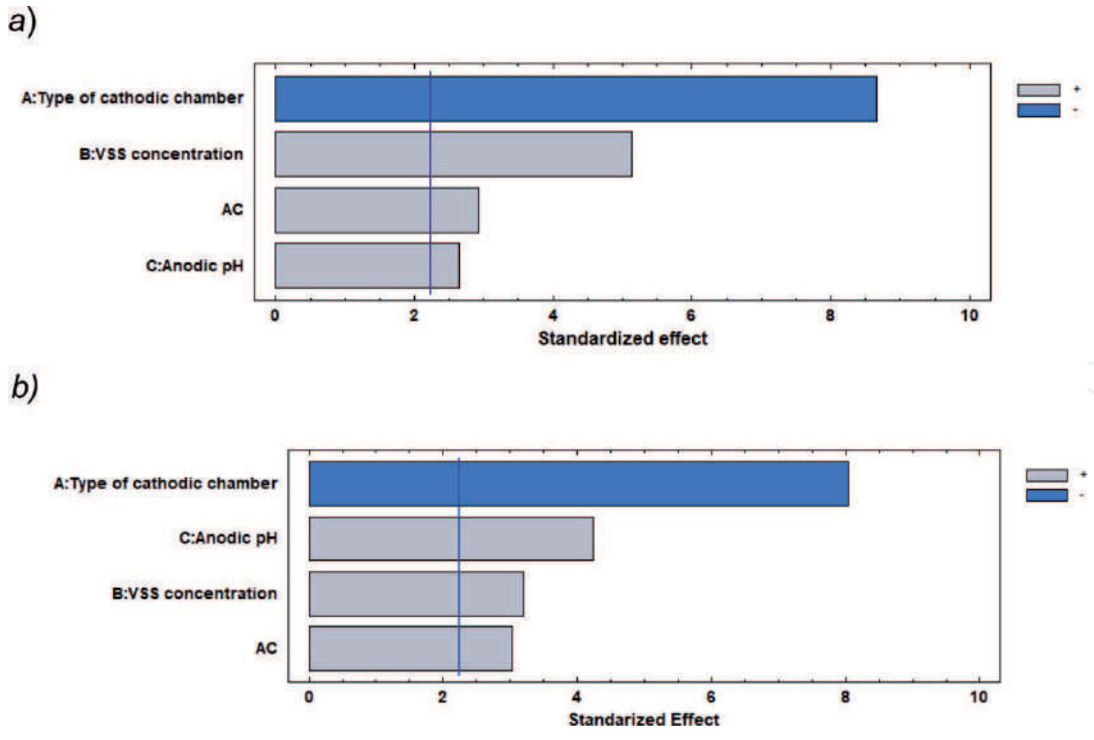


**Figure 6.**
*Standardized Pareto diagrams for PD (a) and for CD (b). For the cathodic zone chamber, the blue color represents the effect of Ae.C.Ch.*

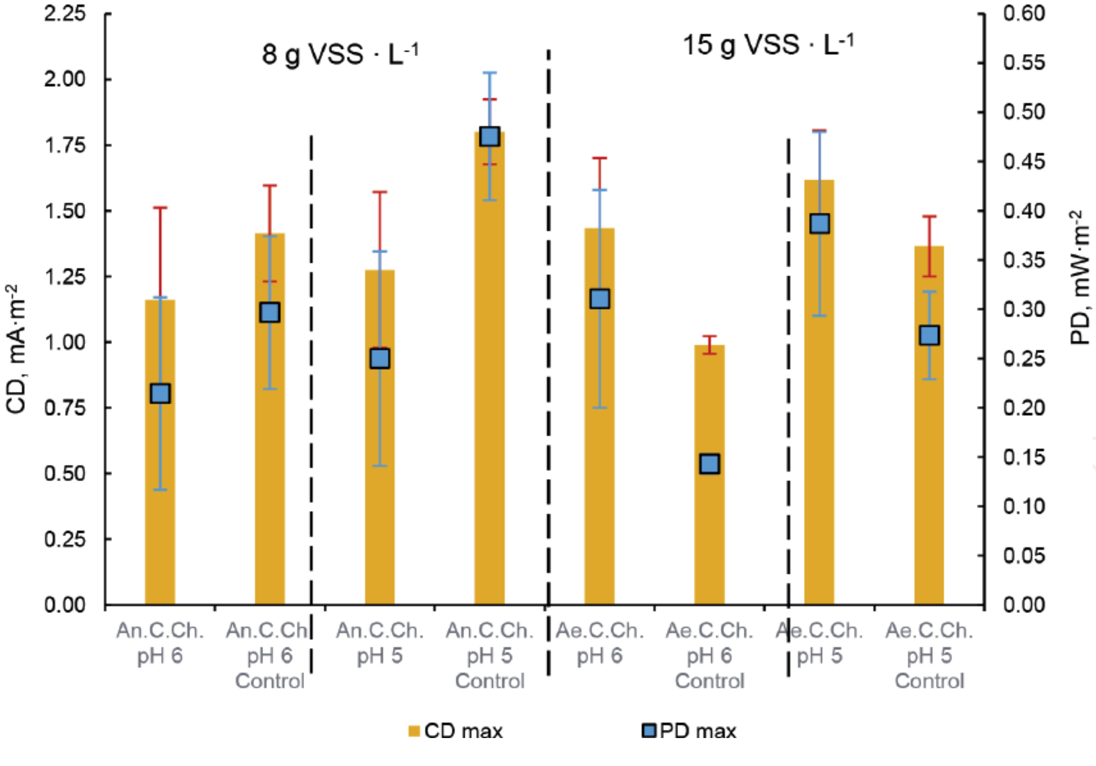


**Figure 7.**
*Comparison of power generation with respect to abiotic cathode controls.*

with aerobic cathodic chambers and MFCs with abiotic cathode, operated with 16 g VSS·L$^{-1}$ and pH of 5, showed that there is no statistically significant difference between the results with and without biocathodes for both variables (p-value >0.1).

For bMFCs with anaerobic cathodic chambers operated with 8 g SSV·L$^{-1}$ and pH of 6, the statistical tests indicated that there was not statistically significant difference between the use of abiotic cathode or biocathode (p-value >0.1). However, for bMFCs with anaerobic cathodic chambers operated with 16 g SSV·$L^{-1}$ and pH of 5, the values of both PD and the CD were lower than the obtained in the MFCs with abiotic cathode (p-value of 0.0302892 and 0.0455172 respectively) with a 90% of confidence.

### 3.3 Organic matter removal and Coloumbic efficiency

The average TCOD and VSS removals determined in the anodically processed sludge, and the coulombic efficiencies obtained using different initial pH and VSS concentrations, and in bMFCs with aerobic and anaerobic chambers, are illustrated in **Figure 8**. As it can be seen the obtained TCOD and VSS removals were higher than 75%, reaching values up to 92%, which indicates that the sludge stabilization process was successful in all the operational conditions.

Based on the obtained results for TCOD removal, the empirical relationship between the response and variables was expressed by a polynomial equation, with determination coefficient ($R^2$) of 0.997 and adjusted determination coefficient (adj-$R^2$) of 0.982, which indicated a good capability of the model to predict the response within the proposed experimental ranges. The calculated effect analysis, with a 96% of confidence and a factor of significance (p) of 0.04, indicated as the most significant factor the interaction of pH with the concentration of VSS, both with positive effects.

For the VSS removal, the model had $R^2 = 0.999$ and adj-$R^2$ of 0.997, and with a 97% of confidence, the initial VSS concentration had the major effect, followed by the pH. There was not statistically significant effect of the type of the cathodic zone. There was a statistically significant difference between the VSS removals obtained with different initial VSS concentrations ($p = 0.03$) and with different initial pH values in the anode chamber, being p of 0.04 and 0.03 respectively. There was not statistically significant difference between the results obtained in bMFCs with different type of cathodic zone.

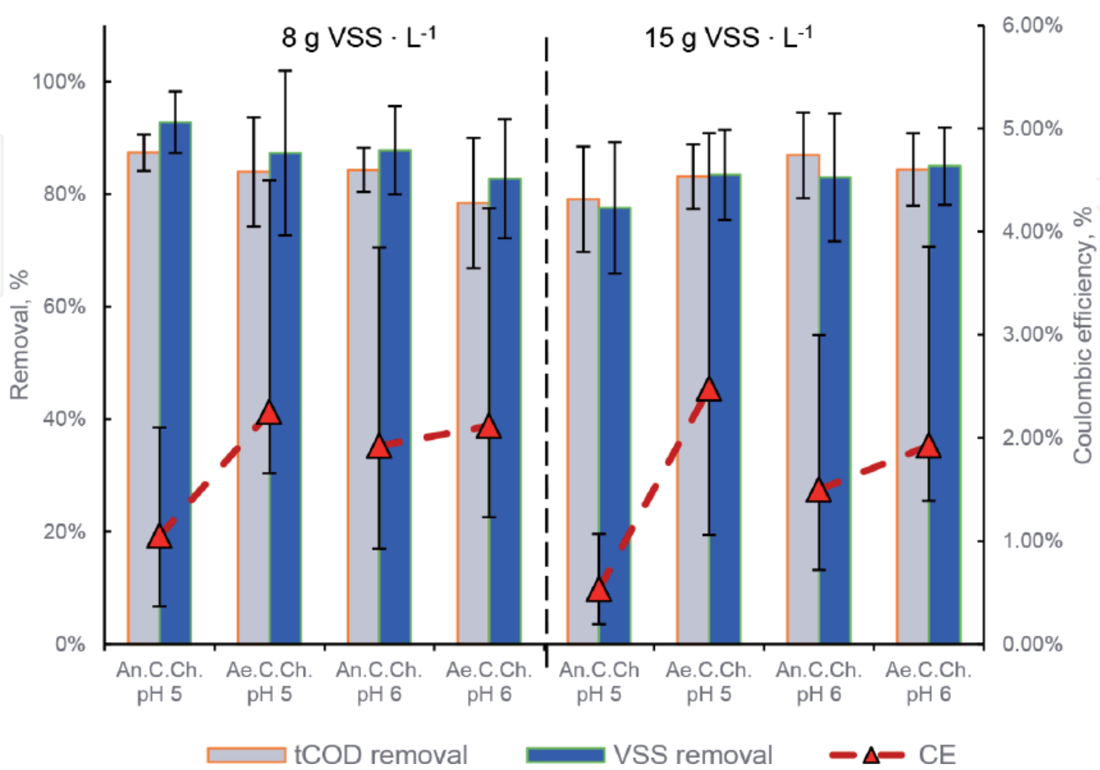


**Figure 8.**
*TCOD and VSS removals, and coulombic efficiencies obtained in the experimental bMFCs.*

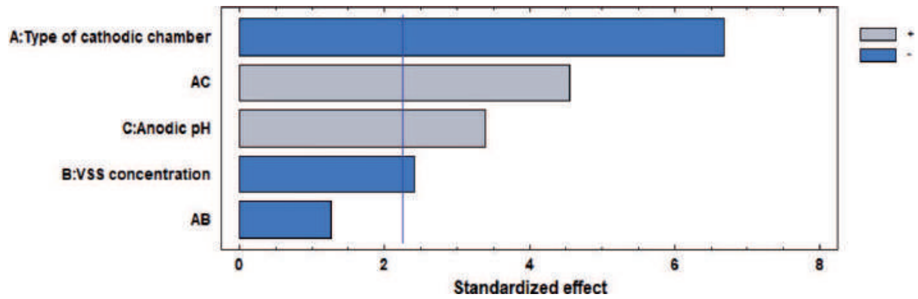


**Figure 9.**
*Standardized Pareto diagrams for CE.*

The performed statistical analysis for the Coulombic Efficiency (CE) using a model with $R^2$ of 0.975 and adj-$R^2$ of 0.941, indicated that the factors which strongly influenced CE are the type of cathodic zone and the initial pH (**Figure 9**). The use of aerobic cathodic zone and initial pH of 6 allows obtaining of better coulombic efficiencies. The highest coulombic efficiency averages reached in the bMFCs were 2.1–2.3%. These results are lower than those reported by Zhang et al. [18], who reached CE up to 19.4%, although with removals of TCOD up to 40.8%, using a double chamber MFCs with sludge as anodic substrate and biocathodes. On the other hand, the obtaining of small CE values with high COD removals indicates that the electrons released from the organic matter were consumed by processes other than those carried out by electrogenic biofilms, such as fermentative and methanogenic biofilms [24]. This is also consistent with the results obtained by Freguia et al. [25], who indicated that fermentation and methanogenesis are not electrode-dependent reactions, so they could occur with any external resistance as long as the redox potential in the solution is low enough and there are bacteria present that derive more energy from these processes than from electrode-driven oxidation of the substrate. Further research is needed to better understand competitive microbial processes such as exoelectrogenic, biomass growth, fermentative, and methanogenic at the anode to minimize their effects and increase power generation and CE.

### 3.4 Electrochemical performance of the bMFCs

Polarization curves and power curves generated in the experimental bMFCs are presented in **Figures 10** and **11** respectively. The values of maximum power (Pmax), internal resistance (IR) and open circuit voltages, obtained from the figures are reported in **Table 3**. The graphs indicated that bMFC with aerobic cathodic chamber, initial sludge VSS concentration of 15 g $\cdot L^{-1}$ and pH of 6 was the one who obtained the highest open circuit voltage (553 mV), as well as the highest maximum PD of 0.21 $mW{\cdot}m^{-2}$ at a CD of 0.55 $mA{\cdot}m^{-2}$. The maximum power in the rest of the bMFCs was 0.05–0.15 $mW{\cdot}m^{-2}$ with current densities of 0.25–0.60 $mA{\cdot}m^{-2}$. The maximum CD up to 0.67 $mA{\cdot}m^{-2}$ and PD of 0.14 $mW{\cdot}m^{-2}$ was reached with the lowest applied resistance (46 Ohms) in bMFC with anaerobic cathodic chamber, initial sludge VSS concentration of 15 g $\cdot L^{-1}$ and pH of 5. These values are lower than with the reported for MFCs with similar structural and biotic characteristics which reached 38 mW $m^{-2}$ [26], 43.6 mW $m^{-2}$ [27].

The results of **Table 4** show that for all reactor configurations, both, the internal resistance, and the open circuit voltages (OCV) were higher when the aerobic cathodic chamber was used. For the case of maximum power density, the results do not show a clear pattern that could help relate the configuration to the observed result.

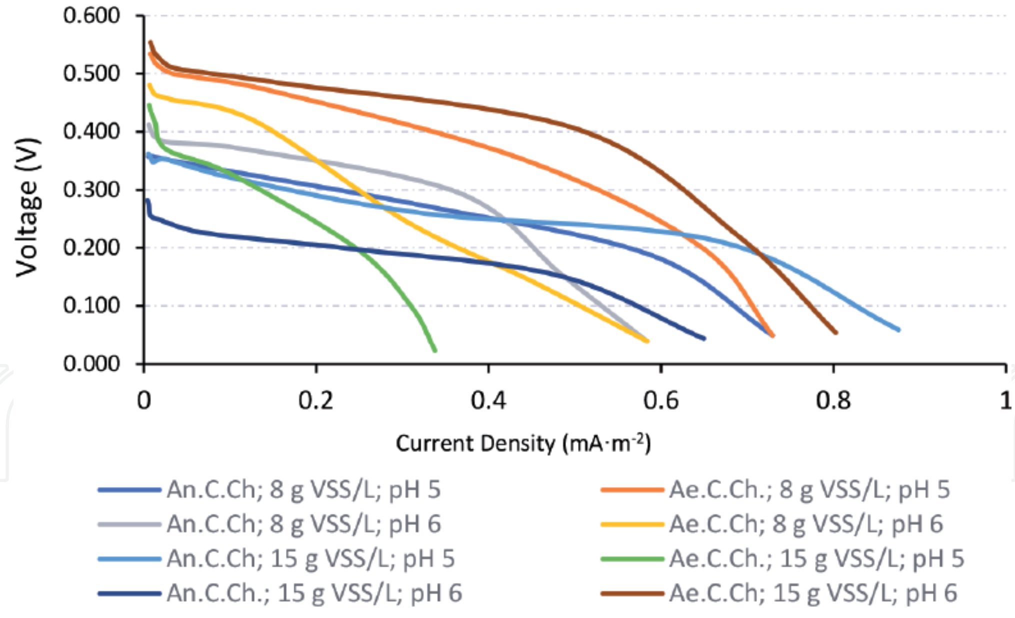


**Figure 10.**
*Polarization curves.*

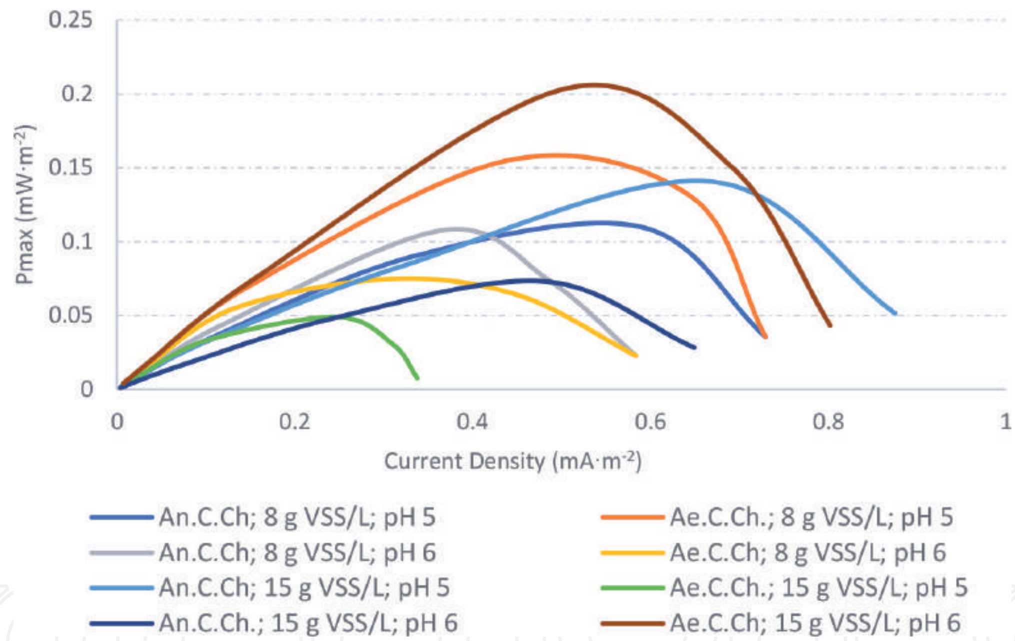


**Figure 11.**
*Power curves.*

The voltamperogram generated from all evaluated operating conditions is shown in **Figure 12**. In green, the operating conditions that included Aerobic Cathodic Chamber (Ae.C.Ch.) and in purple those that included Anaerobic Cathodic Chamber (An.C.Ch.). It was also found that at the potentials −800 mV and 800 mV the maximum and maximum current densities of −21.1 $\mu A \cdot cm^{-2}$ and 7.11 $\mu A \cdot cm^{-2}$ were achieved (corresponding to −307.9 and 103.8 mA shown in the graph) respectively. These values correspond to the Ae.C.Ch. configuration; 8 g $VSS \cdot L^{-1}$; pH 6 and agree with the previous analysis for CDmax where the type of cathodic zone and the pH have significant effects. The shape of the graph agrees with what is observed in [28] where the reduction of oxygen shows the fall of the curve on left section. Under anaerobic conditions this does not happen as markedly since nitrogen has a lower oxidation capacity than oxygen.

| bMFC | $R_{int}$ (Ohms) | $PD_{max}$ ($mW \cdot m^{-2}$) | OCV (mV) |
|---|---|---|---|
| An.C.Ch; 8 g VSS/L; pH 5 | 223.920 | 0.110 | 357.0 |
| Ae.C.Ch; 8 g VSS/L; pH 5 | 498.200 | 0.150 | 534.0 |
| An.C.Ch; 8 g VSS/L; pH 6 | 207.990 | 0.110 | 412.0 |
| Ae.C.Ch; 8 g VSS/L; pH 6 | 484.430 | 0.070 | 480.0 |
| An.C.Ch; 15 g VSS/L; pH 5 | 97.360 | 0.140 | 361.0 |
| Ae.C.Ch; 15 g VSS/L; pH 5 | 1081.320 | 0.050 | 446.0 |
| An.C.Ch; 15 g VSS/L; pH 6 | 132.410 | 0.070 | 282.0 |
| Ae.C.Ch; 15 g VSS/L; pH 6 | 154.250 | 0.210 | 553.0 |

**Table 4.**
*Internal resistance, OCV and maximum power density.*

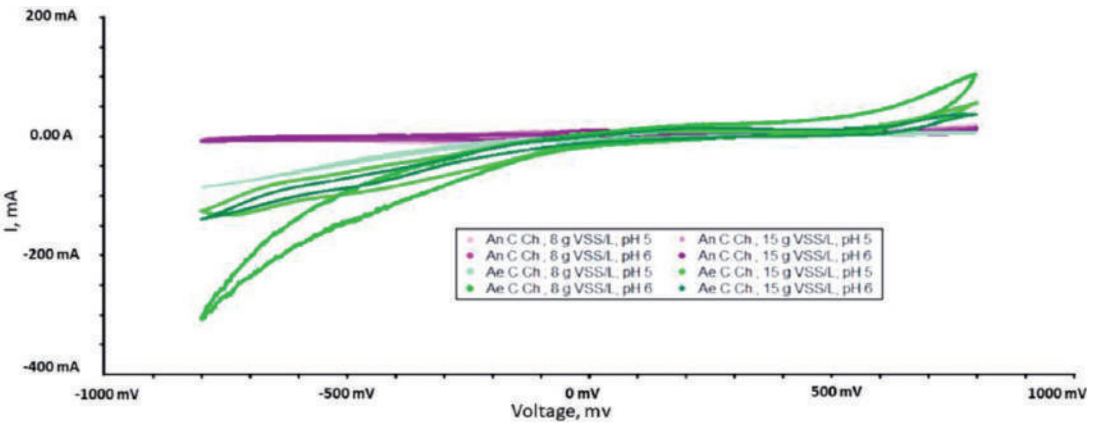


**Figure 12.**
*Cyclic voltammetry obtained in the experimental bMFCs.*

## 4. Conclusions

This study showed that it is possible to stabilize successfully secondary sludge with VSS concentration up to 15 $g \cdot L^{-1}$ using microbial fuel cells with biocathodes. The highest organic matter removals reached in the anode chamber, up to 92%, indicates a very good microbial activity in the anodic chambers. The statistical analyses of the obtained results indicated that the kind of the anodic chamber, the variations of VSS concentration in the secondary sludge between 8 and 15 $g \cdot L^{-1}$, as well as the variations of pH between 5 an6 do not influenced significatively the organic matter removal.

The simultaneous generation of electricity is possible together with the degradation of organic matter, which contributes to the sustainability of this method. The bio-cathodic microbial fuel cells with aerobic cathodic chambers allows obtaining of higher voltages, current densities, power densities and coulombic efficiencies compared with the microbial fuel cells with anaerobic cathodic chambers (up to 450 mV, 0.43 $mW \cdot m^{-2}$, 1.80 $A \cdot m^{-2}$ and 4% respectively).

The effects of the VSS concentrations and pH values were much lower than the type of the cathodic chamber, but statistically significant, greater results were obtained using sludge with higher VSS concentration (of 15 $g \cdot L^{-1}$) and higher pH (pH of 6). The lowest effect on the power density was the one of pH and on the current density was the one of VSS concentration. The best configuration for operating MCCs varied according to the parameter of interest that is desired as a response variable. For the power density, the best configuration is aerobic cathodic chamber, 15 g VSS·$L^{-1}$ and sludge pH of 5. For the current density the best configuration is aerobic cathodic chamber, 15 g VSS·$L^{-1}$ and pH of 6. For the case of the coulombic efficiency, the best configuration is aerobic cathodic chamber, 8 g VSS·$L^{-1}$ and pH of 6,

The performance comparison of the microbial fuel cells with biotic and abiotic cathodes indicated that there was not statistically significant improvement of the response parameters, and there was even a configuration (anaerobic cathodic chambers, 16 g SSV·$L^{-1}$ and pH of 5) for which better results were obtained with abiotic cathode.

The electrochemical tests confirmed that the configuration with aerobic cathodic chamber, initial sludge VSS concentration of 15 g ·$L^{-1}$ and pH of 6 was the one who obtained the highest open circuit voltage (553 mV), as well as the highest maximum power density of 0.21 mW·$m^{-2}$ and current density of 0.55 mA·$m^{-2}$. The internal resistance and the open circuit voltages were higher when the aerobic cathodic chambers were used.

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## References

[1] Zhen G, Lu X, Kato H, Zhao Y, Li YY. Overview of pretreatment strategies for enhancing sewage sludge disintegration and subsequent anaerobic digestion: Current advances, full-scale application and future perspectives. Renew. Sust. Energ. Rev. 2017; 69: 559-577. DOI: 10.1016/j.rser.2016.11.187

[2] Carstea EM, Bridgeman J, Baker A, Reynolds DM. Fluorescence spectroscopy for wastewater monitoring: A review. Water Res. 2016; 95: 205-219.

[3] Xue S, Jin W, Zhang Z, Liu H. 2017. Reductions of dissolved organic matter and disinfection by-product precursors in full-scale wastewater treatment plants in winter. Chemosphere. 2017; 179: 395-404. DOI: 10.1016/j.chemosphere.2017.02.106

[4] Maspolim Y, Zhou Y, Guo C, Xiao K, Ng WJ. Comparison of single-stage and two-phase anaerobic sludge digestion systems –Performance and microbial community dynamics. Chemosphere. 2015; 140: 54-62. DOI: 10.1016/j.chemosphere.2014.07.028

[5] Alvarado A, West S, Abbt-Braun G, Horn H. Hydrolysis of particulate organic matter from municipal wastewater under aerobic treatment. Chemosphere. 2021; 263, 128329. DOI: 10.1016/j.chemosphere. 2020. 128329

[6] Mohan SV, Velvizhi G, Modestra JA, Srikanth S. Microbial fuel cell: critical factors regulating bio-catalyzed electrochemical process and recent advancements. Renewable and Sustainable Energy Reviews. 2014. 40: 779-797. DOI: 10.1016/j.rser.2014.07.109

[7] Rai M, Ingle AP. Sustainable bioenergy: advances and impacts. 1st ed. Elsevier; 2019. 416 p. eBook ISBN: 9780128176559. DOI:

[8] Harnisch F, Schröder U. From MFC to MXC: Chemical and biological cathodes and their potential for microbial bioelectrochemical systems. Chemical Society Reviews. 2010; 39(11): 4433-4448. DOI: 10.1039/c003068f

[9] Du Z, Li H, Gu T. A state of the art review on microbial fuel cells: A promising technology for wastewater treatment and bioenergy. Biotechnology advances. 2007; 25: 464-482. DOI: 10.1016/j.biotechadv.2007.05.004

[10] Huang L, Regan JM, Quan X. Electron transfer mechanisms, new applications, and performance of biocathode microbial fuel cells. Bioresource Technology. 2011; 102: 316-323. DOI: 10.1016/j.biortech.2010.06.096

[11] Zaybak Z, Pisciotta JM, Tokash JC, Logan BE. Enhanced start-up of anaerobic facultatively autotrophic biocathodes in bioelectrochemical systems. Journal of Biotechnology. 2013; 168 (4): 478-485. DOI: 10.1016/j.jbiotec.2013.10.001

[12] Estrada, E. B., Salazar, M. d. (2013). Generación de energía eléctrica a partir del tratamiento de aguas residuales por medio de bioceldas. Jiutepec, Morelos, México.: IMTA.

[13] Meng F, Zhao Q, Zheng Z, Wei L, Wang K, Jiang J, Ding J, Na X. (2019). Simultaneous sludge degradation, desalination and bioelectricity generation in two-phase microbial desalination cells. Chemical Engineering Journal. 2018; 361: 180-188.

[14] Metcalf & Eddy, Inc. (2014). Wastewater engineering. Treatment and reuse recovery. 5th ed. United States of America: McGraw Hill; 2014. Print ISBN: 9780073401188. p. 1952.

[15] Yu H, Zhao Q, Dong Q, Jiang J, Wang K, Zhang Y. Electronic and metagenomic insights into the performance of bioelectrochemical reactor simultaneously treating sewage sludge and Cr (VI)-laden wastewater. Chemical Engineering Journal. 2018; 341: 495-504. DOI: 10.1016/j.cej.2018.01.159

[16] Zhang G, Zhao Q, Jiao Y, Wang K, Lee, DJ, Ren N. Efficient electricity generation from sewage sludge using biocathode microbial fuel cell. Water Research. 2012; 46: 43-52. DOI: 10.1016/j.watres.2011.10.036

[17] Huarachi-Olivera R, Dueñas-Gonza A, Yapo-Pari U, Vega P, Romero-Ugarte, M, Tapia J, Molina L, Lazarte-Rivera A, Pacheco-Salazar DG, Esparza M. Bioelectrogenesis with microbial fuel cells (MFCs) using the microalga Chlorella vulgaris and bacterial communities. Electronic Journal of Biotechnology. 2018; 31: 34-43. DOI: 10.1016/j.ejbt.2017.10.013

[18] Feng Y, Yang Q, Wang X, Logan BE. Treatment of carbon fiber brush anodes for improving power generation in air-cathode microbial fuel cells. Journal of Power Sources. 2010; 195: 184-1844. DOI:10.1016/j.jpowsour.2009.10.030

[19] Rabaey K, Ossieur W, Verhaege M, Verstraete W. (2005). Continuous microbial fuel cells convert carbohydrates to electricity. Water Science & Technology. 2005; 52(1-2): 515-523. DOI: 10.2166/wst.2005.0561

[20] Zhao H, Zhao J, Li F, Li X. Performance of denitrifying microbial fuel cell with biocathode over nitrite. Frontiers in Microbiology. 2016; 7(344): 1-7. DOI: 10.3389/fmicb.2016.00344

[21] APHA. Standards methods for the examination of water and wastewater. 23th ed. Washington, DC, USA: American Public Health Asociation; 2017. ISBN: 9780875532875; p. 2076.

[22] Revelo DM, Hurtado NH, Ruiz JO, López S. (2015). Uso de microorganismos nativos en la remoción simultánea de materia orgánica y Cr(VI) en una celda de combustible microbiana de biocátodo (CCM). Información Tecnológica. 2015; 26: 77-88. DOI:

[23] Varanasi JL, Veerubhotla R, Das D. Diagnostic tools for the assessment of MFC. In Debabrata D, Microbial fuel cell: A bioelectrochemical system that converts waste to watts. Kharagpur, India: Springer, 2018. p. 249-262. Ch13.

[24] Al-Mamun A, Jafary T, Baawain MS, Rahman S, Rahman M, Tabatabaei M, Lam SS. Energy recovery and carbon/nitrogen removal from sewage and contaminated groundwater in a coupled hydrolytic-acidogenic sequencing batch reactor and denitrifying biocathode microbial fuel cell. Environmental Research. 2020; 183: 1-11. DOI: 10.1016/j.envres.2020.109273

[25] Freguia S, Rabaey K, Yuan Z, Keller J. Electron and carbon balances in microbial fuel cells reveal temporary bacterial storage behavior during electricity generation. Environmental Science & Technology. 2007; 41: 2915-2921. DOI: 10.1021/es062611i

[26] Min B, Cheng S, Logan BE. Electricity generation using membrane and salt bridge microbial fuel cells. Water Research. 2005; 39(9): 1675-1686. DOI: 10.1016/j.watres.2005.02.002

[27] Tang X, Guo K, Li H, Du Z, Tian J. (2010). Microfiltration membrane performance in two-chamber microbial fuel cells. Biochem. Eng. 2010; 52: 194-198. DOI: 10.1016/j.bej.2010.08.007

[28] Chen S, Patil SA, Schröder U. A high-performance rotating graphite fiber brush air-cathode for microbial fuel cells. Applied Energy Journal. 2018; 211:1089-1094. DOI: 10.1016/j.apenergy.2017.12.013)10.1016/j.apenergy.2017.12.013)

Chapter

# An Overview of Occurrence and Removal of Pharmaceuticals from Sewage/Wastewater

*Mohd Salim Mahtab and Izharul Haq Farooqi*

## Abstract

Nowadays, the occurrence of pharmaceuticals in sewage/wastewater is a major environmental concern. Their precise characterization and suitable treatment/disposal is a must else it pollutes the surface water bodies and causes major distress on aquatic lives and human health. Also, the up-gradation of the sewage/wastewater treatment plant (WWTP) is a must to consider the removal of these pollutants and to provide the best quality effluent for various reuse purposes. Mostly, the conventional treatment methods are inefficient for their removal, and hence, the most advanced and refined treatment options are needed for their effective treatment. In this chapter, we have highlighted the occurrence of pharmaceuticals in various water samples and their treatment options are reviewed. It was recommended that integrated treatment systems are more efficient, economical, and environmental friendly than single stand-alone treatment. Further advancement and modifications in the treatment options are required to overcome the shortcomings regarding pharmaceutical removal to achieve the legal standard discharge limit.

**Keywords:** advanced oxidation process, biological treatment, emerging contaminants, wastewater, recalcitrant compounds, sewage

## 1. Introduction

Nowadays, the problems associated with the widespread occurrence of pharmaceuticals in the aquatic environment have been recognized as an emerging environmental issue [1–3]. The increasing usage of pharmaceuticals and their improper discharge is one of the major environmental concerns. Pharmaceuticals are a large and diverse group of compounds designed to prevent, cure, and treat disease and improve health. Their usage and consumption are increasing consistently due to the discoveries of new drugs, the expanding population, etc. [2, 3]. After intake, these pharmaceutically active compounds undergo metabolic processes in the organism. Significant fractions of the parent compound are excreted in un-metabolized form into raw sewage and wastewater treatment systems. The most commonly occurring pharmaceuticals in the environment are given in **Table 1** [4]. Thus, body metabolization and excretion followed by wastewater treatment are considered to be the primary pathway of pharmaceuticals to the environment [1–3, 5–7]. Disposal of drug leftovers into sewage and trash is another source of entry [8]. In addition, sewer leaking [9], sewer overflow [10], and surface runoff [11] are also considered

| S. no. | Class of drugs | Name of drugs |
|---|---|---|
| 1. | Antibiotics | Erythromycin, ofloxacin, streptomycin, flumequine, ciprofloxacin, trimethoprim, sulfamethoxazole, lincomycin, penicillin, and amoxicillin |
| 2. | Antidepressants | Mianserin |
| 3. | Anticancer drugs | Cyclophosphamide and ifosphamide |
| 4. | Anti-inflammatory drugs | Acetylsalicylic acid (aspirin), diclofenac, ibuprofen, acetaminophen, naproxen, and phenazone |
| 5. | Beta-blockers | Metoprolol, propranolol, nadolol, and atenolol |
| 6. | Diuretics | Furosemide |
| 7. | Lipid regulators | Bezafibrate, gemfibrozil, clofibric acid, and fenofibrate |
| 8. | Steroids and related hormones | 17-β-estradiol, estrone, and diethylstilbestrol |
| 9. | Tranquilizers | Diazepam |

**Table 1.**
*Some common pharmaceuticals are found in the environment [4].*

as additional sources contributing to the presence of pharmaceuticals in the aquatic environment [5].

Their detection techniques and proper characterization are relatively difficult which required distinctive procedures and sophisticated instruments due to their low concentration levels in different environmental matrices [7, 11, 12]. Several studies investigated the occurrence and distribution of pharmaceuticals in soil irrigated with reclaimed water [13, 14] and soil that received biosolids from urban sewage treatment plants [15, 16]. These studies confirmed that the conventional systems are not enough to completely remove such micro-pollutants from wastewater and sludge, and as a result, they find their way into the environment [17]. Once entered the environment, pharmaceutically active compounds can produce subtle effects on aquatic and terrestrial organisms. Therefore, the occurrence of pharmaceutical compounds and the extent to which they can be eliminated during wastewater treatment have become the active subject matter of actual research [1, 3–7].

Domestic sewage is relatively simple to treat with conventional methods due to the absence of any recalcitrant compounds. The conventional treatment options are widely applicable for their effective treatment [1, 18–20]. The sewage/wastewater treatment plants are generally not designed to consider the specific pharmaceuticals, emerging compounds, etc., during the treatment. Hence, their presence in the sewage water is very problematic for the treatment performance of the plant [1, 5–7, 21]. Furthermore, the presence of pharmaceuticals in the effluents of sewage/wastewater treatment plants is very toxic in many ways to the soil and surrounding water bodies [1–5, 21]. To overcome the abovementioned problems, firstly, we have to stop the improper disposal of pharmaceuticals and their proper monitoring/collection system should be designed [3]. The accurate characterization and suitable treatment options should be provided to obtain the legal effluent discharge standards. The constant discharge of various pharmaceuticals into the water bodies and their persistent nature and bioaccumulation potential cause serious effects to aquatic lives and human health [21–23]. Therefore, in this chapter, we have highlighted the occurrence and some of the removal techniques specifically for the pharmaceuticals from sewage/wastewater. The scope for future research directions is also highlighted in the conclusion part.

## 2. Occurrence of pharmaceuticals in sewage/wastewater

The huge variation in the concentrations of pharmaceutically active compounds (PhACs) was observed due to various factors viz. environmental persistency, dilution, treatment efficiency [21, 24, 25]. In some studies, the reported amounts of pharmaceuticals are estimated to be 5.6, 2.0, and 0.4 g/day/1000 equivalent inhabitants [1, 21]. In one of the studies, the highest levels at the influent of WWTPs were observed for nonsteroidal anti-inflammatory drugs (NSAIDs) that were expected due to their high consumption [1]. Lower but still significant levels of lipid-modifying agents (7–12%), diuretics (8–10%), and beta-blockers (5–9%) were detected entering the WWTPs [1]. Atenolol and carbamazepine were quantified in the influent samples of WWTPs in average concentrations ranging from 0.4 to 1.4 mg/L [1]. The amount found in effluent or sludge depended on the removal efficiency of the plant and/or the physicochemical properties of the compounds. In the effluent waters, NSAIDs were present in the highest percentage (35–44%), followed by the lipid-modifying agents (8–29%) and psychiatric drugs (17–30%) [1]. The highest concentrations in the effluents were found for naproxen, diclofenac, and carbamazepine [1].

It has been reported that from the list of detected samples of the emerging contaminants about 70% are PACs and personal care products (PCPs) [26]. Globally, more than 200 PhACs have been reported in river waters with a maximum concentration of 6 mg/L for ciprofloxacin antibiotics [27]. Similarly, tamoxifen was detected in the range of 25–38 ng/L [28]. Also, the concentrations of antibiotics, hormones, antidepressants, and chemotherapy drugs range from 0.04 to 6.3 μg/L [29]. Out of the various sources of the PhACs into the environment, the domestic discharge and effluents of the manufacturing units of pharmaceuticals are well-thought-out major sources [22]. Various categories for the occurrence of the PhACs have been reported viz. wastewater treatment plants (WWTPs), wastewater,

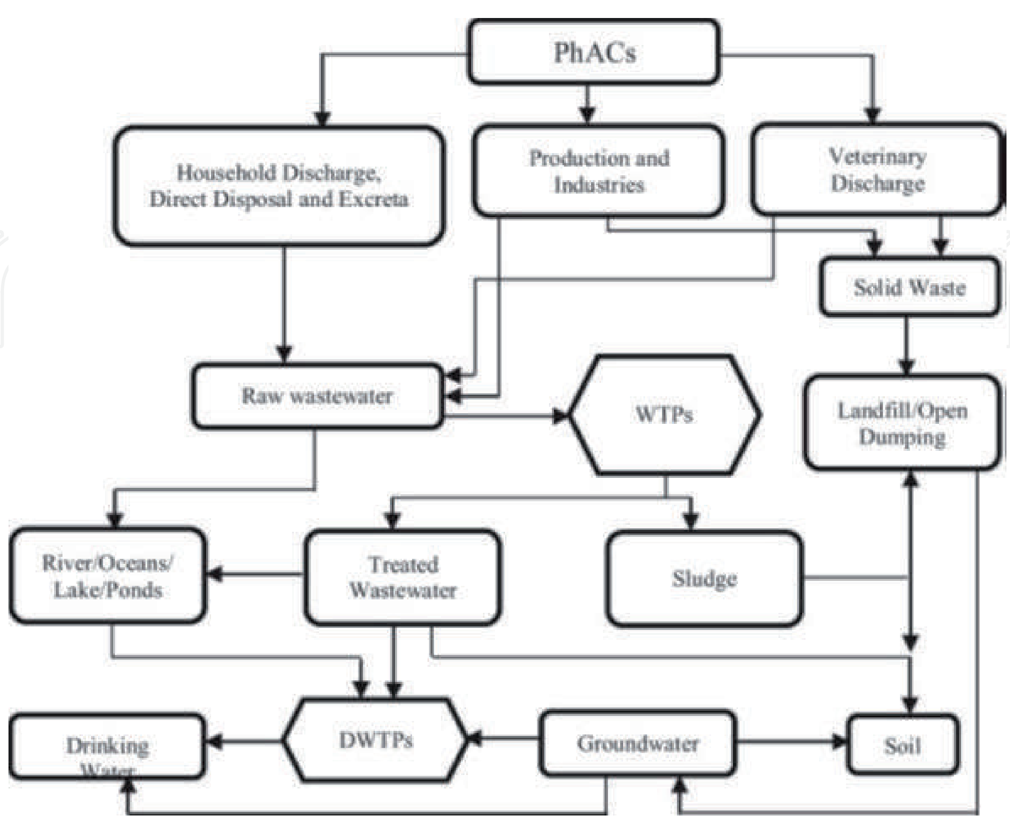


**Figure 1.**
*Flowchart showing PhACs pathways in the environment [30, 31].*

sewage, sewage sludge, groundwater, surface water, and drinking water [24, 30, 31]. So, WWTPs are considered as one of the prominent anthropogenic sources emitting pharmaceuticals into the environment along with industrial discharges, hospital effluents, etc. [22, 25]. Furthermore, the inefficient management and treatments of PhACs risk the prospect of sustainable reuse of treated wastewater and sludge [21]. **Figure 1** shows the flowchart showing PhACs pathways in the environment [30, 31].

## 3. Removal of pharmaceuticals from sewage/wastewater

It was well recognized in the literature that the conventional biological treatment systems alone are not sufficient enough to completely remove the pharmaceuticals and therefore, some additional steps are required for their proper treatment. It was reported that among the conventional activated sludge process (ASP) and membrane bioreactor (MBR) systems, the MBR system appeared to have a higher removal efficiency for many of the pharmaceuticals [1, 32]. On the other hand, carbamazepine and hydrochlorothiazide showed poor removal efficiencies in either ASP or MBR systems [1, 32]. O'Brien et al. [33] have found that compounds such as atenolol, carbamazepine, and ibuprofen appeared to be persistent in the sewer system. It was recommended to use a composite sampling approach in wastewater treatment plants [5, 33]. The superior performance of MBR in the removal of some target pharmaceuticals is due to the result of the higher biomass concentration, longer solid retention time (SRT), and better-retaining capacity of solids and microbes [32, 34]. On the other hand, the integration approach of membrane technology is called electrochemical membrane bioreactors (EMBR). It was observed that EMBRs are more efficient with low energy consumptions as compared to MBRs and ASPs [21, 35]. But the common problem with the advanced technologies is their limited applications only at laboratory and pilot scales. Besides, membrane fouling, high energy demand, and costly membrane materials are some limitations of MBRs, which need to be overcome for their extensive full-scale applications [21].

The term removal of pharmaceuticals used here means the conversion of the parent compound. Thus, the overall removal refers to the losses of a parent compound by different mechanisms of chemical and physical transformation, biodegradation, and sorption to solid matter [1]. The most analyzed carbamazepine showed very low removal (<25%) regardless of the treatment applied [32]. The pharmaceuticals removal efficiencies are based on the characteristics of the wastewater, treatment types used, and other operational conditions [1, 21]. The addition of the occasional tertiary treatment improves the removal efficiencies of the pharmaceuticals. The lower removal efficiency of diclofenac was reported in some studies [1, 36, 37]. Better performances of WWTP may be due to longer both hydraulic and solid retention times. As a compound spends more time in reactors wherein bacteria growth is promoted, the biological transformation may occur to a greater extent [38]. It has been proven that longer SRT, especially, improves the elimination of most of the pharmaceuticals during sewage treatment [1, 39].

A variety of treatment techniques for pharmaceuticals removal have been considered in the past studies such as natural, conventional and advanced treatment approaches. Dilution, volatilization, photolysis, sorption, biodegradation, etc., are cost-effective and natural processes [21]. However, the natural processes are proved less efficient [22]. On the other hand, the conventional approaches viz. adsorption, ozonation, membrane filtration, showed high pharmaceuticals removal efficacies [23]. But these approaches are having some disadvantages like oxidation by-products formation in the ozonation process may be more toxic than the parent compounds, and high operational costs in addition to the concentrate disposal are required in the membrane filtration process [25]. The widespread applications of various advanced treatment approaches viz. advanced oxidation processes (AOPs), constructed wetlands, bioelectrical systems, enzymatic treatment, have been recommended in the past few years [21]. Also, the up-gradation of the conventional WWTPs might further minimize the environmental release of the various pharmaceuticals [21, 23, 40]. Although the AOPs are considered one of the most effective treatment options for a variety of pharmaceuticals removal, their full-scale applications are still limited due to the number of challenges [18–21, 25, 41].

The WWTPs generally considered the primary, secondary, and sometimes tertiary treatment stages. The pharmaceuticals entered into the plants undergo several treatment stages, and their fraction is degraded/removed [21, 24, 42]. In the secondary stage, the pharmaceuticals are subjected to several processes such as biodegradation, sorption, dispersion, dilution, photodegradation, and volatilization [21, 22, 24]. Likewise, the tertiary treatment steps are reported to exhibit significant pharmaceuticals removal efficiency via ozonation-like conventional oxidation processes [21, 43, 44].

The importance of the tertiary treatment in the WWTPs is versatile as it supplements the secondary treatment and those pollutants that are not removed in the second stage are removed in the tertiary stage. Several advanced technologies are employed to remove the pharmaceuticals in the WWTPs themselves to produce high-quality effluent for reuse purposes [21, 44, 45]. Among the tertiary treatment, AOPs have been considered that oxidize/mineralize the various pharmaceuticals and their by-products to $CO_2$, $H_2O$, and simple inorganic ions [18, 21]. The various types are AOPs are now widely applied for various applications of high strength and pharmaceuticals removal viz. Fenton process, Photo-Fenton process, Electro-Fenton process, Sono-Fenton process, ozonation process, UV-based treatment [21, 46]. Also, a range of commercially available adsorbents, such as activated carbon (AC), biochar, carbon nanotubes, clay minerals, are used for the adsorption of various pharmaceuticals [21, 47]. The usages of AC for a broad-spectrum pharmaceutical adsorption were found most suitable due to reduced interference from the organic materials for the adsorption active sites [21, 48]. The adsorption efficiency depends on the types of PhACs, properties of AC, and other environmental conditions [21, 24].

Among the mentioned options, ozonation and AC treatment are found to be the economically feasible option and utilized in some WWTPs [21, 25]. The main reactive species in AOPs for the degradation/mineralization of the pharmaceuticals are hydroxyl radicals ($OH^{\bullet}$) and the number of parallel reactions is reported in their mechanism [18–20, 49, 50]. The suitability of the various adoption of the AOPs is mainly based on wastewater characteristics, recalcitrant nature of the target compounds, available resources, and economic conditions [50]. It was well recognized in the literature that the integrated processes are more efficient and environmental friendly [18, 50]. A very high removal efficiency (>95%) of diclofenac, carbamazepine, sulpiride, at an ozone dose of 5 mg/L, was observed [51]. All the AOPs are having their limitations/disadvantages as well; hence, the suitable/optimized treatment options should be designed and implemented to achieve the target removal efficacies etc. [18, 41, 50]. Some of the disadvantages of the Fenton process are low-working pH requirement and high sludge production, the chances of the pharmaceuticals accumulate in the iron sludge produced after the treatment [41]. On the other hand, when the applied ozone dosages are inadequate, it will result in the formation of transformation products [18], and the toxicity can further be reduced by a subsequent biological treatment [21, 52]. The combined approach of the ozonation-biological process is found most efficient for the removal of pharmaceuticals from secondary urban wastewater [21, 52, 53]. Currently, many treatment technologies are available as mentioned in **Table 2** [54, 55].

| Treatment technologies | Classification |
|---|---|
| Physical treatment | Primary treatment |
| Aerobic process<br>Anaerobic process | Secondary biological treatment |
| Activated carbon<br>Membrane distillation<br>Membrane technology | Tertiary treatments |
| Fenton process<br>Ozone/hydrogen peroxide treatment<br>Photocatalysis Electrochemical oxidation<br>Ultrasound irradiation<br>Wet air oxidation | Advanced oxidation processes |
| Mixed primary, secondary and tertiary treatments | Hybrid technologies |

**Table 2.**
*Some treatment technologies for pharmaceutical wastewater treatment [54, 55].*

## 4. Conclusion

This chapter provides a brief overview regarding the problems associated with the pharmaceuticals present in the sewage/wastewater and their suitable treatment options. From the literature, it was understood that the problems related to the emerging contaminants and particularly for the pharmaceuticals are of great concern and require specific attention to protecting the environment and public health. Out of the various categories of pharmaceuticals, different treatment options are required and one single option is not sufficient to remove all the types of pharmaceuticals. The challenges associated with their accurate analysis, detection, and extraction due to their low concentration are also an important domain for further research. Regarding the treatment options in various studies, it was reported that the integrated processes are more advantageous in many ways for pharmaceuticals removal. For example, the post-biological treatment option after the ozonation process significantly improves the pharmaceutical removal. The other options like ASP and MBR are also considered useful but not efficient enough for their complete mineralization and removal. Also, the activated carbon-adsorption process is just a phase change mechanism system and required extensive research for further improvement. Various transformation/intermediate products are formed in AOPs treatment, hence required more advancements to remove those toxic intermediates from the water matrix. The up-gradation of the WWTPs is a very important step to improve the effluent quality considering the problems of the pharmaceuticals. The single and combined AOPs are limited to lab/pilot scale only and their full-scale applications are required, which should be focused on in future research for the best-fit alternative both economically and environmental friendly.


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## Conflict of interest

No potential conflict of interest was reported by the authors.

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## References

[1] Jelic A, Gros M, Ginebreda A, Cespedes-Sànchez R, Ventura F, Petrovic M, et al. Occurrence, partition and removal of pharmaceuticals in sewage water and sludge during wastewater treatment. Water Research. 2011;**45**(3):1165-1176. DOI: 10.1016/j.watres.2010.11.010

[2] Husain Khan A, Abdul Aziz H, Khan NA, Ahmed S, Mehtab MS, Vambol S, et al. Pharmaceuticals of emerging concern in hospital wastewater: Removal of Ibuprofen and Ofloxacin drugs using MBBR method. International Journal of Environmental Analytical Chemistry. 2020;**19**:1-5. DOI: 10.1080/03067319.2020.1855333

[3] Khan AH, Aziz HA, Khan NA, Hasan MA, Ahmed S, Farooqi IH, et al. Impact, disease outbreak and the eco-hazards associated with pharmaceutical residues: A Critical review. International Journal of Environmental Science and Technology. 2021;**10**:1-2. DOI: 10.1007/s13762-021-03158-9

[4] Nikolaou A, Meric S, Fatta D. Occurrence patterns of pharmaceuticals in water and wastewater environments. Analytical and Bioanalytical Chemistry. 2007;**387**(4):1225-1234. DOI: 10.1007/s00216-006-1035-8

[5] Tran NH, Gin KY. Occurrence and removal of pharmaceuticals, hormones, personal care products, and endocrine disrupters in a full-scale water reclamation plant. Science of the Total Environment. 2017;**599**:1503-1516. DOI: 10.1016/j.scitotenv.2017.05.097

[6] Madikizela LM, Ncube S, Chimuka L. Analysis, occurrence and removal of pharmaceuticals in African water resources: A current status. Journal of Environmental Management. 2020;**253**:109741. DOI: 10.1016/j.jenvman.2019.109741

[7] Mousel D, Bastian D, Firk J, Palmowski L, Pinnekamp J. Removal of pharmaceuticals from wastewater of health care facilities. Science of the Total Environment. 2021;**751**:141310. DOI: 10.1016/j.scitotenv.2020.141310

[8] Ruhoy IS, Daughton CG. Beyond the medicine cabinet: An analysis of where and why medications accumulate. Environment International. 2008;**34**(8):1157-1169. DOI: 10.1016/j.envint.2008.05.002

[9] Wolf L, Zwiener C, Zemann M. Tracking artificial sweeteners and pharmaceuticals introduced into urban groundwater by leaking sewer networks. Science of the Total Environment. 2012;**430**:8-19. DOI: 10.1016/j.scitotenv.2012.04.059

[10] Launay MA, Dittmer U, Steinmetz H. Organic micropollutants discharged by combined sewer overflows–characterisation of pollutant sources and stormwater-related processes. Water Research. 2016;**104**:82-92. DOI: 10.1016/j.watres.2016.07.068

[11] Pedersen JA, Soliman M, Suffet IH. Human pharmaceuticals, hormones, and personal care product ingredients in runoff from agricultural fields irrigated with treated wastewater. Journal of Agricultural and Food Chemistry. 2005;**53**(5):1625-1632. DOI: 10.1021/jf049228m

[12] Majumder A, Gupta AK, Ghosal PS, Varma M. A review on hospital wastewater treatment: A special emphasis on occurrence and removal of pharmaceutically active compounds, resistant microorganisms, and SARS-CoV-2. Journal of Environmental Chemical Engineering. 2020;**22**:104812. DOI: 10.1016/j.jece.2020.104812

[13] Gielen GJ, van den Heuvel MR, Clinton PW, Greenfield LG. Factors

impacting on pharmaceutical leaching following sewage application to land. Chemosphere. 2009;**74**(4):537-542. DOI: 10.1016/j.chemosphere.2008.09.048

[14] Kinney CA, Furlong ET, Werner SL, Cahill JD. Presence and distribution of wastewater-derived pharmaceuticals in soil irrigated with reclaimed water. Environmental Toxicology and Chemistry: An International Journal. 2006;**25**(2):317-326. DOI: 10.1897/05-187R.1

[15] Carbonell G, Pro J, Gómez N, Babín MM, Fernández C, Alonso E, et al. Sewage sludge applied to agricultural soil: Ecotoxicological effects on representative soil organisms. Ecotoxicology and Environmental Safety. 2009;**72**(4):1309-1319. DOI: 10.1016/j.ecoenv.2009.01.007

[16] Lapen DR, Topp E, Metcalfe CD, Li H, Edwards M, Gottschall N, et al. Pharmaceutical and personal care products in tile drainage following land application of municipal biosolids. Science of the Total Environment. 2008;**399**(1-3):50-65. DOI: 10.1016/j.scitotenv.2008.02.025

[17] Wick A, Fink G, Joss A, Siegrist H, Ternes TA. Fate of beta blockers and psycho-active drugs in conventional wastewater treatment. Water Research. 2009;**43**(4):1060-1074. DOI: 10.1016/j.watres.2008.11.031

[18] Hussain M, Mahtab MS, Farooqi IH. The applications of ozone-based advanced oxidation processes for wastewater treatment: A review. Advances in Environmental Research. 2020;**9**(3):191-214. DOI: 10.12989/aer.2020.9.3.191

[19] Mahtab MS, Farooqi IH, Khursheed A. Sustainable approaches to the Fenton process for wastewater treatment: A review. Materials Today: Proceedings. 2021;**47**(7):1480-1484. DOI: 10.1016/j.matpr.2021.04.215

[20] Hussain M, Mahtab MS, Farooqi IH. A comprehensive review of the Fenton-based approaches focusing on landfill leachate treatment. Advances in Environmental Research. 2021;**10**(1):59-86. DOI: 10.12989/aer.2021.10.1.059

[21] Rout PR, Zhang TC, Bhunia P, Surampalli RY. Treatment technologies for emerging contaminants in wastewater treatment plants: A review. Science of the Total Environment. 2021;**753**:141990. DOI: 10.1016/j.scitotenv.2020.141990

[22] Barbosa MO, Moreira NF, Ribeiro AR, Pereira MF, Silva AM. Occurrence and removal of organic micropollutants: An overview of the watch list of EU Decision 2015/495. Water Research. 2016;**94**:257-279. DOI: 10.1016/j.watres.2016.02.047

[23] Pesqueira JF, Pereira MF, Silva AM. Environmental impact assessment of advanced urban wastewater treatment technologies for the removal of priority substances and contaminants of emerging concern: A review. Journal of Cleaner Production. 2020;**261**:121078. DOI: 10.1016/j.jclepro.2020.121078

[24] Luo Y, Guo W, Ngo HH, Nghiem LD, Hai FI, Zhang J, et al. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. Science of the Total Environment. 2014;**473**:619-641. DOI: 10.1016/j.scitotenv.2013.12.065

[25] Rizzo L, Malato S, Antakyali D, Beretsou VG, Đolić MB, Gernjak W, et al. Consolidated vs new advanced treatment methods for the removal of contaminants of emerging concern from urban wastewater. Science of the Total Environment. 2019;**655**:986-1008. DOI: 10.1016/j.scitotenv.2018.11.265

[26] Das S, Ray NM, Wan J, Khan A, Chakraborty T, Ray MB. Micropollutants in wastewater: Fate and

removal processes. Physico-chemical Wastewater Treatment and Resource Recovery. 2017;**3**:75

[27] Petrie B, Barden R, Kasprzyk-Hordern B. A review on emerging contaminants in wastewaters and the environment: Current knowledge, understudied areas and recommendations for future monitoring. Water Research. 2015;**72**:3-27. DOI: 10.1016/j.watres.2014.08.053

[28] Ferrando-Climent L, Rodriguez-Mozaz S, Barceló D. Incidence of anticancer drugs in an aquatic urban system: From hospital effluents through urban wastewater to natural environment. Environmental Pollution. 2014;**193**:216-223. DOI: 10.1016/j.envpol.2014.07.002

[29] Jones OA, Voulvoulis N, Lester JN. Human pharmaceuticals in the aquatic environment: A review. Environmental Technology. 2001;**22**(12):1383-1394. DOI: 10.1080/09593332208618186

[30] Balakrishna K, Rath A, Praveenkumarreddy Y, Guruge KS, Subedi B. A review of the occurrence of pharmaceuticals and personal care products in Indian water bodies. Ecotoxicology and Environmental Safety. 2017;**137**:113-120. DOI: 10.1016/j.ecoenv.2016.11.014

[31] Khan SU, Rameez H, Basheer F, Farooqi IH. Eco-toxicity and health issues associated with the pharmaceuticals in aqueous environments: A global scenario. Pharmaceutical Wastewater Treatment Technologies: Concepts and Implementation Strategies. 2021:145-179. DOI: 10.2166/9781789061338

[32] Radjenović J, Petrović M, Barceló D. Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment. Water Research. 2009;**43**(3):831-841. DOI: 10.1016/j.watres.2008.11.043

[33] O'Brien JW, Banks AP, Novic AJ, Mueller JF, Jiang G, Ort C, et al. Impact of in-sewer degradation of pharmaceutical and personal care products (PPCPs) population markers on a population model. Environmental Science & Technology. 2017;**51**(7):3816-3823. DOI: 10.1021/acs.est.6b02755

[34] Joss A, Zabczynski S, Göbel A, Hoffmann B, Löffler D, McArdell CS, et al. Biological degradation of pharmaceuticals in municipal wastewater treatment: Proposing a classification scheme. Water Research. 2006;**40**(8):1686-1696. DOI: 10.1016/j.watres.2006.02.014

[35] Asif MB, Maqbool T, Zhang Z. Electrochemical membrane bioreactors: State-of-the-art and future prospects. Science of the Total Environment. 2020;**741**:140233

[36] Cirja M, Ivashechkin P, Schäffer A, Corvini PF. Factors affecting the removal of organic micropollutants from wastewater in conventional treatment plants (CTP) and membrane bioreactors (MBR). Reviews in Environmental Science and Bio/Technology. 2008;**7**(1):61-78. DOI: 10.1007/s11157-007-9121-8

[37] Kimura K, Hara H, Watanabe Y. Elimination of selected acidic pharmaceuticals from municipal wastewater by an activated sludge system and membrane bioreactors. Environmental Science & Technology. 2007;**41**(10):3708-3714. DOI: 10.1021/es061684z

[38] Reif R, Suárez S, Omil F, Lema JM. Fate of pharmaceuticals and cosmetic ingredients during the operation of a MBR treating sewage. Desalination. 2008;**221**(1-3):511-517. DOI: 10.1016/j.desal.2007.01.111

[39] Göbel A, McArdell CS, Joss A, Siegrist H, Giger W. Fate of sulfonamides, macrolides, and trimethoprim in different wastewater treatment technologies. Science of the Total Environment. 2007;**372**(2-3):361-371. DOI: 10.1016/j.scitotenv.2006.07.039

[40] Roccaro P. Treatment processes for municipal wastewater reclamation: The challenges of emerging contaminants and direct potable reuse. Current Opinion in Environmental Science & Health. 2018;**2**:46-54. DOI: 10.1016/j.coesh.2018.02.003

[41] Mahtab MS, Farooqi IH, Khursheed A. Zero Fenton sludge discharge: A review on reuse approach during wastewater treatment by the advanced oxidation process. International Journal of Environmental Science and Technology. 2021;**13**:1-4. DOI: 10.1007/s13762-020-03121-0

[42] Tran NH, Reinhard M, Gin KY. Occurrence and fate of emerging contaminants in municipal wastewater treatment plants from different geographical regions—A review. Water Research. 2018;**133**:182-207. DOI: 10.1016/j.watres.2017.12.029

[43] Rout PR, Bhunia P, Dash RR. Response surface optimization of phosphate removal from aqueous solution using a natural adsorbent. Trends in Asian Water Environmental Science and Technology. 2017:93-104. DOI: 10.1007/978-3-319-39259-2_8

[44] Ahmed MB, Zhou JL, Ngo HH, Guo W, Thomaidis NS, Xu J. Progress in the biological and chemical treatment technologies for emerging contaminant removal from wastewater: A critical review. Journal of Hazardous Materials. 2017;**323**:274-298. DOI: 10.1016/j.jhazmat.2016.04.045

[45] Wang J, Wang S. Removal of pharmaceuticals and personal care products (PPCPs) from wastewater: A review. Journal of Environmental Management. 2016;**182**:620-640. DOI: 10.1016/j.jenvman.2016.07.049

[46] de Oliveira M, Frihling BE, Velasques J, Magalhães Filho FJ, Cavalheri PS, Migliolo L. Pharmaceuticals residues and xenobiotics contaminants: Occurrence, analytical techniques and sustainable alternatives for wastewater treatment. Science of the Total Environment. 2020;**705**:135568. DOI: 10.1016/j.scitotenv.2019.135568

[47] Rodriguez-Narvaez OM, Peralta-Hernandez JM, Goonetilleke A, Bandala ER. Treatment technologies for emerging contaminants in water: A review. Chemical Engineering Journal. 2017;**323**:361-380. DOI: 10.1016/j.cej.2017.04.106

[48] Budimirović D, Veličković ZS, Djokić VR, Milosavljević M, Markovski J, Lević S, et al. Efficient As(V) removal by α-FeOOH and α-FeOOH/α-$MnO_2$ embedded PEG-6-arm functionalized multiwall carbon nanotubes. Chemical Engineering Research and Design. 2017;**119**:75-86. DOI: 10.1016/j.cherd.2017.01.010

[49] Mahtab MS, Farooqi IH. UV-$TiO_2$ process for landfill leachate treatment: Optimization by response surface methodology. International Journal for Research in Engineering Application & Management. 2020;**5**(12):14-18. DOI: 10.35291/2454-9150.2020.0160

[50] Mahtab MS, Islam DT, Farooqi IH. Optimization of the process variables for landfill leachate treatment using Fenton based advanced oxidation technique. Engineering Science and Technology, an International Journal. 2021;**24**(2):428-435. DOI: 10.1016/j.jestch.2020.08.013

[51] Sui Q, Huang J, Deng S, Yu G, Fan Q. Occurrence and removal of

pharmaceuticals, caffeine and DEET in wastewater treatment plants of Beijing, China. Water Research. 2010;**44**(2):417-426. DOI: 10.1016/j.watres.2009.07.010

[52] Knopp G, Prasse C, Ternes TA, Cornel P. Elimination of micropollutants and transformation products from a wastewater treatment plant effluent through pilot scale ozonation followed by various activated carbon and biological filters. Water Research. 2016;**100**:580-592. DOI: 10.1016/j.watres.2016.04.069

[53] McArdell C. The first full-scale advanced ozonation plant in the Dübendorf WWTP running; the new Swiss water protection act approved. Norman Bulletin. 2015;**4**:36-37

[54] Mahmood Q, Khan MS, Riaz N. Existing treatment—Globally in full scale plants. Pharmaceutical Wastewater Treatment Technologies: Concepts and Implementation Strategies. 2021:402-428. DOI: 10.2166/9781789061338

[55] Khan NA, Ahmed S, Vambol V, Vambol S. Pharmaceutical Wastewater Treatment Technologies: Concepts and Implementation Strategies2021. DOI: 10.2166/9781789061338

Chapter

# Implications of Sewage Discharge on Freshwater Ecosystems

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## Abstract

Freshwater ecosystems such as lakes and rivers are among the sensitive ecosystems, which host rich biodiversity. Being major freshwater resources, they provide a wide range of ecosystem services, making their existence essential for the well-being of human societies. However, in the past few decades, there have been adverse impacts on the health of these ecosystems due to uncontrolled sewage disposal throughout the world. This is increasingly becoming a tough challenge to protect the freshwater ecosystems from the ramifications of the entry of untreated sewage. Loss of biodiversity, physiological and behavioral changes in species, community shifts, and fish mortality have been witnessed in aquatic ecosystems, which are the recipients of untreated or partially treated sewage. Nutrients such as nitrogen and phosphorus are abundant in sewage and are one of the leading causes of eutrophication of water bodies. Several freshwater ecosystems around the world have become a victim of eutrophication due to untreated sewage disposal, leading to a change in trophic status.

**Keywords:** biodiversity, eutrophication, phosphorus, species

## 1. Introduction

One of the biggest challenges we are confronting in the twenty-first century is the inaccessibility of clean water and improved sanitation [1]. Although safe drinking water, sanitation and hygiene (WASH) are required for an improved standard of living, they are equally important for the protection of health and environment. As the countries improvise their sanitation coverage, it is also important that they reduce the release of untreated sewage into the environment by exploiting the energy and nutrients present in it. Water plays an important role in various aspects of socio-economic development such as food production, economy, domestic water supply, environmental sustainability, health systems, and industrial applications. Lack of access to WASH could have a negative impact on the economy, health, and environment. Water pollution from sources such as agriculture, industries, urban runoffs, and waste disposal threatens clean drinking water supplies with detrimental impacts on freshwater ecosystems [2]. Several water bodies in developing countries such as rivers, streams, and lakes, which are located close to highly populated areas, have become filled with waste, which have turned them into dead or sewage streams. Most aquatic ecosystems have a natural tendency to dilute pollution to some extent, but severe contamination of aquatic ecosystems results in the alteration of their fauna and flora community [3]. The amount of nutrients received by aquatic ecosystems varies throughout the world depending on the characteristics of the ecosystem. Most of them receive varying quantities of a wide range of nutrients that are unloaded from human settlements. Sewage is the used water-containing solids deposited from households, commercials, and industries, which is transported in sewers and disposed off into watercourses. Sewage disposal in a particular region depends on the accessibility of natural watercourses in that particular area. Worldwide around 65% of the river stretches are polluted [4], which have resulted in the degradation as well as loss of biodiversity in the water bodies and cannot be neglected.

Poorly managed human excreta has several detrimental consequences on the environment, polluting surface water such as lakes and rivers. Heavily polluted water has a serious impact on freshwater ecosystems, food webs, and biodiversity. Water bodies located in highly populated urban areas have a considerable amount of biological oxygen demand contributed mostly from wastewater. Untreated or partly treated urban wastewater consists of high concentration of nutrients as well as organic matter [5], which upon decomposition releases additional nutrients. Increased levels of nutrients especially nitrogen and phosphorus in aquatic ecosystems are associated with eutrophication. Algal blooms especially those of cyanophytes release cyanotoxins [6], which are known to have harmful effects on aquatic life, wildlife, livestock, agricultural crops, and humans [7]. Several toxins are liberated from sewage into the water, which are consumed by fishes and other forms of aquatic life thereby increasing their possibility of entering into the food chain. Several toxic substances including heavy metals have a high concentration in the wastewater generated from industries [8]. Due to their non-degradable nature, they tend to display high toxicity in aquatic systems and accumulate in the food webs. Thus, water pollution has received more attention during the past few years owing to their ecologic, biodiversity, economic, and social perspectives.

## 2. Composition of sewage

Sewage is composed of domestic effluent consisting of black water (excreta, urine, and fecal sludge) and gray water (used water from washing and bathing); water from commercial establishments and institutions, including hospitals; industrial effluent, stormwater and other urban runoff; and agricultural, horticultural and aquaculture runoff [9]. Sewage comprises 99.9% of water and 0.1% of solids, which includes dissolved as well as suspended organic and inorganic solids. Dissolved solids constitute a major portion as compared to suspended solids, while organic fraction consists of fats, carbohydrates, proteins, lignin, and their decomposition products. Similarly, the inorganic part includes several constituents derived from industrial as well as domestic sources including heavy metals like cadmium, mercury, arsenic, zinc, and copper. A varied and abundant diversity of microbes are present in sewage [10] and is contributed in human sewage from sources like human domestic waste such as feces, washing, bathing urine, and sweat. These microorganisms are added from the human body present in the skin, respiratory tract, oral cavity, gastrointestinal tract, and urogenital tract. Wastewater is considered as an important reservoir of pathogens, [11, 12], which includes Fecal Coliform, *E coli,* Salmonella, Shigella, Vibrio cholera, parasitic eggs and cysts, viruses and fungi [13, 14], intestinal nematodes like hookworm (Ancylostoma duodenale), roundworm (Ascaris lumbricoides), and whipworms (Trichuris). Sewage contains a rich concentration of nutrients such as nitrogen (N) and phosphorus (P). Around, 16.6 Tg (Tg = million metric ton) of nitrogen and 3.0 Tg of phosphorus are present in wastewater produced throughout the world annually. Human urine consists of a high concentration of nutrients such as nitrogen and phosphorus than the amount present in the feces [15]. Thus, human urine is responsible for 50% of the phosphorus load and 80% of the nitrogen load in the sewage [16].

## 3. Sewage generation and treatment scenario throughout the world

Despite being a major factor in water quality, proper wastewater treatment is lacking in many developing countries of the world and it is estimated that 90% of developing countries do not treat wastewater before disposal into the receiving waters be it lakes or rivers. A large amount of untreated industrial, agricultural, and domestic wastes is discharged into the world's waterways due to which low-income countries are hit by contaminated water supplies and disease. Water sources such as rivers, lakes, and oceans are the major recipients of domestic and industrial wastes across the world. Country-specific data on wastewater generation reveal that around 390 billion $m^3$ of wastewater is generated throughout the world, which is fivefold the amount of water released by Niagara Falls annually [17]. However, the amount of wastewater generated is projected to increase by 24% by 2020 and further about 51% by 2050 [18]. It is estimated that worldwide about 80% of the wastewater generated is discharged directly without any proper treatment into water bodies [19]. Around two million tons of sewage, industrial and agricultural waste is discharged into the world's waterways. Water sources such as rivers, lakes, and oceans are the major recipients of domestic and industrial wastes across the world. With regard to the wastewater generation and treatment in the world, it has been stated that high-income countries on an average treat around 70% of the wastewater generated by them, and upper- and lower middle-income countries provide treatment to 38% and 28% of the wastewater generated respectively, while as low-income countries treat only 8% of total wastewater generated [20]. Available figures reveal a shocking scenario of sewage disposal into water bodies across the world. Venezuela discharges 97% of sewage generated directly into the environment without providing any treatment. Developed nations like Turkey discharge 75% of the wastewater generated from industries directly into the environment. About 71% of the wastewater generated in European countries receives treatment owing to public awareness toward health and environmental or partly due to technological advancements. In Latin American countries, only 20% of the wastewater generated is being treated, while the rest is disposed off untreated into the water bodies. The Middle East and North Africa provide treatment to 51% [20], while Asian countries treat only 32% of generated wastewater. Asia is the largest producer of wastewater and generates 42% of wastewater produced globally with an annual estimate of 159 billion $m^3$. North American countries generate 67 billion $m^3$, while Europe generates 68 billion $m^3$ [18]. With the ongoing freshwater crisis throughout the world, the available freshwater resources cannot be polluted and made unfit for human consumption. Proper treatment and disposal of wastewater should be regarded as a matter of urgency throughout the world [21].

## 4. Effects of sewage on freshwater biodiversity

Now a day's there is an increasing recognition that freshwater is a valuable resource due to overexploitation and pollution. Wastewater discharge contain several harmful substances or chemicals, which may cause adverse environmental impacts such as changes in aquatic habitats, species composition, and decrease in biodiversity. All of these impacts lead to a less valuable environment, a less prosperous economy, and ultimately, a diminished quality of life. Several substances are present in sewage, which can potentially impact plant and animal communities in different ways.

### 4.1 Temperature

#### *4.1.1 Physical changes*

Sewage discharge is often associated with physical changes in water bodies. Aquatic life sustains under an optimum temperature and an increase in the average temperature of the water body has ecological impacts resulting in thermal enhancement [22]. The shift in water temperature can seriously affect aquatic life, such as microbes, invertebrates, algae, and fish [23]. Temperature also affects the solubility and consequently, the availability of oxygen in the water. An increase in temperature results in less dissolution of oxygen in the water and hence, oxygen demand required by the bacteria for the degradation of wastes also increases. Tissue anoxia can occur at higher lethal temperatures in aquatic animals. Temperature also affects key physicochemical conditions such as oxygen concentrations as well as energetic processes associated with primary production and litter decomposition [24, 25].

#### *4.1.2 Chemical changes*

The effects of certain toxic substances like copper that increases metabolic demand or zinc which blocks oxygen uptake at the gill level for fish get enhanced by an increase in temperature. Toxicants that act on cellular enzymes involved in energy metabolism or that cause a change in the rate of uptake may also have their effect potentiated by a temperature increase. High water temperature also affects the toxicity of some chemicals in the water as well as the sensitivity of living organisms to toxic substances [26, 27].

#### *4.1.3 Biological changes*

Causes of thermal death include failure of osmoregulatory processes, alterations in cellular enzymes and membrane lipids, and protein denaturation. In addition, temperature controls the growth rates of phytoplankton, macrophytes, and epiphytes, making freshwater ecosystems sensitive to rising temperatures [28, 29]. Because most river organisms are ectotherms, changes in temperature have profound effects on their growth, phenology, survival, and distribution [30, 31].

### 4.2 Dissolved oxygen

#### *4.2.1 Physical changes*

Dissolved oxygen (DO) is a key parameter that determines the water quality as well as the health of an aquatic ecosystem. The presence of a certain amount of DO in water is important for the survival of higher forms of biodiversity [32]. A fluctuation in DO near its saturation is an indication of relatively healthy waters while as low dissolved oxygen indicates potential danger to the water body [33]. Oxygen-demanding wastes in the sewage are responsible for the depletion of DO levels, which impact both water quality and biodiversity in the water body [34]. The aquatic ecosystem suffering from hypoxic or anoxic conditions is responsible for the depletion of fish stocks and other forms of aquatic life. These losses can have harmful effects on ecological health, economy, and stability of the ecosystem [35].

#### *4.2.2 Chemical changes*

Development of hypoxic and anoxic conditions, increase in metal and phosphate release from sediments creation of hypoxic (reduced dissolved oxygen), anoxic (extremely low or no dissolved oxygen) and euxinic (sulfide production in the absence of oxygen) conditions take place in the water body [36, 37]. Low DO level affects the metabolic processes of species. Low levels of DO in receiving water bodies can result in the release of toxic substances, biomagnification in organisms, and increased nutrient loads.

#### *4.2.3 Biological changes*

Fish are among the most affected species as low DO concentration increases their susceptibility toward diseases, retarding their growth, hindering their swimming ability, changes in feeding habits, migration, and in extreme cases results in death.

It significantly affect mortality, reproduction, behavior, and physiological response in fishes [38]. If the decrease in oxygen continues for a long time, it can result in a change in species composition [39]. Among planktonic organisms most likely to suffer mortality from exposure to low oxygen in bottom waters are fish larvae lacking fully developed sensory and motor capabilities.

### 4.3 Total suspended solids

#### *4.3.1 Physical changes*

Suspended solids (SS) comprise of a fine particulate matter having a diameter of less than 62 mm. They can cause physical damage to fish gills [40]. Blockage of filter-feeding apparatus of zooplankton, gills of the most sensitive benthic invertebrates like epibenthos, living on or above the sediment can be clogged by sediment particles.

#### *4.3.2 Chemical changes*

They can pose a number of direct as well as indirect environmental impacts like reduced sunlight penetration, which in turn affects photosynthesis, toxic effects due to contaminants attached with suspended solids [22]. A high concentration of salts can result in increase in the salt content of the water body with harmful effects on aquatic organisms and a brackish, salty taste to its consumers.

#### *4.3.3 Biological changes*

A high level of SS in receiving water body can cause flocculation and sinking of phytoplankton, reduced primary productivity in macrophytes and algae [41, 42], egg mortality in fish [43]. Further, SS in zooplankton can cause toxicity, as well as ingestion of sediment particles having no nutritional value, causing zooplankton starvation and death.

### 4.4 Cyanide

This substance is an important toxicant to fish and other aquatic animals and its salts are frequently found in effluents from industrial wastes. Certain forms of cyanide are acutely toxic to many aquatic life forms and concentrations

<0.1 mg/l can be toxic to some sensitive aquatic species. At the cellular level, cyanide blocks the oxygen consumption of metabolizing cells, which is due to inhibition of the enzyme cytochrome oxidase catalyzing the final oxidation step in cellular respiration. Cyanide forms complexes with some heavy metals such as Zn, Pb, and Cd and is highly toxic. Several cyanide-containing substances display acute toxicity toward aquatic life [38]. However, it has been observed that cyanide-containing compounds also have effects on aquatic life at sublethal concentrations.

### 4.5 Pharmaceuticals

Pharmaceuticals are among the emerging contaminants in wastewater and are one of the most relevant group of substances having a possible impact on aquatic ecosystems due to their chemicophysical properties [44]. Water bodies that receive wastewater discharges are found to be heavily impacted by annual loadings of these substances. Pharmaceuticals along with their metabolites are readily excreted with urine and feces. While the main concern about pharmaceuticals and their metabolites is that they are being added continuously into lakes and rivers as pollutants, they can have certain adverse effects on aquatic ecosystems and harm freshwater resources including drinking water supplies on a long-term basis. Although concentrations of pharmaceutical compounds in aquatic ecosystems are low, they can cause toxic effects on organisms [45]. Uptake of pharmaceuticals into fish can occur *via* both dermal and gill surfaces for water-borne/sediment-associated pharmaceuticals, orally through the diet, or maternally, *via* the transfer of contaminants through the lipid reserve of eggs. Pharmaceutical drugs are generally designed to have low toxicity but there is the potential for unintended side effects. The active ingredients in pharmaceuticals are known to have potential risks to the aquatic ecosystem and are suspected to have direct toxicity to certain aquatic organisms. There is a global concern about the presence of estrogenic residues in the aquatic ecosystems. The source of these estrogenic residues is industrial wastes and medicines, and as additives in animal feed [46]. The effect of these traces is remarkable on aquatic animals and consequently on humans. Fishes are considered more susceptible to the high concentration of pharmaceuticals. It has been reported that substances such as diclofenac and 17a-ethinylestradiol are responsible for inducing structural disruption in the kidney and intestine and also modify the expression genes, which are associated with the process-controlling metabolism [47, 48]. Their chronic exposure to fishes might affect their survival and reproduction. Another research stated that the presence of antibiotic compounds such as sulfamethoxazole might cause chronic toxicity effects on the photosynthetic apparatus of algae [49]. Therefore, the pharmaceuticals have an effect on the survival of algae due to their rate reduction of photosynthesis by affecting the functions of chloroplasts. A large amount of dead algae lead to secondary effects on the ecosystem such as eutrophication and disruption of the food chain. It threatens the equilibrium of the entire aquatic ecosystem [50].

### 4.6 Nitrogen

Some water-soluble forms of inorganic nitrogen, such as ionized ammonium, ammonia, nitrite, and nitrate, are present in waste streams, which can exert oxygen demand in surface water resources. Molecular ammonia or $NH_4OH$ is considered as a most toxic form of ammonia, while the dissociated ammonium ion ($NH_4$) is relatively nontoxic. The discharge of ammonia is mostly from industries, agriculture, and domestic wastewater. Organic wastes contributed from these sources are responsible for the increases in oxygen demand as a result of the increase in biological decomposition and production of ammonia due to the decomposition of organic nitrogen-containing compounds. Ammonia has toxic effects on aquatic life and high concentration can impair aquatic communities [51]. It encourages eutrophication in receiving water bodies. Ammonia and nitrate are principal forms of nitrogen and in the presence of oxygen, ammonia is converted into nitrate creating low dissolved oxygen conditions in surface waters [52, 53]. Excess ammoniacal nitrogen is damaging to aquatic life due to its ability to destroy the aquatic enzyme hydrolysis reaction apart from damaging certain tissues and organs in organisms. Its elevated concentration can cause certain symptoms in aquatic organisms such as hypoxia, coma, and reduced immunity, resulting in slow growth and even large numbers of deaths [54]. Ammonia concentrations >2 mg/l are toxic to aquatic life, especially fishes. Several works done on ammonia toxicity on freshwater vegetation have shown that concentrations >2.4 mg/l inhibit photosynthesis. Further, nitrate causes a decline in amphibian populations and in adverse cases causes poor larval growth, reduced body size, and impaired swimming ability. Direct toxic effects from ammonia are those with a direct impact on individual organisms, typically death, reduced growth rate, or reduced reproductive success.

### 4.7 Heavy metals

Heavy metals comprise one of the most toxic pollutants in aquatic ecosystems due to the detrimental impacts they display in aquatic biota [55]. The heavy metal present in sewage has severe detrimental effects on the ecological balance of the aquatic environment including organisms [56]. Fishes are among the severely affected species and cannot escape from the detrimental impacts of metals. They accumulate a considerable amount of heavy metals in their body tissues and represent a major dietary source of this element for humans. The presence of heavy metals can inhibit the growth of fish as well as its larvae, reduce the size of fish populations, and can threaten the entire fish population if present in high concentration. A high concentration of aluminum can result in osmoregulatory failure in aquatic animals like fishes [57, 58]. It has the potential to bind with fish gills causing several kinds of diseases, suffocation and ultimately death, change in blood plasma levels, and decrease in nutrient intake at gills. More residence time of water in lakes results in the accumulation of heavy metals in biota, while a significant portion finds its way into the sediments. Mercury has carcinogenic and neuro-toxic properties with the ability to accumulate in living organisms, which gradually increases in the food web. Apart from its toxic effects on humans due to biomagnification in fish, mercury compounds have certain toxic effects on aquatic animals as well.

### 4.8 Phosphorus

One of the major pollutants found in aquatic environments is phosphorus. The average amount of phosphorus in water resources is <1 mg/l; exceeding the amounts permitted in water causes a serious threat to the environment, animals, and aquatic life. Phosphorous is one of the essential nutrients which promotes algal blooms in rivers and lakes and finally leads to eutrophication which causes oxygen depletion in water *via* algal decay, which has harmful effects on aquatic life. A little rise in the content of this nutrient influences toxin production since it increases the growth of the algae.

## 5. Eutrophication

### 5.1 Classification of lakes

Lakes are often classified according to their trophy or degree of enrichment with nutrients and organic matter. They are classified by their trophic state with the main classes of oligotrophic, mesotrophic, eutrophic, and dystrophic (**Table 1**).

Several natural water bodies referred as oligotrophic have clearwater ecosystems with limited primary and secondary productivities due to a shortage of major nutrients [60]. These water bodies under natural succession will require thousands of years to transform into eutrophic. The oligotrophic lake is deep and receiving effluents that are nutrient-poor from its drainage basin. Organic matter production is less in the well-illuminated epilimnion. Therefore, the material sinking into the hypolimnion is the small quantity and little oxygen is consumed there during the summer. In contrast, a eutrophic lake is often, but not necessarily, shallower, the drainage basin is richer, and rivers and groundwater discharge into its epilimnion a substantial amount of nutrients. Primary productivity is higher as compared to that of oligotrophic lakes, and therefore, more organic material settles into the hypolimnion resulting in oxygen depletion. As a result, the deeper layers of water of a eutrophic lake become anoxic during summer. Oligotrophic water bodies have <5–10 μg $l^{-1}$ of phosphorus and < 250–600 μg $l^{-1}$ nitrogen. Oligotrophic water bodies have mean primary productivity ranging between 50 and 300 mg carbon $m^{-2}$ $day^{-1}$. In eutrophic water bodies, the phosphorus concentration is 10–30 μg $l^{-1}$, while nitrogen concentration content is 500–100 μg $l^{-1}$. Primary productivity in eutrophic water bodies is >1 g carbon $m^{-2}/day^{-1}$. If excessive quantities of phosphorus and nitrogen are added to the water, excessive growth of aquatic plants and

| Trophic status | Characteristics | TP (mg $m^{-2}$) | TN (mg $m^{-2}$) |
|---|---|---|---|
| **Oligotrophic** | Oligotrophic lakes have poor nutrients and support little plant growth due to which biological productivity is usually low. The waters are clear and the bottom layers have a good oxygen supply throughout the year. | 3.0–17.7 | 307_1630 |
| **Mesotrophic** | Mesotrophic lakes have transitional characteristics. They are moderately enriched with nutrients and have moderate plant growth. | 10.9–95.6 | 361_1387 |
| **Eutrophic** | Eutrophic lakes have a rich supply of nutrients that support dense plant growths due to which biological productivity is usually high. The waters are turbid, which support heavy growths of phytoplankton and an abundance of rooted aquatic vegetation. Deepwaters have less concentrations of dissolved oxygen during the seasons of restricted circulation. | 16–386 | 393_6100 |
| **Dystrophic** | Lakes in the dystrophic state have highly polluted water quality due to which oxygen is absent and the presence of toxins that support no desirable species. | 750–1200 | — |

**Table 1.**
*Lake classification on the basis of trophy or degree of enrichment with nutrients and in relation to P and N [59].*

algae takes place. As these algae die, they are decomposed by bacteria and in this process, dissolved oxygen is utilized. The decomposers use up the dissolved oxygen of the water body. Due to this dissolved oxygen, concentrations often fall considerably for fish to breathe resulting in fish kills [61].

### 5.2 Causes of eutrophication

The term "eutrophic" has been derived from the Greek words eu meaning "well" and trophe meaning "nourishment." Eutrophication refers to the abundant growth of phytoplanktons causing imbalanced primary as well as secondary productivity with a high rate of succession from the existing seral stage to a higher seral stage as a result of nutrient enrichment from fertilizer runoff and humans waste. It takes place at the point when a water body moves toward becoming enriched in key-limiting nutrients, such as nitrates, phosphates, and initiating symptomatic changes, including the expanded production of algae (**Figure 1**). Nitrogen (N) and phosphorus (P) are present in all aquatic ecosystems in some limited amount and are considered as an essential nutrient for the biological growth of organisms. Phosphorus being a macronutrient is essential for all living cells as it is an important constituent of adenosine diphosphate, adenosine triphosphate, nicotinamide adenosine dinucleotide phosphate, nucleic acids as well as phospholipids in the cell wall. Phosphorus is stored as polyphosphates in intracellular volutin granules in prokaryotes as well as eukaryotes. Both N and P are essential nutrients that are required by plants and animals for maintaining their growth and metabolism. However, in wastewater, these essential nutrients are available in abundant as phosphates, combined organic nitrogen, nitrates, and ammonia. On discharge into some receiving water body, their increased concentration can initiate

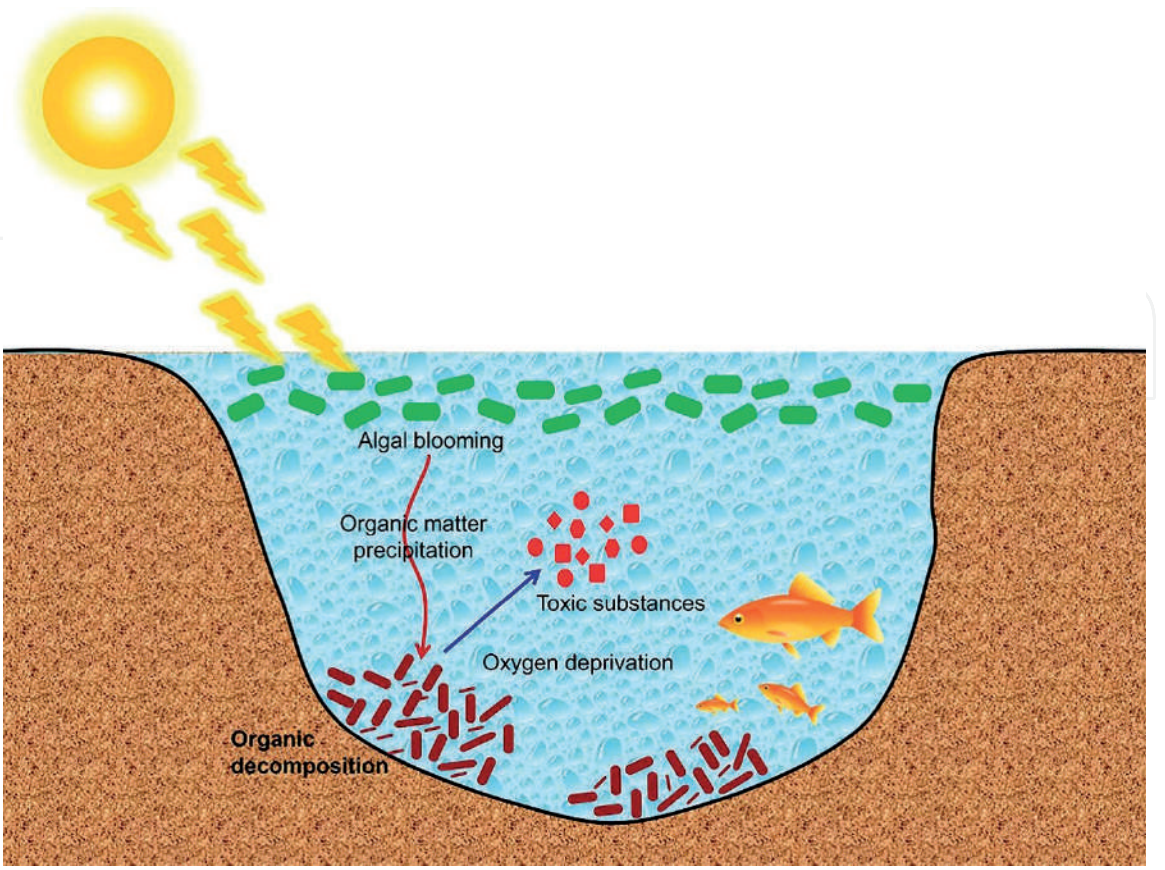


**Figure 1.**
*Eutrophication process [62].*

eutrophication with several adverse consequences on the ecological health of the water body [63, 64]. Eutrophication is a natural phenomenon that takes thousands of years to occur in water bodies such as lakes, rivers, and reservoirs. However, an increased rate of nutrient input as a result of anthropogenic activities initiates the process of completing it within a short time period, which is referred to as artificial or cultural eutrophication [65]. Natural eutrophication pushes the succession from open water lake to the marsh to the meadow to the forest, which may take place anywhere within a time period of 500–10,000 years or more depending on the initial condition of that area. Human activities accelerate the rate at which the influx of nutrients into the ecosystems takes place. Runoff resulting from agriculture, urban, and industrial development, mainly from septic systems, sewers, and other human-related actions, increases the rate of entry of both inorganic nutrients and organic substances into aquatic ecosystems.

### 5.3 Nutrients in aquatic ecosystems

The minimum acceptable concentration of total inorganic phosphate in water is 0.03–0.04 mg $l^{-1}$ and in many lakes, streams, and rivers where the problem of eutrophication is found to occur and its value has been found to increase by 20–25 times during the past 10–15 years especially in cities and industries. Around 60% of the phosphate present in the waterways of the US is contributed from domestic sewage. Phosphate is also contributed from mines, fertilizer runoff, and domestic sewage containing a high concentration of phosphate with about 50% resulting from human waste and 20–30% from detergents. Animal wastes are also rich in nitrate as well as phosphates [66]. Phosphorus resulting from agriculture runoff is the major source of phosphorus loading in riverine sediments, which is being utilized by benthic algae and rooted plants. Eutrophication has become a major concern in many developed as well as developing countries, especially in highly populated countries such as India, China, Bangladesh, Indonesia, and Pakistan. Lakes as well as reservoirs of several industrialized countries of Europe and North America including the Great Lakes of USA and Canada are facing severe threats due to eutrophication. Several lakes of Asia (54%), Europe (53%), North America (48%), South America (41%), and Africa (28%) are eutrophic. As compared to point source pollution, management of diffuse sources is far more challenging due to the difficulty in controlling nutrients contributing from runoff arising from agricultural and urban areas. Most of the phosphorus enters to water body *via* runoff and erosion taking during winter storm events. Thus, phosphorus influx from diffuse sources may be of little significance in the eutrophication of rivers due to the fact that the timing of the transfers does not usually overlap with the period of maximum biological demand. On the other hand, phosphorus being a significant element in the process of eutrophication needs to be identified and quantified from various sources during periods of low flow. Symptoms of eutrophication mostly take place during the plant growing season, that is, spring and summer, when there is a low flow, high water residence times, abundant sunlight light levels, and water temperature is on the higher side, which cause fast algal growth. During the growing period, phosphorus originating from point discharge in rivers is a source of high concentrations of dissolved, bioavailable phosphorus fractions into the water body. According to Meybeck [67], streams and rivers around the world have nearly doubled their concentration of nutrients that is, nitrogen and phosphorus, with local increases of about 50 times. Overall, cultural eutrophication of river ecosystems is a global phenomenon that has, during the past few years, gained much less attention than lake eutrophication. This may be partly due to the effects of increased nutrient concentrations in rivers that are least affected because some factors apart from the nutrients limit algal growth. Although some progress has been made, still there is a less conceptual understanding of eutrophication in rivers and streams. Hydraulic flushing of nutrients, water velocity, and light limitation are indeed significant in regulatory algal growth interacting in several ways. Moreover, short residence time in rivers (<3 days) will have different effects in comparison with longer residence time in impounded rivers or riverine lakes (>3 days). In comparison with lakes (>30 days retention time) and considering some of the factors mentioned above, Hilton [68] devised a conceptual model of how the process of eutrophication takes place in rivers. Since natural streams are net heterotrophic, Dodds [69] formulated the trophic state of rivers into autotrophic, nutrient controlled, and heterotrophic, external carbon-regulated state. The autotrophic state in lotic water bodies is mostly dependent on phosphorus and nitrogen values. Algal biomass is positively correlated with gross primary production in streams and rivers. Eutrophication is a problem that is persistent worldwide. In Spain for example, 80% of the lakes, 70% of the reservoirs, and 60% of the river sites were eutrophic in the 1990s with hypertrophy increasing downstream [70]. There may be several deleterious effects of eutrophication on the environment, which have adverse consequences on the health of the exposed animal population apart from humans through several pathways. Certain health risks appear when extracted freshwater from eutrophic water bodies is supplied for drinking purposes. A severe impact can also occur during animal watering from eutrophic waters.

### 5.4 Symptoms and effects of eutrophication

The following are the symptoms of eutrophication:

1. Release of limiting nutrients such as phosphorus and nitrogen into the water body.

2. Degradation of water quality such as the appearance of red tides or excessive foam over the surface of the water.

3. Increase in the productivity of the ecosystem along with biomass of phytoplankton, macrophytes, and harmful algal blooms.

4. Reduction in the water clarity and sediments are visible from a depth of few feet. Due to the greenish color of water, turbidity, and high levels of planktonic algae, the clarity of the water is drastically reduced.

5. Oxygen depletion due to increased production of organic matter and formation and release of hydrogen sulfide.

6. Shifts in the composition of species, for example, increased concentration of nitrogen causes new and more competitive forms to invade and compete with original ones.

The following are the effects of eutrophication:

1. Microcystins are certain toxins produced by various genera of cyanobacteria, the predominant one being Microcystis sp. These toxins are highly water-stable and resistant to boiling, and thus pose a threat to water and food quality if not properly monitored. Exposure to microcystins represents a health risk to aquatic organisms, wildlife, domestic animals, and humans upon drinking or

ingesting cyanobacteria in the water. These substances can enter the food chain and cause mortality in an animal apart from other health effects in humans.

2. If the water body affected by eutrophication is used for supplying drinking water to a community, it can cause an increase in the cost of treatment due to prevailing taste and odor problems. Raw water is a source of algae and several other aquatic plants, which also increases the treatment cost, while the quality of water supply may decrease. Planktonic algae when present can shorten filter runs.

3. Certain algae have been found to release organic compounds that are supposed to cause tastes and odors problems besides which they also produce trihalomethanes (THMs) and halo acetic acid (HAA) precursors which are considered as human carcinogens. These compounds react with chlorine, which is used during the disinfection process in wastewater treatment plants and is released with the treated effluent.

4. As the algae die, they become a source of food for the bacterial population, which consumes oxygen during the process. This may cause hypoxia, especially during the night due to which animals especially fish may suffocate resulting in fish kills. Mass deaths are also due to the release of hydrogen sulfide.

5. Aquatic weeds have been often found to block irrigation canals and other water supplies.

6. Excessive growth of macrophytes and algae can impair recreational purposes of water such as swimming, boating, and fishing. Odor problems can arise due to water weeds, dead decaying algae as well as algal scum.

7. Economic loss is also suffered due to change in the composition of species, fish kills, loss of recreational value, and reduction in tourism activities.

## 6. Conclusion

There has been a continuous increase in the sewage generation throughout the world from domestic, industrial as well as agricultural sources. This has put a serious threat on the freshwater ecosystems as a significant part of them goes untreated into freshwater ecosystems. Due to the presence of a wide variety of contaminants such as suspended solids, pharmaceuticals, heavy metals, sewage disposal has affected several aspects of flora and fauna. It has taken a heavy toll on aquatic life causing several undesirable changes in their structure and composition. Sewage disposal is regarded as a primary culprit in the deterioration of the health of freshwater bodies around the world. It is responsible for the process of eutrophication, which has several negative repercussions on the water bodies including harmful algal blooms, the decline in water quality, loss of economic as well as the esthetic value of the water body.

## Conflict of interest

The authors declare no conflict of interest.

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## References

[1] Kookana RS, Drechsel P, Jamwal P, Vanderzalm J. Urbanisation and emerging economies: Issues and potential solutions for water and food security. Science of the Total Environment. 2020;**732**:139057. DOI: 10.1016/j.scitotenv.2020.139057

[2] Beiras R, Bellas J, Cachot J, Cormier B, Cousin X, Engwall M, et al. Ingestion and contact with polyethylene microplastics does not cause acute toxicity on marine zooplankton. Journal of Hazardous Materials. 2018;**360**: 452-460. DOI: 10.1016/j.jhazmat.2018. 07.101

[3] Mateo-Sagasta J, Zadeh SM, Turral H, Burke J. Water pollution from agriculture: A global review. Executive Summary. Food and Agriculture Organization of the United Nations Rome and International Water Management Institute, 2017

[4] Vörösmarty CJ, McIntyre PB, Gessner MO, Dudgeon D, Prusevich A, Green P, et al. Global threats to human water security and river biodiversity. Nature. 2010;**467**(7315):555-561. DOI: 10.1038/nature09440

[5] Qayoom U, Bhat SU, Ahmad I. Efficiency evaluation of sewage treatment technologies: Implications on aquatic ecosystem health. Journal of Water and Health. 2020;**19**(1):29-46

[6] Mhlanga L, Day J, Cronberg G, Chimbari M, Siziba N, Annadotter H. Cyanobacteria and cyanotoxins in the source water from Lake Chivero, Harare, Zimbabwe, and the presence of cyanotoxins in drinking water. African Journal of Aquatic Science. 2006;**31**(2): 165-173. DOI: 10.2989/1608591060950 3888

[7] Havens K.E. Cyanobacteria blooms: effects on aquatic ecosystems. In: Hudnell H.K. (eds) Cyanobacterial Harmful Algal Blooms: State of the Science and Research Needs. Advances in Experimental Medicine and Biology. New York, NY: Springer; 2008. vol 619. https://doi.org/10.1007/978-0-387-75865-7_33

[8] Zhang X, Yang L, Li Y, Li H, Wang W, Ye B. Impacts of lead/zinc mining and smelting on the environment and human health in China. Environmental Monitoring and Assessment. 2012;**184**(4):2261-2273. DOI: 10.1007/s10661-011-2115-6

[9] Raschid-Sally L, Jayakody P. Drivers and Characteristics of Wastewater Agriculture in Developing Countries: Results from a Global Assessment. Colombo, Sri Lanka: International Water Management Institute; 2009

[10] Yu S, Miao C, Song H, Huang Y, Chen W, He X. Efficiency of nitrogen and phosphorus removal by six macrophytes from eutrophic water. International Journal of Phytore mediation. 2019;**21**(7):643-651. DOI: 10.1080/15226514.2018.1556582

[11] Ajonina C, Buzie C, Rubiandini RH, Otterpohl R. Microbial pathogens in wastewater treatment plants (WWTP) in Hamburg. Journal of Toxicology and Environmental Health, Part A. 2015;**78**(6):381-387. DOI: 10.1080/ 15287394.2014.989626

[12] Al-Gheethi AA, Efaq AN, Bala JD, Norli I, Abdel-Monem MO, Kadir MA. Removal of pathogenic bacteria from sewage-treated effluent and biosolids for agricultural purposes. Applied Water Science. 2018;**8**(2):1-25. DOI: 10.1007/ s13201-018-0698-6

[13] Grandclément C, Seyssiecq I, Piram A, Wong-Wah-Chung P, Vanot G, Tiliacos N, et al. From the conventional biological wastewater treatment to hybrid processes, the evaluation of

organic micropollutant removal: A review. Water Research. 2017;**111**:297-317. DOI: 10.1016/j.watres.2017.01.005

[14] Osuolale O, Okoh A. Human enteric bacteria and viruses in five wastewater treatment plants in the Eastern Cape, South Africa. Journal of Infection and Public Health. 2017;**10**(5):541-547. DOI: 10.1016/j.jiph.2016.11.012

[15] Kirchmann H, Pettersson S. Human urine-chemical composition and fertilizer use efficiency. Fertilizer Research. 1994;**40**(2):149-154. DOI: 10.1007/BF00750100

[16] Larsen TA, Alder AC, Eggen RI, Maurer M, Lienert J. Source separation: Will we see a paradigm shift in wastewater handling? Environ. Sci. Technol. 2009, 43, 6121-6125. DOI: 10.1021/ es803001r

[17] World Waterfall Database. (2017). Niagara Falls, Ontario, Canada. Retrieved from: https://www.worldwaterfalldatabase.com/index.php/waterfall/Niagara–Falls–106

[18] Qadri R, Faiq MA. Freshwater pollution: Effects on aquatic life and human health. In: Fresh water pollution dynamics and remediation. Singapore: Springer; 2020. pp. 15-26. DOI: 10.1007/978-981-13-8277-2_2

[19] World Water Assessment Programme (UNESCO WWAP) 2017. Available from: http://www.unesco.org/new/en/natural-sciences/environment/water/wwap

[20] Sato T, Qadir M, Yamamoto S, Endo T, Zahoor A. Global, regional, and country level need for data on wastewater generation, treatment, and use. Agricultural Water Management. 2013;**130**:1-3. DOI: 10.1016/j.agwat.2013.08.007

[21] Reckson K, Tawanda MS. Effect of sewage disposal on the water quality in Marimba River and Lake Chivero: The case of Crowborough grazing land of Harare. Zimbabwe. International Researcher. 2012;**1**(3):53-57

[22] Horner RR, Skupien JJ, Livingstone EH and Shaver HE. Fundamentals of Urban Runoff Management: Technical and Institutional Issues. Prepared by the Terrene Institute, Washington, DC, in cooperation with the U.S. Environmental Protection Agency. 1994. EPA/840/B-92/002

[23] Gupta P, Vishwakarma M, Rawtani PM. Assessment of water quality parameters of Kerwa Dam for drinking suitability. International Journal of Theoretical and Applied Sciences. 2009;**1**(2):53-55

[24] Lecerf A, Risnoveanu G, Popescu C, Gessner MO, Chauvet E. Decomposition of diverse litter mixtures in streams. Ecology. 2007;**88**(1):219-227

[25] Baerlocher F, Seena S, Wilson KP, Dudley WD. Raised water temperature lowers diversity of hyporheic aquatic hyphomycetes. Freshwater Biology. Feb 2008;**53**(2):368-379

[26] Dojlido J, Best GA. Chemistry of Water and Water Pollution. Ellis Horwood Limited; 1993

[27] Mayer FL Jr, Ellersieck MR. Experiences with single-species tests for acute toxic effects on freshwater animals. Ambio. 1988;**17**:367-375

[28] Whitehead PG, Hornberger GM. Modelling algal behaviour in the River Thames. Water Research. 1984;**18**(8):945-953

[29] Wade AJ, Whitehead PG, Hornberger GM, Snook DL. On modelling the flow controls on macrophyte and epiphyte dynamics in a lowland permeable catchment: The River Kennet, southern England.

Science of the Total Environment. 2002;**282**:375-393

[30] Hawkins CP, Hogue JN, Decker LM, Feminella JW. Channel morphology, water temperature, and assemblage structure of stream insects. Journal of the North American Benthological Society. 1997;**16**(4):728-749

[31] Daufresne M, Roger MC, Capra H, Lamouroux N. Long-term changes within the invertebrate and fish communities of the Upper Rhône River: Effects of climatic factors. Global Change Biology. 2004;**10**(1):124-140

[32] Connolly NM, Crossland MR, Pearson RG. Effect of low dissolved oxygen on survival, emergence, and drift of tropical stream macro invertebrates. Journal of the North American Benthological Society. 2004;**23**(2):251-270

[33] Olabode GS, OF O, Somerset VS. Physicochemical properties of wastewater effluent from two selected wastewater treatment plants (Cape Town) for water quality improvement. International journal of Environmental Science and Technology. 2020;**17**: 4745-4758. DOI: 10.1007/s13762-020-02788-9

[34] Suthar S, Sharma J, Chabukdhara M, Nema AK. Water quality assessment of river Hindon at Ghaziabad, India: Impact of industrial and urban wastewater. Environmental Monitoring and Assessment. 2010;**165**(1):103-112. DOI: 10.1007/s10661-009-0930-9

[35] Nelsen TA, Blackwelder P, Hood T, McKee B, Romer N, Alvarez-Zarikian C, et al. Time-based correlation of biogenic, lithogenic and authigenic sediment components with anthropogenic inputs in the Gulf of Mexico NECOP study area. Estuaries. 1994;**17**(4):873-885. DOI: 10.2307/1352755

[36] Frodge JD, Thamas GL, Pauley GB. Effects of canopy formation by floating and submergent aquatic macrophytes on the water quality of two shallow Pacific Northwest lakes. Aquatic Botany. 1990;**38**:231-248

[37] Lovley DR, Giovannoni SJ, White DC, Champine JE, Phillips EJ, Gorby YA, et al. Geobacter metallireducens gen. nov. sp. nov., a microorganism capable of coupling the complete oxidation of organic compounds to the reduction of iron and other metals. Archives of Microbiology. 1993;**159**(4):336-344. DOI: 10.1007/BF00290916

[38] Brett JR, Blackburn JM. Oxygen requirements for growth of young coho (Oncorhynchus kisutch) and sockeye (O. nerka) salmon at 15 C. Canadian Journal of Fisheries and Aquatic Sciences. 1981;**38**(4):399-404. DOI: 10.1139/f81-056

[39] Chambers PA, Mill TA. Dissolved oxygen conditions and fish requirements in the Athabasca, Peace and Slave Rivers: Assessment of present conditions and future trends. In: Northern River Basins Study, Edmonton, Alberta; 1996

[40] Lake RG, Hinch SG. Acute effects of suspended sediment angularity on juvenile coho salmon (Oncorhynchus kisutch). Canadian Journal of Fisheries and Aquatic Sciences. 1999;**56**(5):862-867. DOI: 10.1139/f99-024

[41] Van Nieuwenhuyse EE, LaPerriere JD. Effects of placer gold mining on primary production in subarctic streams of alaska 1. Jawra Journal of the American Water Resources Association. 1986;**22**(1):91-99. DOI: 10.1111/j.1752-1688.1986.tb01864.x

[42] Birkett C, Tollner EW, Gattie DK. Total suspended solids and flow regime

effects on periphyton development in a laboratory channel. Transactions of the ASABE. 2007;**50**(3):1095-1104

[43] Slaney PA, Halsey TG, Tautz AF. Effects of forest harvesting practices on spawning habitat of stream salmonids in the Centennial Creek watershed, British Columbia. Ministry of Recreation and Conservation, Victoria, B.C. Fish Manage Rep; 1997;**73**:45

[44] Bottoni P, Caroli S, Caracciolo AB. Pharmaceuticals as priority water contaminants. Toxicological and Environmental Chemistry. 2010;**92**(3): 549-565. DOI: 10.1080/0277224100 3614320

[45] Peñuela GA, Martínez-López E. Enzymatic activity changes in striped catfish Pseudoplatystoma magdaleniatum, induced by exposure to different concentrations of ibuprofen and triclosan. Chemosphere. 2021;**271**:129399. DOI: 10.1016/j. chemosphere.2020.129399

[46] Seelig B. Water Resource Impacts from Medicines and Other Biologically Active Substances. Available from: http://www.ag.ndsu.edu/pubs/h2oqual/watgrnd/wq1278.pdf

[47] Mehinto AC, Hill EM, Tyler CR. Uptake and biological effects of environmentally relevant concentrations of the nonsteroidal anti-inflammatory pharmaceutical diclofenac in rainbow trout (Oncorhynchus mykiss). Environmental Science and Technology. 2010;**44**(6): 2176-2182

[48] Lyssimachou A, Arukwe A. Alteration of brain and interrenal StAR protein, P450 scc, and Cyp11β mRNA levels in atlantic salmon after nominal waterborne exposure to the synthetic pharmaceutical estrogen ethynylestradiol. Journal of Toxicology and Environmental Health, Part A. 2007;**70**(7):606-613

[49] Liu BY, Nie XP, Liu WQ, Snoeijs P, Guan C, Tsui MT. Toxic effects of erythromycin, ciprofloxacin and sulfamethoxazole on photosynthetic apparatus in Selenastrum capricornutum. Ecotoxicology and Environmental Safety. 2011;**74**(4): 1027-1035

[50] Lanzky PF, Halting-Sørensen B. The toxic effect of the antibiotic metronidazole on aquatic organisms. Chemosphere. 1997;**35**(11):2553-2561

[51] Versteeg DJ, Belanger SE, Carr GJ. Understanding single-species and model ecosystem sensitivity: Data-based comparison. Environmental Toxicology and Chemistry: An International Journal. 1999;**18**(6):1329-1346. DOI: 10.1002/etc.5620180636

[52] Sabalowsky AR. An investigation of the feasibility of nitrification and denitrification of a complex industrial wastewater with high seasonal temperatures [Doctoral dissertation]. Virginia Tech

[53] Kurosu O (2001) Nitrogen removal from wastewaters in microalgalbacterial-treatment ponds. Available from: http://www.socrates.berkeley.edu/es196/projects/2001final/kurosu.pdf

[54] Krakat N, Demirel B, Anjum R, Dietz D. Methods of ammonia removal in anaerobic digestion: A review. Water Science and Technology. 2017;**76**(8): 1925-1938. DOI: 10.2166/wst.2017.406

[55] Qayoom U, Bhat SU, Ahmad I, Kumar A. Assessment of potential risks of heavy metals from wastewater treatment plants of Srinagar city, Kashmir. International journal of Environmental Science and Technology. 2021;**30**:1-20

[56] Farombi EO, Adelowo OA, Ajimoko YR. Biomarkers of oxidative stress and heavy metal levels as

indicators of environmental pollution in African cat fish (Clarias gariepinus) from Nigeria Ogun River. International Journal of Environmental Research and Public Health. 2007;**4**(2):158-165. DOI: 10.3390/ijerph2007040011

[57] Vosylienė MZ, Mikalajūnė A. Effect of heavy metal model mixture on rainbow trout biological parameters. Ekologija. 2006;**4**:12-17

[58] Rosseland BO, Eldhuset TD, Staurnes MJ. Environmental effects of aluminium. Environmental Geochemistry and Health. 1990;**12**(1): 17-27

[59] Salameh E, Harahsheh S. Eutrophication processes in arid climates. In: Eutrophication: Causes, Consequences and Control. Dordrecht: Springer; 2010. pp. 69-90

[60] Beeby A. What do sentinels stand for? Environmental Pollution. 2001; **112**(2):285-298

[61] Murphy KJ. Plant communities and plant diversity in softwater lakes of northern Europe. Aquatic Botany. 2002;**73**(4):287-324. DOI: 10.1016/ S0304-3770(02)00028-1

[62] Umbria A. Stato di qualità ambientale del laghi e analisi dei trend evolutivi. In: Documento Tecnico. 2009. Available from: http://www.arpa.umbria.it/resources/documenti/Acqua/Rapporto%20laghi%202005-2006-2007.pdf

[63] Khan FA, Ansari AA. Eutrophication: An ecological vision. The Botanical Review. 2005;**71**(4): 449-482

[64] Fink G, Alcamo J, Flörke M, Reder K. Phosphorus loadings to the world's largest lakes: Sources and trends. Global Biogeochemical Cycles. 2018;**32**(4):617-634. DOI: 10.1002/ 2017GB005858

[65] Rovira JL, Pardo P. Nutrient pollution of waters: Eutrophication trends in European marine and coastal environments. Contributions to Science. 2006:181-186. DOI: 10.2436/20. 7010.01.4

[66] Penelope RV, Charles RV. Water resources and the quality of natural waters. London: Jones and Bartbett Publishers; 1992

[67] Meybeck M. Carbon, nitrogen, and phosphorus transport by world rivers. American Journal of Science. 1982; **282**(4):401-450

[68] Hilton J, O'Hare M, Bowes MJ, Jones JI. How green is my river? A new paradigm of eutrophication in rivers. Science of the Total Environment. 2006;**365**(1-3):66-83. DOI: 10.1016/j. scitotenv.2006.02.055

[69] Dodds WK. Eutrophication and trophic state in rivers and streams. Limnology and Oceanography. 2006;**51**(1part2):671-680

[70] Cobelas MA, Jacobsen BA. Hypertrophic phytoplankton: An overview. Freshwater Forum. 1992;**2**(3):184-199

Chapter

# Biological versus Physicochemical Technologies for Industrial Sewage Treatment: Which Is the Most Efficient and Inexpensive?

*Karima Elkarrach, Fatima Atia, Anass Omor, Omar Laidi, Saloua Biyada, Mohamed Benlmelih and Mohammed Merzouki*

## Abstract

Industries play a major role in the development of countries' economy. However, they are known as the biggest source of water pollution in the whole world. In fact, several industries use a huge amount of water in their manufacturing operations, and then, they reject a large volume of wastewaters such as tanneries, brassware, olive mills … etc. The sewage of these industries may contain organic/inorganic matters or toxic components that harm human health and the environment. Therefore, the treatment of these effluents is necessary. For that, there are many treatment processes, including biological and physicochemical processes or both. The choice of adequate process is depending on many reasons, especially on the biodegradability degree of each effluent, as well as the presence of recalcitrant pollutants. Nevertheless, biological technologies, particularly bioremediation, are recently an emerging technology for the elimination of recalcitrant pollutants like heavy metals. Furthermore, these biotechnologies are simple, efficient, eco-friendly and inexpensive. Therefore, this environmental biotechnology may be a new approach for the treatment of industrial sewage, so, it can successfully replace physicochemical technologies that are very expensive.

**Keywords:** Industries, sewage, biological technologies, physicochemical processes

## 1. Introduction

Water is so essential in our daily life. However, water resources and their quality are progressively decreasing because of human activities, and then several countries are threatened by water scarcity, including Morocco. So, the rational management of these water resources is a big challenge in the whole world. Nowadays, the treatment and reuse of wastewater are known as the best solutions to deal with this lack of water. The constraint of this issue is pollution, especially industrial pollution, because industries generate high toxic substances, which may reduce the performance of the treatment [1]. For example in Morocco, the large hydraulic basin 'Sebou' receives more than 40% of pollution from industries of Fez city such as tanneries, textiles, brassware, olive mill … etc.

Industries release organic and inorganic pollutants namely heavy metals, dyes, polyphenols ... etc. Heavy metals are toxic, in which their toxicity depends on several factors, particularly the metal dose and the time exposition. Arsenic, cadmium, chromium, lead, and mercury, have ranked as carcinogenic metals, because they may damage multiple organs even at lower exposure doses [2]. Likewise, textile dyes are highly toxic and potentially carcinogenic [3]. Thus, they can lead to various animal and human diseases, as well as the environmental degradation. Therefore, recalcitrant substances harm the environment and human health, and then their removal from wastewaters is mandatory.

The literature has shown several physicochemical and biological processes for the treatment of industrial sewage. Among physicochemical processes, there is coagulation [4], electrocoagulation [5], forward osmosis [6], chemical precipitation [7], adsorption [8], and oxidation [9]. As for biological systems, there are many technologies such as sequencing batch reactor [10], bioaugmentation [11], biosorption [12], membrane bioreactor [13], anaerobic digestion [14]... etc. In fact, each process has its advantages and disadvantages; hence the process performance is highly dependent on the nature of the effluent and the flow to be treated. For example, physical–chemical treatments are known for their high performance, but they are very expensive and can generate another serious pollution. Biological treatments are also efficient and ecological, but the presence of recalcitrant substances in huge amount can decrease their efficient. So, the issue is complex, because it is necessary to find a treatment process that will be eco-friendly, efficient, and economical at the same time.

Taking into account the above, this chapter focuses on various physicochemical and biological processes for the treatment of industrial sewage. Moreover, this chapter will show the effectiveness of biological technologies for the removal of toxic substances.

## 2. Treatment of industrial wastewaters

The treatment of industrial effluents is essential before their discharge into the natural environment. Several physicochemical and biological treatments of these effluents have been studied in the literature. These techniques have been considered simple, efficient, or even advanced, but each system has certain advantages over the other. Moreover, these treatment systems can be applied independently or combined.

### 2.1 Physicochemical treatments

#### *2.1.1 Membrane filtration*

##### *2.1.1.1 Reverse osmosis*

This technology is based on the use of a semi-permeable membrane, wherein pollutants will be captured. This treatment system is known for its high purification rate, and it may be used for the treatment of all industrial sewage [15]. A study has shown that reverse osmosis is an advanced and promising technique for industrial wastewaters. Despite the qualities of this treatment system, it presents certain disadvantages, particularly the high cost.

##### *2.1.1.2 Membrane filtration*

Currently, this technique is well developed; it is based on the physical separation of pollutants under hydraulic pressure. This treatment system is very efficient for industrial sewage treatment such as pharmaceutical [16], textile [17], pulp and paper effluents [18]…etc. The separation is based on three principles, which are adsorption, electrostatic phenomenon, and sieving [19].

According to the membrane's pore size, there are three filtration types:

- Microfiltration: it refers to remove substances with a size greater than 10 μm through a membrane with pores between 0.1–10 μm. It is characterized by the tangential passage, and it is done under low pressure gradient of 1–3 bars. This technique is effective for sewage purification and the elimination of microorganisms, especially bacteria.

- Ultrafiltration: the pores of the membrane are between 0.001 and 0.1 μm. Thanks to these small pores, only water and small molecules (Ions) can pass through this membrane, while macromolecules such as proteins, polymers, bacteria, and viruses, will be retained [20].

- Nanofiltration: the pore size of the membrane is less than 1 nm. This technique is effective for industrial sewage treatment. It may remove heavy metals and ions as chromium and nickel [21]. It can also retain organic substances with a molecular weight fewer than 300 daltons. Nevertheless, it could not produce demineralized water as the reverse osmosis technique.

Otherwise, the membrane can be mineral (metallic, ceramic, etc.) or organic (polyamides, cellulose acetate, etc.). Its structure can be uniform (Isotropic) or composite (Anisotropic). Indeed, organic membranes are the most used because of their low cost, but mineral membranes can resist extreme conditions (Temperature, pH, etc.).

Consequently, membrane filtration has several qualities, namely the removal of micro-organisms, heavy metals, turbidity, dyes, and also odors from industrial sewage. Despite these advantages, the technique has also some limits such as rapid membrane fouling, production of high amount of sludge, high investment costs, and high energy consumption.

#### *2.1.2 Coagulation-flocculation*

The coagulation-flocculation process involves the use of coagulant and flocculant agents that can regroup the pollutants together as heavy flocs. These flocs will be eliminated by precipitation or filtration. These agents may be iron or aluminum chemicals. According to Junio et al. [4], coagulation-flocculation is a simple, fast, and effective technique for removing pollutants from industrial wastewaters. In this study, ferric chloride was used as a coagulant agent for the treatment of tannery sewage, wherein the abatement rates of COD and suspended solids were above 80%. Nevertheless, this technique has several disadvantages, namely the production of high sludge and the increase of acidity and conductivity within the treated effluent. On the other hand, the use of bio-coagulants and bio-flocculants is a new approach of this technique in order to reduce the massive use of chemicals and their harmful effects. According to previous study, cactus juice can be used as a bio-flocculant to reduce chromium, in which chromium VI removal was around 98% [22].

#### *2.1.3 Electrocoagulation*

Electrocoagulation has considered as a new alternative of chemical coagulation, and it is a promising process for the treatment of industrial sewage [23]. This technique is based on the principle of soluble anodes, and it induces the electrochemical separation of pollutants. These anodes are often made of aluminum or iron, from where metal cations ($Fe^{3+}$ or $Al^{3+}$) are generated by imposing an electric current between these anodes. These metal cations react as a coagulant to destabilize the suspended particles, and then, the formation of flocs that will subsequently precipitate. Indeed, this technique has several advantages, but the production of sludge in high amount and the consumption of high energy are its main disadvantages.

#### *2.1.4 Oxidation*

Oxidation is based on electrochemical reactions between the oxidizing agent and the pollutant by changing the electrons. This technique aims to modify the characterization of refractory pollutants by making them insoluble to facilitate their elimination, or soluble but non-toxic. The most commonly used chemical oxidants are oxygen, hydrogen peroxide, chlorine, ozone, potassium permanganate, and ferric chloride. This system is known for its strong elimination of bad odors, either natural or produced during anaerobic conditions. In addition, the combination of ozone with ultraviolet rays (UV) or hydrogen peroxide produces free radicals that are powerful oxidants and can eliminate a large part of the COD [24]. The advantages and disadvantages of this process are depending on the oxidant agent and the type of pollutant (**Table 1**).

According to the literature, several types of research have shown the efficiency of this process for the elimination of sulfides, of which hydrogen peroxide is the most used. This oxidant can eliminate 85–100% of sulfides by using 1.3 to 4.0 mg/L of $H_2O_2$ for 1 mg/L of sulfides [26].

In recent decades, this process has been developed using the combination of two powerful chemical oxidants ($H_2O_2/Fe^{2+}$ and $H_2O_2/O_3$), photo-catalysis (UV),

| Oxidant | Advantages | Disadvantages |
|---|---|---|
| Oxygen | Low investment costs.<br>Simple process | Incomplete oxidation.<br>Production of colloidal sulfur and poly-sulfides.<br>Difficult to control and build.<br>Increase of the turbidity. |
| Chlorine | Low investment costs.<br>Simple process | Incomplete oxidation.<br>Use of high dose.<br>Lack of security.<br>Increase the turbidity |
| Ozone | Easy process<br>Production of high water quality | Expensive process<br>Increase the turbidity<br>Ozone concentration is low than 2 mg/L |
| Potassium Permanganate | Easy and economical process | Requires the use of filters for the removal of residual $MnO_2$.<br>Increase the turbidity.<br>Use of a large quantity of the product.<br>Expensive product. |
| Hydrogen peroxide | Easy and economical process | Incomplete oxidation.<br>Increase the turbidity<br>Use of high amount of products.<br>Requires a long contact time. |
| Ferric chloride | Economical and powerful oxidant | This process has not been demonstrated on a pilot scale for the treatment of drinking water. |

**Table 1.**
*Advantages and disadvantages of oxidation agents [25].*

sonochemical oxidation, or electrochemical oxidation. As a result, this oxidation is called advanced oxidation (POA), which is considered an innovative process and an emerging technology for the treatment of industrial sewage. The principle of advanced oxidation is based on the production of hydroxyl radicals, which are very active and react rapidly on organic and inorganic compounds [9]. This advanced process has several qualities like high removal rates in a short time and minimal sludge production. However, it also has some disadvantages namely the high operating and investment costs, as well as the treatment efficiency depends on nature and pollutant concentration.

#### *2.1.5 Adsorption*

Adsorption is well known for the treatment of industrial sewage, so it is characterized by its high purifying capacity [27]. This process is based on the use of a material that will retain pollutants. This material can be applied as a fixed bed or can be used in suspension with the effluent (Fluidized Bed). The adsorption material can be inorganic (rocks, ashes ...), or organic (fruit, vegetables, wood, bacteria ....). Moreover, it can be used natural or activated.

The activation of a material can be carried out with a physical process (Pyrolysis, calcination, carbonization), a chemical process (Acids, bases), or the both. Physical activation involves high temperatures (800–1000°C), whereas chemical activation requires low temperatures. The most commonly used chemical agents are potassium hydroxide, sodium bicarbonate, sodium hydroxide, zinc chloride, sulfuric and phosphoric acids. However, phosphoric acid is frequently used comparing to other agents because of its low cost and activation temperature, as well as this acid can be recoverable (< 600°C) [27]. On the other hand, the activation of materials with potassium hydroxide is considered as the most effective [28]. In fact, chemical activation has several advantages, especially the increase in the specific exchange surface and the material porosity [8]. Although the activated carbon is a powerful adsorbent, its use is so limited due to its high cost. For that, this technique will be very attractive and promising if the material will be efficient and inexpensive at the same time. Thus, several attempts have been made to find novel materials such as organic waste, fly ash [29], olive pomace [30], and sawdust [31].

##### *2.1.5.1 Adsorption types*

According to the literature, the principle of adsorption is based on the binding forces between ions of adsorbent and adsorbate. Consequently, the involved forces divide adsorption into two types:

- Physical adsorption or physisorption: this type of adsorption is characterized by the absence of electron exchange between the adsorbent and the adsorbate. However, the adsorbate is retained by the adsorbent through non-specific physical forces of Van der Waals type, where multiple layers can be formed. This adsorption type requires low heat and it is reversible and non-specific.

- Chemical adsorption or chemisorptions: it is based on the exchange of electrons between the adsorbent and the adsorbate. This process requires high energy compared to physical adsorption. This energy corresponds to the eternal covalent bonds between ions of the adsorbent and the adsorbate, and then the phenomena of ion exchange and protonation/deprotonation are the main mechanisms. Moreover, a single layer could be only formed through this adsorption type, while other layers can be retained by physisorption.

*2.1.5.2 Adsorption isotherms and kinetics*

The study of isotherms is essential because it expresses the static adsorption capacity for an adsorbent/adsorbate couple. There are four main types of isotherms, which are as follows (**Figure 1**):

- Type a, which reveals cooperative adsorption of the adsorbate molecules.
- Type b or "Langmuir type", which is observed in the case of progressive microporous adsorption.
- Type c, which is observed in the case of a strong interaction between the adsorbate and the surface of the solid.
- Type d or linear isotherm, which occurs when the solutes penetrate more easily into the solid than into the solvent [32].

On the other hand, several mathematical models describe the adsorption mechanisms, where Langmuir, Freundlich, and Temkin are widely used.

- Langmuir's model: indicates that the adsorption is monolayer and into homogeneous surface. It is the oldest and the most common model. A limited adsorption capacity (qmax) is retained by the solid.
- Freundlich model: this empirical model reveals that the material surface is heterogeneous.
- Temkin's model: It takes into account adsorbant-adsorbate interactions.

Adsorption kinetics allows also a better understanding of the adsorption mechanism. As well, it describes the adsorption rate that leads to the control of the equilibrium time. The mathematical models of the adsorption kinetics are numerous and they can be used for the optimization of treatment models. Among these models, we quote pseudo-first-order, pseudo-second-order, and Elovich.

**2.2 Biological treatments**

Although the COD/$BOD_5$ ratio reveals that physicochemical treatments are the most suitable for inorganic industrial sewage, the literature has shown that

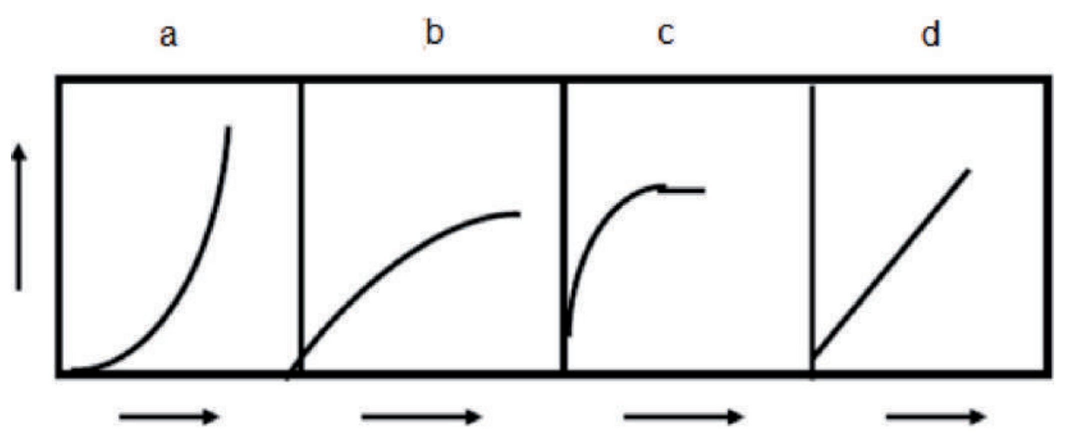


**Figure 1.**
*Main types of adsorption isotherms according to [32].*

biological treatments are also efficient and promising for the treatment of these effluents. Biological treatment involves the use of non-specific microorganisms (Activated sludge), well-selected microorganisms (Bio-augmentation), algae, or plants (Phytoremediation). These microorganisms can be bacteria, yeasts, fungi, etc.

Biological treatment consists of the use of pollutants of industrial sewage as a source of nutrition and energy by these microorganisms for their growth. This type of treatment has several advantages comparing to physicochemical treatments. Among these qualities, there are:

- Easy installation and control on a large scale.
- Attractive and economical processes.
- Ecological processes.
- Very effective for the removal of biodegradable organic matter, nitrogen, and phosphorus in particular.

Furthermore, the presence or absence of oxygen divides these biological treatments into two categories, which are aerobic and anaerobic treatments.

#### *2.2.1 Aerobic treatments*

##### *2.2.1.1 Classical process of activated sludge*

The activated sludge process is the most classic and most famous process since the 20th century. It is based on the treatment with aerobic micro-organisms. These micro-organisms are generally autotrophic or heterotrophic, and they are composed of several groups like bacteria (Gram-positive and/or Gram-negative), fungi, yeasts, protozoa, and metazoa. Consequently, activated sludge is composed of micro-organisms plus inert, organic or mineral matters. These elements are grouped through mucilaginous substances. In fact, those micro-organisms degrade the organic matter of wastewaters into carbon dioxide, water, new cells, and other non-toxic by-products. The separation between the treated effluent and the activated sludge takes place in a clarifier or decanter.

Even this process is very effective in the degradation of organic sewage like agri-food sewage; it also has some disadvantages, particularly the bulking phenomenon, the presence of high amount of recalcitrant pollutants, as well as nitrogen and phosphorus are not reduced at the same time and in the same reactor. This requires the addition of another tank to remove them, and subsequently the increase of installation and operation costs.

##### *2.2.1.2 Sequencing batch reactor*

The Sequencing Batch Reactor (SBR) is an emerging approach that has been well developed recently. This technique has the same treatment principle as the previous process, so it is based on the treatment by activated sludge under aerobic conditions. However, this process differs from the other one, because all treatment steps are performed in a single reactor, including nitrogen and phosphorus removal. In addition, the separation liquid/solid is done in the same reactor, where the good separation is linked to the presence of an adequate quantity of filamentous bacteria.

The treatment through this system is by cycle that involves four successive phases, which are:

- Phase one is the supply of the reactor with the effluent to be treated.
- Phase two is the aeration or treatment phase. In this phase, the effluent is brought into contact with the activated sludge in the presence of oxygen. During this stage, the effluent will be degraded by micro-organisms.
- Phase three is the settling phase during which the treated effluent will be separated from the activated sludge.
- Phase four is the withdrawal phase, from which the treated effluent will be withdrawn and the new cycle will be started.

The performance of this system depends on many parameters such as the volumetric organic load, daily cycle number of the treatment, level of dissolved oxygen, sludge index, sludge age, and time of the settling phase. The optimization of these parameters leads to very high abatement rates.

The reference [33] showed that SBR is a promising technique for the treatment of several types of sewage such as agri-food, pharmaceutical, pulp/paper, textile, tannery, chemical, and petrochemical effluents, ... etc.

Another study shows the efficiency of the SBR system compared to the conventional activated sludge process (**Table 2**). So, the SBR is the most efficient due to very high removal rates, and also the system is capable to remove nitrogen and phosphorus at the same time. Thus, this system is inexpensive and useful than the classic process. Furthermore, aerobic denitrification was highlighted within this reactor [10, 35]. In recent decades, this phenomenon has been very attractive and advanced according to various studies. The literature showed more than 37 aerobic denitrifying bacteria, where *Bacillus pulminus*, *Arthrobacter sp*., and *Streptomyces lusitanus* were the latest shown [36].

Heavy metals could also be removed by this biological system. The reference [11] has shown that this system is capable to remove chromium from a tannery effluent with a removal rate of 96.1% using a low volumetric organic load. As well, [37] has indicated that several heavy metals (Nickel, chromium, cadmium, cobalt, zinc, and silver) were eliminated from brassware effluent through this system with high removal rates that reached more than 60%.

This system has many advantages such as low cost, short treatment time compared to the classic process, high removal of organic and mineral matter, simplicity of the process, the possibility of spreading excess sludge, limitation of bad odors,

| Parameters | Abatement rate (%) | |
|---|---|---|
| | Sequencing batch reactor | Classic process of activated sludge |
| $BOD_5$ | 89–99 | 85–95 |
| Suspended solids | 85–97 | 85–90 |
| Total nitrogen | >75 | Untreated |
| Phosphorus | 57–69 | Untreated |
| Total coliforms | 99 | 90–96 |

**Table 2.**
*Average abatement rates obtained by the sequential batch reactor and the conventional activated sludge process [34].*

etc. … Despite all these advantages, it also has some shortcomings like the bulking phenomenon.

#### *2.2.1.3 Membrane bioreactor*

The membrane bioreactor is a new alternative to the classic activated sludge process, so it is based on the same principle of activated sludge treatment. However, the solid/liquid separation is done through membrane column instead of clarifier. Consequently, this technique is the combination of an activated sludge biological reactor and a membrane process such as microfiltration. It is widely used for the treatment of industrial sewage [13]. Furthermore, the use of membrane filtration increases the rate of effluent purification due to its removing capacity of high concentrations of suspended solids, nitrogen and phosphorus, as well as bacteria and viruses. However, membrane cleaning or regeneration after plugging is essential, so it increases considerably the process cost.

#### *2.2.1.4 Bioremediation*

The presence of a high concentration of heavy metals, salts, or other toxic substances, reduces or prevents the treatment by the activated sludge because of these extreme conditions. This issue allows us to highlight biotechnological technique that is bioremediation. This biotechnology regroups some processes like bio-augmentation, biosorption and phytoremediation. These techniques use a powerful microorganism, consortium, or plant, which can resist these extreme conditions.

Bioaugmentation is based only on the use of living microorganisms, whereas biosorption involves living or non-living microorganisms. Moreover, biosorption is one of the various mechanisms of bioaugmentation. For biosorption, the microorganisms can replace the activated carbon, and then reduce process cost. This method depends on cell wall compositions such as polysaccharides, which include amino, carboxyl, phosphate, and sulfate groups. According to a previous study, the biosorption method was applied to remove heavy metals using natural microorganisms [38], or as a bio-nanocomposite material, which were synthesized from microorganisms [39]. Biosorption depends on some mechanisms, namely adsorption, ion exchange, chelation, and complexation. While bioaugmentation, it is based on the metabolic capabilities of microorganisms for the detoxification of several compounds, including recalcitrant pollutants. Therefore, microorganisms can resist these toxic substances of industrial sewage through some mechanisms, among which figure biosorption, bioaccumulation, enzymatic reduction, SOS response, and enzymatic DNA repair system… etc. [40]. So, these mechanisms can be an effective way to remove the toxicity of the industrial sewage.

Furthermore, there are three approaches of bioaugmentation depending on the origin of these added microorganisms:

- Autochthonous bioaugmentation: It indicates that the microorganism is isolated from the same contaminated medium to be treated (native or indigenous microorganism).

- Allochthonous bioaugmentation: where the medium of isolation is different from the contaminated medium to be treated (endogenous microorganism).

- Gene bioaugmentation: this is when the inoculated microorganism is genetically modified to have certain functions.

Tannery effluents are known for their high salinity, due to the high use of salts during the tanning process. Therefore, [41] added a consortium of halophytic bacteria in the sequencing batch reactor to treat this tannery sewage. Despite the use of a high salt concentration of 34 g/L, the treatment achieved great abatement rates of 95%, 93%, 96%, and 92% respectively for COD, orthophosphate ions, NTK, and suspended solids.

*Enterobacter sp.* DU17 was isolated from the tannery effluent [42]. This bacterium was used to reduce hexavalent chromium. Indeed, the reduction rate of Cr(VI) could reach 100% when the initial chromium VI concentration is around 100 mg/L, and when glucose or fructose are carbon source. This high Cr(VI) reduction capacity by *Enterobacter sp.* DU17 has been justified by the presence of chromium reductase enzyme.

Several bacterial have shown their capacity to biosorb heavy metals such as chromium. Likewise, [11] showed that *Bacillus sp., Enterobactera erogenes,* and *Bacillus pumilus* are also chromate bacteria.

In conclusion, this biotechnology may be the most efficient and inexpensive technique for the treatment of industrial sewage because it involves the use of the most efficient microorganisms for each pollutant type.

#### *2.2.2 Anaerobic treatments*

Anaerobic treatments are generally the same as aerobic treatments but in the absence of oxygen. So, they consist of the degradation of effluents by anaerobic microorganisms. Although these anaerobic treatments have a low removal of COD and $BOD_5$, anaerobic co-digestion produces biogas from the organic matters. Indeed, biogas production passes through four stages under the intervention of fermentative bacteria, then acidogenic bacteria, followed by acetogenic and methanogenic bacteria [43]. The produced biogas contains a mixture of methane (50–75%), carbon dioxide (30–40%), and some traces of other components [43].

This anaerobic process can treat industrial sewage such as mill olive, agrifood, domestic, and tannery effluents [44]. According to several studies, sulfides inhibit the proliferation of methanogenic bacteria [45]. Nevertheless, a study has shown that tannery effluents can be anaerobically degraded [44]. In this study, tannery effluents were mixed with the plant of *Phragmites karka*, and then they were incubated in the SBR under anaerobic conditions using different concentrations of the plant. This co-digestion of this mixture produced 0.26 L of methane per 1 g of COD eliminated (71%), where the plant percentage was about 25%. This rate of produced biogas decreased when the concentration of the plant increases.

In conclusion, anaerobic treatment becomes very attractive due to its production of renewable energy.

### 2.3 Coupled treatments

Although physicochemical and biological treatments are efficient, certain limits reduce their performance. Industrial sewage is very complex and toxic, so a physicochemical or even biological process is unable to eliminate the entire pollutant load, especially inorganic pollutants. For this reason, several researchers have combined two processes or more in order to increase the purification of these effluents and to obtain an effluent that fully meets discharge standards.

In the reference [46], they coupled the chemical process of ozone oxidation with the membrane bioreactor for the treatment of tannery effluents. The coupled treatment of these two processes produced a small amount of sludge (0.03 Kg sludge/kg COD removed), which was considered to be the lowest.

On the other hand, [47] has combined chemical coagulation using ferric chloride with advanced oxidation techniques (photo-oxidation, homogeneous oxidation, and photo-fenton) for the treatment of industrial sewage, where the coagulation coupled to photo-fenton is considered the best.

In another study, aluminum sulfate and ferric chloride were used to remove organic carbon and chromium before biological treatment of tannery effluents by the SBR. This study showed that aluminum sulfate is more effective than ferric chloride in terms of COD removal [48]. However, [36] has used ferric chloride as a coagulant following by the treatment through the SBR. This combined treatment gave 99.89%, 99.98%, and 99.99% respectively for the COD, the sulfide ions, and the total chromium, and then the treated effluent was well conformed to standards.

In [49], they have coupled coagulation with activated carbon adsorption to treat industrial effluents, where lime was used as a coagulating agent. This combined treatment removed 97% of suspended solids, 99% of color and turbidity, 98% of total phosphorus, and 99.7% of chromium.

On the other hand, [50] has studied the treatment of tannery effluents by coupling 3 processes: 2 anaerobic bioreactors, followed by ozone oxidation, followed by biofiltration. The filtration is carried out under aeration into ceramic-lined column, which is inoculated with activated sludge. The optimization of this system has led to the production of a satisfactory rate of biogas and a good elimination of COD, total chromium, chromium VI, total nitrogen, and suspended solids.

## 3. Conclusion

The pollution generated by industries has harmful impacts on the environment and human health. In addition, their effluents were classified as very dangerous due to the presence of recalcitrant pollutants. This imposes a prior treatment of these effluents before their discharge into the environment. In this regards, different physicochemical and biological techniques for the treatment of these effluents have been shown in this chapter such as reverse osmosis, membrane filtration, oxidation, adsorption coagulation, classic activated sludge, sequencing batch reactor, membrane bioreactor, bioremediation, and anaerobic processes. Indeed, each technique has advantages but also has certain limits. For that, the choice of a treatment system is linked to numerous criteria namely the nature of the effluent, the presence of toxic substances, the operating and investigation costs and the possibility of its application at a large scale. Generally, although physicochemical techniques are very efficient and well adapt with industrial sewage, they are expensive and could generate other pollutants. Otherwise, the presence of huge amount of recalcitrant pollutants is the main limit of biological but they are also more efficient, simple, eco-friendly and especially inexpensive.

Based on this study, we considered further investigating the treatment of industrial sewage through biological processes, bioremediation techniques in particular, because they are promising, attractive and emerging technologies.

## Conflict of interest

The authors declare no conflict of interest.

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## References

[1] Naushad M. A new generation material grapheme: applications in water technology. 1st ed. Springer international publishing, 2019. 476 p. Doi: 10.1007/978-3-319-75484-0

[2] Tchounwou PB, Yedjou CG, Patlolla AK, Sutton DJ. Heavy metal toxicity and the environment. Exp Suppl. 2012; 101:133-164. Doi:10.1007/978-3-7643-8340-4_6

[3] Sharma B, Dangi AK, Shukla P. Contemporary enzyme based technologies for bioremediation: A review. Journal of environment Management. 2018;210: 10-18. DOI: 10.1016/j.jenvman.2017.12.075

[4] Junior OG, Santos MGB, Nossol ABS, Starling MCVM, Trovo AG. Decontamination and toxicity removal of an industrial effluent containing pesticides via multistage treatment: Coagulation-flocculation-settling and photo-fenton process. Process safety and environmental protection. 2021;147:674-683. https://doi.org/10.1016/j.psep.2020.12.021

[5] Asaithambi P, Govindarajan R, Yesuf MB, Selvakumar P, Alemayehu E. Investigation of direct and alternating current-electrocoagulation process for the treatment of distillery industrial effluent: Studies on operating parameters. Journal of Environmental Chemical Engineering. 2020. https://doi.org/10.1016/j.jece.2020.104811

[6] Mahto A, Aruchamy K, Meena R, Kamili M. et al. Forward osmosis for industrial effluents treatment-sustainability considerations. Separation and purification technology. 2021; 254: 117568. https://doi.org/10.1016/j.seppur.2020.117568

[7] Omor A, Rais Z, El Rhazi K, Merzouki M, El Karrach K, Elallaoui N, Taleb M. Optimization of the method wastewater treatment of unit bovine hides's unhairing liming. Journal of Materials and Environmental Sciences. 2017; 8:1235-1246

[8] Kebede TG, Mengistie AA, Dube S, Nkambule TTI, Nindi MM. Study on adsorption of some common metal ions present in industrial effluent by *Moringa stenopetala* seed powder. Journal of environment chemical engineering. 2017;6 (1): 1378-1389. https://doi.org/10.1016/j.jece.2018.01.012

[9] Boczkaj G, Fernandes A. Wastewater treatment by means of advanced oxidation processes at basic pH conditions: A review. Chemical Engineering journal. 2017;15:608-633. https://doi.org/10.1016/j.cej.2017.03.084

[10] Elkarrach K, Merzouki M, Laidi O, Biyada S, Omor A, Benlemlih M. Sequencing Batch Reactor: Inexpensive and efficient treatment for tannery effluents of fez city in morocco, Desalination Water Treat. J. 2020a;203:1-7. Doi: 10.5004/Dwt.2020.26151

[11] Elkarrach K, Merzouki M, Biyada S, Benlemlih M. Bioaugmentation process for the treatment of tannery effluents in fez, morocco: an eco-friendly treatment using novel chromate bacteria, Water Process Eng. 2020b;38:101-589. Https://Doi.Org/10.1016/J.Jwpe.2020.101598

[12] Castro L, Blazquez ML, Gonzalez F, Munoz JA, Ballester A. Biosorption of Zn(II) from industrial effluents using sugar beet pulp and F. vesiculosus: From laboratory tests to a pilot approach. Science of the total environment. 2017;15: 856-866. Doi:10.1016/j.scitotenv.2017.04.138

[13] Chandrasekhar SS, Vaishnavi D, Sahu N, Sridhar S. Design of integrated membrane bioreactor process for effective and environmantally safe

treatment of highly complex coffee industrial effluent. Journal of Water process engineering. 2020;37:101436. https://doi.org/10.1016/j.jwpe.2020.101436

[14] Sani K, Kongjan P, Pakhathirathien C, Cheirslip B, et al. Effectiveness of using two-stage anaerobic to recover bio-energy from high strength palm oil mill effluents with simultaneous treatment. Journal of Water process engineering. 2021; 39: 101661. https://doi.org/10.1016/j.jwpe.2020.101661

[15] Trishitman D, Cassano A, Basile A, Rastogi NK. Reverse osmosis for industrial wastewater treatment, Current and forward osmosiss: Principles, Applications, Advances. 2020;207-228. https://doi.org/10.1016/B978-0-12-816777-9.00009-5

[16] Ravikumar YVL., Kalyani S, Satyanarayana SV, Sridhar S. Processing of pharmaceutical effluent condensate by nanofiltration and reverse osmosis membrane techniques', Journal Of The Taiwan Institute Of Chemical Engineers. Taiwan Institute of Chemical Engineers. 2014;45(1):50Ŕ56. DOI: 10.1016/J.Jtice.2013.09.021

[17] Buscio V, Crespi M, Gutiérrez-Bouzán C. Sustainable dyeing of denim using indigo dye recovered with polyvinylidene difluoride ultrafiltration membranes, J. Clean. Prod. 2015;91:201-207. Doi: 10.1016/J.Jclepro.2014.12.016

[18] Gönder ZB, Arayici S, Barles H. Advanced treatment of pulp and paper mill wastewater by nanofiltration process: effects of operating conditions on membrane fouling, Separ. And purification Technol. 2011; 76(3): 292-302. DOI:10.1016/j.seppur.2010.10.018

[19] Padaki M et al. Membrane technology enhancement in oil-water separation. a review, Desalination. 2015; 357: 197Ŕ207. Doi: 10.1016/J.Desal.2014.11.023

[20] Miller DJ, Kasemset S, Paul DR, Freeman BD. Comparison of membrane fouling at constant flux and constant transmembrane pressure conditions. J. Membr. Sci. 2014; 454: 505-515. https://doi.org/10.1016/j.memsci.2013.12.027

[21] Basaran G, Kavak D, Dizge N, Asci Y, Solener M, Ozbey B. Comparative study of the removal of nickel (II) and chromium (VI) heavy metals from metal plating wastewater by two nanofiltration membranes. Desalination Water Treat. 2016;57(46): 1-11. https://doi.org/10.1080/19443994.2015.1127778

[22] Aziza A, Abdeljalil Z, Abdelali I. Utilisation d'un nouveau bio-floculant extrait de cactus marocain dans le traitement des rejets chargés de chrome (VI) par le procédé de coagulation floculation. Afrique SCIENCE. 2009;05(3):25 - 35

[23] Gaogui J, Shuai R, Stephen P, Wei S, Przemyslaw B, Zhiong G. Electrocoagulation for industrial wastewater treatment: an updated review, Environ.Sci.: Water res. Technol. 2021. https://doi.org/10.1039/D1EW00158B

[24] Kalra SS, Mohan S, Sinha A, Singh G. Advanced oxidation processes for treatment of textile and dye wastewater: a review. 2nd Int. Conference on Environmental Science and Development. 2011; 4: 271-275

[25] Duranceau SJ, Trupiano VM, Lowenstine M, Whidden S, Hopp J. Innovative hydrogen sulfide treatment methods : Moving beyond packed tower aeration. FLORIDA Water Resour. J. 2010;1-8

[26] Snyder EG. Elimination of odor at six major wastewater treatment plants. Water Environ. Federation, 2016;57(10):1027-1032

[27] Malwade K, Lataye D, Mhaisalkar V, et al. Adsorption of hexavalent chromium onto activated carbon derived from leucaena leucocephala waste sawdust: kinetics, equilibrium and thermodynamics, Int. J. Environ. Sci. Technol. 2016;13(9):2107-2116. Doi: 10.1007/S13762-016-1042-Z

[28] Alvarez-Torrellas S, Munoz M, Zazo JA, Casas JA, Garcia J. Synthesis of high surface area carbon adsorbents prepared from pine sawdust-onopordum acanthium L. for nonsteroidal anti-inflammatory drugs adsorption, J. Enviro. Manage. 2016;183:294Ŕ305. Doi: 10.1016/J. Jenvman.2016.08.077

[29] Zhang Y et al.,Effects of modified fly ash on mercury adsorption ability in an entrained-flow reactor, FUEL. Elsevier Ltd. 2014;128:274-280. Doi: 10.1016/J.Fuel.2014.03.009

[30] Koçer O, Acemioğlu B. Adsorption of basic green 4 from aqueous solution by olive pomace and commercial activated carbon: process design, isotherm, kinetic and thermodynamic studies', Desalination Water Treat. 2016;57(35):16653Ŕ16669. Doi: 10.1080/19443994.2015.1080194

[31] ElMouhri G, Merzouki M, Miyah Y, Elkarrach K, Mejbar F, Elmountassir R, Lahrichi A. Valorization of two biological materials in the treatment of tannery effluents by filtration, Moroccan Journal of chemistry. 2019;7(1):183-193. https://doi.org/10.48317/IMIST.PRSM/morjchem-v7i1.14064

[32] Giles CH et al. Studies in adsorption. Part xi. a system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids, J. Chem. Soc. 1960;846:3973-3993. Doi: 10.1039/Jr9600003973

[33] Patil PG, Kulkarni G, Smt SV, Kore M, Shri V, Kore S. Aerobic sequencing batch reactor for wastewater treatment: a review. IJERT. 2013; 2(10)

[34] Dohare D, Kawale M. Biological treatment of wastewater using activated sludge process and sequential batch reactor process - a review, Int. J. Eng. Sci. Res. Technol. 2014;3(11)

[35] Elkarrach K, Merzouki M, Laidi O, Omor A, Biyada S, Benlemlih M, Combination of chemical and biological processes for the treatment of tannery effluent of Fez city in Morocco, Desalination and Water Treatment. 2021a; 220: 109-115. doi: 10.5004/dwt.2021.26989

[36] Elkarrach K, Merzouki M, Laidi O, Benlemlih M. Aerobic denitrification using Bacillus pulminus, Arthrobacter sp., and *Streptomyces lusitanus*: Novel isolated denitrifying bacteria. Bioresource Technology Reports. 2021b; 14: 100663. https://doi.org/10.1016/j.biteb.2021.100663

[37] Laidi O, Merzouki M, El Karrach K, Benlemlih M. Brassware wastewater treatment optimization in the city of Fez with sequencing batch reactor using activated sludge. JMES. 2015; 6(6):1562-1569

[38] Samuel MS, Abigail MEA, Chidambaram C. Isotherm modelling, kinetic study and optimization of batch parameters using response surface methodology for effective removal of Cr(VI) using fungal biomass. PLoS ONE 2015;10(3)/e0116884. Doi:10.1371/journal.pone.0116884

[39] Samuel SM, Subramaniyan V, Bhattacharya J, Chidambaram R, Qureshi T., Pradeep Singh ND. Ultrasonic-assisted synthesis of Graphene oxide – fungal hyphae: An efficient and reclaimable adsorbent for Chromium (VI) removal from aqueous solution, Ultrasonics Sonochemistry.

2018. Doi: https://doi.org/10.1016/j.ultsonch.2018.06.012

[40] Ramírez-Dírz MI, Díaz-Pérez C, Vargas E, Riveros-Rosas H, Campos-Garcéa J, Cervantes C. Mechanisms of bacterial resistance to chromium compounds. Biometals. 2008;21:321e332. DOI: 10.1007/s10534-007-9121-8

[41] Lefebvre O, Vasudevan N, Torrijos M, Thanasekaran M, Moletta R. Halophilic biological treatment of tannery soak liquor in a sequencing batch reactor. Water Res. 2005;39(8):1471-1480. https://doi.org/10.1016/j.watres.2004.12.038

[42] Rahman Z, Singh VP. Cr(VI) reduction by *Enterobacter sp.* du17 isolated from the tannery waste dump site and characterization of the bacterium and the Cr(VI) reductase . Int. Biodeterior. Biodegradation. 2014;9: 97-103. Http://Dx.Doi.Org/10.1016/J.Ibiod.2014.03.015

[43] Abbasi T, Tauseef SM, Abbasi SA. Anaerobic digestion for global warming control and energy generation-an overview. Renew. Sust. Energ. Rev. 2012;16:3228-3242. DOI: 10.1016/j.rser.2012.02.046

[44] Mekonnen A, Leta S, Njau KN. Co-Digestion of tannery wastewater and *Phragmites Karka* using a laboratory scale anaerobic sequencing batch reactor (ASBR). New York Sci. J. 2016; 9(1)

[45] Hashem MA, Nur-A-Tomal MS, Bushra SA. Oxidation-Coagulation-Filtration processes for the reduction of sulfide from the hair burning liming wastewater in tannery. J. Clean. Produc. 2016; 127, 339 Ŕ342. Available at: Http://Dx.Doi.Org/10.1016/J.Jclepro.2016.03.159

[46] Di Iaconi C, Lopez A, Ramadori R, Di Pinto AC, Passino R. Combined chemical and biological degradation of tannery wastewater by a periodic submerged filter (SBBR), Water Res. 2002;36: 2205Ŕ14. https://doi.org/10.1016/S0043-1354(01)00445-6

[47] Naumczyk J, Rusiniak M. Physicochemical and chemical purification of tannery wastewaters [Thesis]. Technical university of WARSAW of Poland, Faculty of environmental engineering; 2005

[48] Song Z, Williams CJ, Edyvean RGJ. Treatment of tannery wastewater by chemical coagulation, Desalination. 2004;164:249-259, https://doi.org/10.1016/S0011-9164(4)00193-6

[49] Ayoub GM, Hamzeh A, Semerjian L. Post treatment of tannery wastewater using lime/bittern coagulation and activated carbon adsorption. Desalination. 2011; 273:359-365. https://doi.org/10.1016/j.desal.2011.01.045

[50] Chen F, Li X, Luo Z, Jing M, Zhu Q, Zhang S. Treatment of tannery wastewater using a combined UASB (2 stage)-ozonation-BAF system. Desalination Water Treat. 2018;116:277-283. DOI:10.5004/dwt.2018.22610