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TREATMENT OF HIGHLY TOXIC PHARMACEUTICAL EFFLUENT FOR THE CONSERVATION OF SURFACE WATERS

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By

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Abstract

Industries often require large quantities of water for various processes, such as manufacturing, cooling, and cleaning. 22% of the ground water is estimated to be withdrawn and consumed by the industrial sector. Recently one of the fastest growing industries of Pakistan is the Pharmaceuticals Industry. The pharmaceutical market in Pakistan is almost worth PKR 423 billion, with national and international firms comprising 69% and 31% of the sector, respectively. According to Pakistan Credit Rating Agency (PACRA) Report, 2020, the top 25 enterprises hold a 60% market share, while the top 50 enterprises hold an 80% market share. Pakistan has over 650 enterprises in operation, but just 31 of them are multinationals, approximately less than 3%. 99% of these industrial units discharge their wastewater without any sort of treatment. The discharged effluent is contaminated with pharmaceutical compounds, antibiotics and other intermediate drug products. Due to the mixing of this effluent with surface water and ground water these water resources also become contaminated. Long term consumption of this contaminated water leads to multiple diseases in humans and animal. It also results in the development of antibiotic resistant gene (ARG) in bacteria, this gene makes it very difficult and at time impossible to kill these bacteria thus creating a huge threat for our lives. Unfortunately, in Pakistan wastewater treatment system is still in development process, due to which there are only few wastewater treatment facilities available at the present. Nowadays multiple treatment options are available for the pharmaceutical wastewater that include Advanced Oxidation Processes (AOPs), Activated Sludge treatments, Ion Exchange, Adsorption and Ozonation. The government and regulating bodies should enforce strict laws for effluent treatment plants to prevent the exploitation of ground water resources and surface water bodies as they are a shared resource.

Keywords: Pharmaceuticals, Industrial effluent, Coagulation, Ozone, Advanced Oxidation Processes

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1. Introduction

One of the major concerns for the environment has evolved as a result of a fast growth in antibiotic usage throughout the world and subsequent release in pharmaceutical wastewater (Magesh, 2020). Antibiotics possess significant genotoxic, carcinogenic, and Eco toxicological impacts on plants, animals, and human life when released in sewage (Ilyas et al., 2019). Antibiotics in waterways may enhance the growth of antibiotic-resistant bacteria and genes in humans, posing a major threat to public health (Kovalakova, 2020). Antibiotics have such a lasting nature and are difficult to degrade, making them resistant to traditional wastewater treatment technology (Phoon, 2020). As a result, developing efficient and affordable treatment methods for pharmaceutical wastewater consisting antibiotics is necessary.

The pharmaceutical industry has grown at such a rapid pace in recent times that pharmaceuticals are now widely utilized in a variety of industries, including agriculture, poultry farming, fisheries, and human health (Wang et al., 2016; Song and Jhung, 2016). Antibiotics, food additives, pain relievers, personal care items, medicines, and other pharmaceuticals are manufactured by the pharmaceutical sector. The pharmaceutical industry's wastewater effluents are released into the environment and ground water at a rate of 22,000 m^3 per day on average. Pre-treatment of pharmaceutical effluents is required in order to safeguard the environment and ground water from contamination. Various parameters like pH, temperature, TSS, BOD, oil and grease, sulphate, TDS, and chloride are all indicators of the pharmaceutical industry's waste water effluents (Ilyas et al., 2019).

Toxic wastewater is produced by the pharmaceutical industry that poses bad odor and a bright hue. The challenges associated with pharmaceutical industry effluent include a greater chemical oxygen demand (COD) and a lower biological oxygen demand (BOD). A complex framework and a range of organic substances define genuine pharmaceutical wastewater (Barzegar, 2019; Malik, 2017). When certain effluent is discharged directly into the environment, it poses a threat to humans and aquatic life. Pharmaceutical wastewater must be treated in order to save the environment and to satisfy the discharge criteria (Alharbi, 2019). One of the most important phases in the treatment of true pharmaceutical wastewater is to select an effective treatment procedure. It is essential to have data on the efficacy of a certain methodology when doing so. One of the most important phases in the treatment of genuine pharmaceutical wastewater is to choose an effective treatment procedure. It is important to have knowledge on the efficacy of a certain approach when doing so. Multiple strategies for treating pharmaceutical wastewater have been suggested by several researchers. However, because of the complicated matrix of pharmaceutical wastewater, these technologies are less effective (Daghrir, 2016).

Because of its properties of substantial fluctuations in water quality and volume, diverse composition, increasing pollution load, and low biodegradability, the treatment of pharmaceutical wastewater has always been challenging to meet the

effluent water quality requirement (Xu et al., 2016). The harmful compounds in pharmaceutical wastewater can damage the biological process, affecting the outcomes of treatment (Svojitka et al., 2017). Many compounds are heterocyclic organics that are hard to eradicate by biological method.

2. Significance of Pharmaceutical Active Compounds

Pharmaceutically Active Compounds (PhACs) are a type of micro pollutants. They can become biologically active at relatively low concentrations, requiring the use of advanced analysis tools to investigate their prevalence. Additionally, they are typically excreted as metabolites in addition to the natural substrate, which can be much more hazardous than the native compound. Domestic discharges, the pharmaceutical effluents, healthcare institutions, discharges linked with veterinary activities and fish farming, and the disposal of unwanted drugs are all well-known sources of pollution (Wiest et al., 2018). Nonetheless, there is still some uncertainty regarding their specific functions. Moreover, it is well-documented that the Conventional Activated Sludge (CAS) treatment method, that is the most widely employed technology, does not entirely eliminate PhAC (Noguera-Oviedo and Aga, 2016).

2.1. Occurrence of Pharmaceutical Waste

Pharmaceutical contaminants have been found in approximately all environmental conditions across every region over the last three decades. In the European Union, over 3000 medicinal compounds are utilized. Pharmaceuticals in the range of ng (Nano-gram) to g per liter have been found in ground water, urban wastewater, waterways, and drinking water (Jodeh et al., 2016). Pharmaceuticals are hard to eliminate from water sources using sewage treatment procedures due to the relatively low biodegradability and strong surface chemistry (Kalvya et al., 2017; Wang et al., 2020). As a result, disposing of them in wastewater treatment facilities is a serious challenge (Wang et al., 2016). Pharmaceuticals are, in fact, among the most important classes of emerging pollutants to be cautious about.

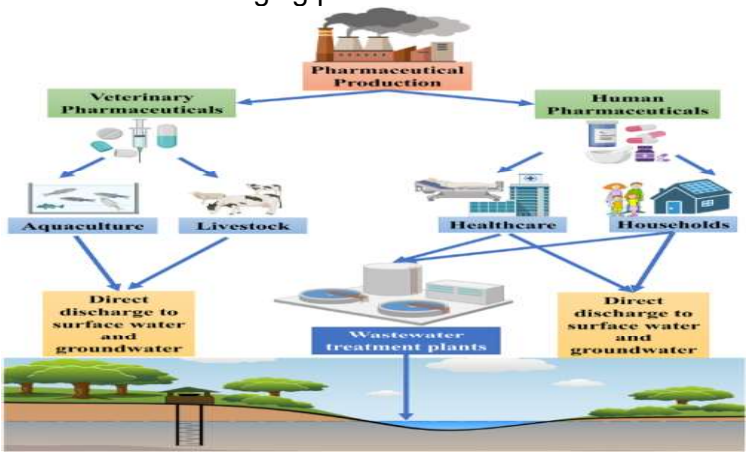


Figure-1: Pathway of pharmaceutical wastewater for contamination of natural water bodies (Kumar et al., 2022)

Few pharmaceuticals have been found in waste streams such as Non-steroidal and anti-inflammatories (i.e., ibuprofen, diclofenac, naproxen, and ketoprofen), which have been reported at extremely low amounts (ng/L and g/L) in surface waters (Guedes-Alonso et al., 2022). Existing data shows a strong emphasis on the occurrence of pharmaceutical effluents in our surroundings. Mostly compounds such as nicotine, caffeine and their derivatives like cotinine and paraxanthine as well as some widely used pharmaceuticals naproxen are typically identified at levels higher (μgL^{-1} range) than those of other ones (Asimakopoulos et al., 2017; Botero-Coy et al., 2018; Greenham et al., 2019). While, several other commonly used pharmaceuticals like diclofenac, erythromycin and carbamazepine are often within the range (Mirzaei et al., 2016). However, most research only look at the short-term occurrence of medicines; very few studies look at these substances over a lengthy period of time to assess seasonal variations and identify patterns from their presence.

2.2. Effects of resistant Antibiotics in Wastewater

Since, the currently used technologies are typically not advanced enough that is why the wastewater treatment plants are not able to eliminate such antimicrobial drugs from their effluents. As a result, when these toxic byproducts are introduced into the environment, they also contain antibiotics, increasing the concentration of environment and eventually caused antibiotic resistance (Danner et al., 2019). With the passage of time, antibiotic resistance becomes prevalent and is predicted to cause a significant rise in the number of death among humans in future (Bondarczuk and Piotrowska-Seget, 2019). According to World Health Organization reports, 200,000 individuals only in the USA contracted antibiotic-resistant germs in 2013, and 23,000 of them passed away (Munita and Arias, 2016). The World Health Organization has stated it to be among the leading three main health threats to public for the 21st century (WHO, 2014). Therefore, it can also pose an economic threat given the extent to which additional funds will be managed to spend on health care (Cristea et al., 2017) to overcome this frequently prevalent anti-biotic resistance.

2.3. Global Impacts of Pharmaceutical Wastewater

According to the present scenario in the USA, the number of fatalities (23,000 annually) related to antibiotic resistance would exceed the total death toll from diabetes and cancer (Dadgostar, 2019). Because of the severely polluted ground water that causes major health issues including cancer, miscarriages, and skin problems, villages next to pharmaceutical companies are in hazardous situation. There have been several instances of fish death in waterways, because humans have developed antibiotic resistance. The National Center for Disease Control (NCDC) of India expressed their concerns over contamination of antibiotics in water in 2018 and urged the environmental ministry to develop strong policies and try to ensure proper discharge and efficient treatment by the antibiotic producers.

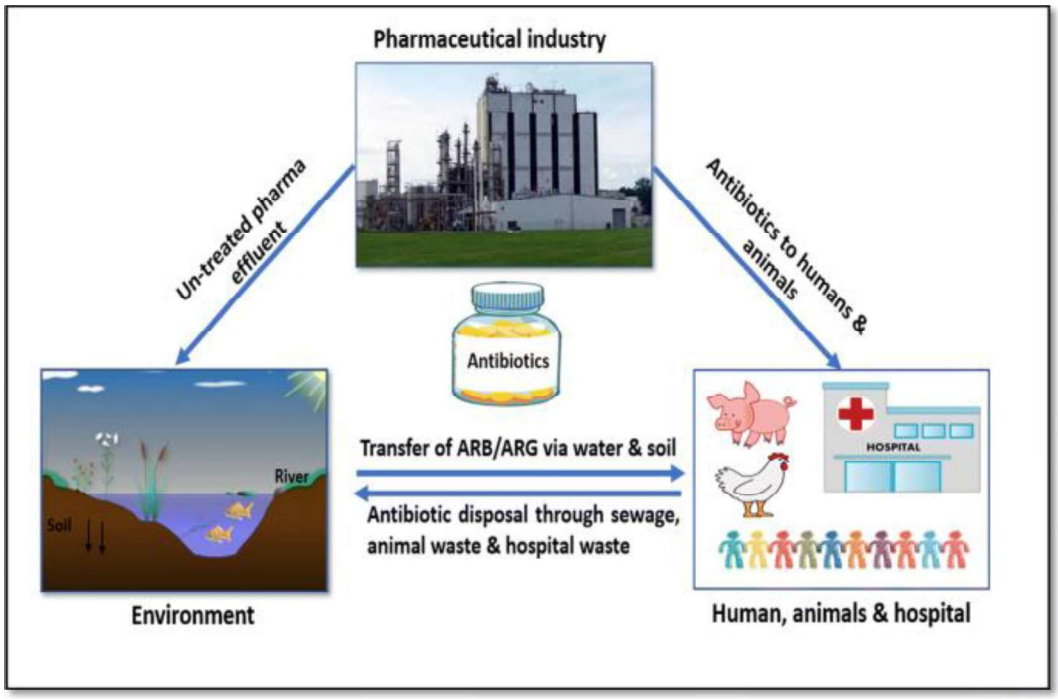


Figure-2: Presence of pharmaceuticals in multiple areas due to untreated wastewater discharge

2.4. Treatment of pharmaceutical waste in Pakistan

Companies in Pakistan's textile, pharmaceutical, ceramic, petrochemical, food processing, steel, and fertilizer sectors are all key contributors to the country's water pollution crisis. Industrial effluent from 400 pharmaceutical factories in Karachi, Pakistan is treated using a sequential batch reactor technology. Another study looked at the effectiveness of using a membrane filtration process in conjunction with an advanced oxidation process (AOP) to get rid of the microorganisms that are inevitably present in pharmaceutical wastewaters because a single process isn't enough to get rid of the harmful chemicals (Ali et al., 2020). Either because of strong biodegradation or poor bioactivity during treatment, active pharmaceutical compounds are often not degraded sufficiently by biological processes during wastewater treatment. Using additional technologies, such as chemical oxidation, to improve wastewater treatment process might be a viable alternative. Oxidation techniques have been found to be effective in eliminating pollutants that cannot be eliminated naturally from wastewater (Shirafkan et al., 2016).

As a developing nation, Pakistan places a premium on the contributions of its manufacturing sector to the country's economic development and growth. Roughly 18% of Pakistan's GDP is generated by the industrial sector (Plecher et al., 2020). As important as the industrial sector is to Pakistan's economy, many citizens are worried about the level of pollution it generates. Pakistan, a mostly agricultural

nation, faces the grave threat of water contamination. Pakistan's pharmaceutical market is predicted to expand by 10% yearly. Despite the expansion, these factories are disobeying environmental regulations by discharging their raw sewage into nearby domestic waters (Ashfaq et al., 2017)

Urban and industrial sewage were the focus of a research that evaluated the quality of the Kabul River in Peshawar. Dumping of solid waste directly into water, sewage effluents, and agricultural operations were all shown to increase pollutant levels in the research, which showed a rise from the upstream (city's origin) to the downstream (city's end) areas (Ali et al., 2020). Most PPCPs that are released into the environment are typically processed by the wastewater treatment system, where some of them are eliminated (Ashfaq et al., 2017b). There are currently insufficient wastewater treatment facilities in Pakistan due to the ongoing building of the country's wastewater treatment infrastructure. The lack of a wastewater treatment facility in Lahore City has led to the direct discharge of sewage water into the surface water, which could increase the concentration of persistent, bio accumulative pollutants (PPCPs) in the water and pose health risks to humans and aquatic life. However, owing to a lack of data on PPCPs in specific regions, risk assessments are very rare (Ashfaq et al., 2017a).

3. Impacts of Pharmaceutical effluents

Recent years have seen medicines and associated compounds become substances of increasing environmental problems. Wastewater treatment is now a top environmental issue. Antibiotics and other pharmaceuticals are widely used in public health settings to improve people's health and well-being. However, the pharmaceutical business may generate and discharge a significant volume of antibiotic-contaminated wastewater. The effluent of the pharmaceutical treatment facility in India, which processes wastewater for 90 pharmaceutical industries, was found to have elevated ciprofloxacin concentrations of 31 mg/L. Because of the potential impact on the environment and human health, scientists all around the globe are studying this category of wastewater. Overflow from various non-point water sources, such as agronomic activity or static water sources, such as municipal or hospital wastewater treatment plants, is a common pathway for pharmaceutical chemicals to make their way into natural water sources (Yang et al., 2016).

3.1. Health Impacts

Low amounts of drugs like ibuprofen, diclofenac, the psychiatrist fluoxetine, and corticosteroids like estrogen and progesterone and progestogens have been associated with abnormal growth patterns in aquatic animals. Reproductive system effects, behavioral abnormalities, and organ failure are only some of the negative consequences. Long-term exposure to trace amounts of drugs has not yet been studied for its toxicological effects on humans. Obesity, neurological problems, infertility, and immune system dysfunctions are only some of the possible side effects of chronic exposure to low doses (Guedes-Alonso and Lopez, 2021).

3.2. Environmental Impacts

The pharmaceutical substances enter aquatic compartments via wastewaters, exposing organisms to them, and causing adverse effects on biota. This vulnerability results from the fact that the purifying procedures used at WWTPs are not intended to get rid of newly discovered contaminants. In addition, the laws in place today do not mandate maximum allowable medication concentrations in water supplies. Because of the wide range of pharmaceutical analytes, their unique characteristics, and the possibility of conjugated compounds being generated during metabolization, removing them from wastewaters is a challenging task (Guedes-Alonso et al., 2020).

4. Physicochemical Parameters of Pharmaceutical Wastewater

Experiments were conducted using an ozone delivery rate of 0.78 mg/s at several pH values (5, 7.5, 9, and 11). Time series data for the pH-dependent elimination of color, ammonia, chloride, or phenol was also recorded. Time-dependent COD decline and COD removal effectiveness over a range of pH values. At a pH of 5, removal rate was 75% (Removal rate = 1950 mg dm^3), at pH 7.5, 85.3% (COD elimination = 2220 mg dm^3), at pH 9 (86.5%), and at pH 11, 88.4% (COD elimination = 2300 mg dm^3). It has been shown in Table-2.1 that molecular ozone interacts with substances in both neutral and acidic environments. A high rate of ozone breakdown causes the production of hydroxyl radicals when the pH rises. It was discovered that the quasi hydroxyl radical was a more effective antioxidant than oxygen itself (Patel et al., 2020).

Table-1: Removal Percentage (%) at different pH

pH	Removal Percentage (%)	COD Elimination
5	75 %	1950 mg dm^3
7.5	85.5 %	2220 mg dm^3
9	86.5 %	----------
11	88.4 %	2300 mg dm^3

Ozone's efficacy is also pH-dependent; at acidic pH, molecule ozone is predicted to attack and destroy the organic molecules, while at alkaline pH, the ozonation process includes the following several oxidation processes through hydroxyl radical production. Jodeh et al., (2016) conducted studies to learn how altering the pH of synthetic sample of citrus wastewater treated by ozone would affect the final product. At a pH of 10, the efficiencies reached 46%, and after 60 min of reaction (the period needed for entire true color removal), they were approximately 40%. The pH of the effluent was lowered when coagulants were added. After adding

PAC and $FeCl_3$, the pH dropped from 8.099 to 6.74 & 7.073, correspondingly. As a result, PAC created an acidic environment, whereas $FeCl_3$ maintained a neutral one. Ozone's production of hydroxyl radicals (OH-) clearly bonded with effluent cationic ions to precipitate metal hydroxyl group (Shirafkan et al., 2016).

Effluent COD was reduced due to the coagulation-flocculation process in all instances. In this point, PAC performed much better than $FeCl_3$ at reducing COD levels, and the decrease was sharper than 50%. Additionally, ozonation maintained a COD reduction in the effluent of around 35% for PAC and 77% for $FeCl_3$. Consequently, this step's findings demonstrated that a better removal effectiveness than PAC was accomplished by ozonation with $FeCl_3$ due to coagulant pH fluctuations inside the neutral and basic regions where free radical process occurred (Shirafkan et al., 2016)

5. Wastewater Treatment Plant Technologies

Most drugs, and antibiotics in particularly, pass through WWTPs partly or untreated since the current technical facilities are mostly based on activated sludge, which was not initially intended to cope with environmental contaminants like pharmaceuticals.

Conventional treatment procedures used to eliminate ECs in WWTPs include accelerated oxidative degradation (AOPs), membrane separation, advanced oxidation, and adsorption (Teodosiu et al., 2018). Conventional wastewater treatment techniques are effective in removing many PPCPs, although secondary-treated effluent still contains trace amounts of these pollutants (Blackbeard et al., 2016). Adsorption, enhanced oxidation, and membrane filtering are only some of the advanced wastewater treatment methods that have been shown to have tremendous promise for further reducing the remaining PPCPs (Luo et al., 2014; Wang et al, 2016).

5.1. Conventional Treatment of pharmaceutical wastewater

Treated wastewater may be recycled into the water supply or reused in other ways; this is the goal of wastewater treatment. Conventional wastewater treatment may be broken down into three main groups: biological, chemical, and physical. Biogas production, aerated lagoons, sludge, antifungal treatment, filtration, and stabilization are all components of the biological approach. Biodegradable organic contaminants in wastewater are broken down by bacteria, nematodes, or other tiny organisms via normal cellular processes, resulting in simple chemicals and extra biomass (Phoon et al., 2020).

A study conducted by Phoon et al., (2020), the physical approach of wastewater treatment involves the use of physical barriers and the use of natural forces including van der Waals, electrical attraction, or gravity to remove unwanted chemicals. The physical approach includes processes including sedimentation, clotting, membrane cleaning, adsorption, distillation, and filtering. Because nicotine, caffeine, and paraxanthine are not only used in drug products but also excreted by smokers and after consuming beverages like coffee, the highest

concentrations of these stimulants are found in influent samples at conventional wastewater treatment plants, which are based on activated sludge technology. In fact, throughout observation, the median amounts of these substances ranged from 45.8 to 95.6 g/L. This pattern of behavior was also shown in other experiments when the greatest doses of the drugs under study were attained for these three stimulants (Ekpeghere et al., 2018; Rico et al., 2019).

5.2. Advanced treatment Processes of pharmaceutical wastewater

Unlike processes like adsorbent and membrane separation, which simply move contaminants from one step (water) to another (adsorbent, membrane surface, or concentrated solution), chemical oxidation, or more particularly AOPs, are highly recommended technologies due to their ability to mineralize water and completely eliminate contaminants (Gimeno et al., 2016).

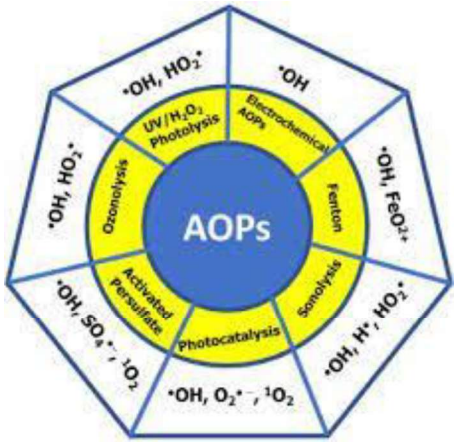


Figure-3: Various Advanced Oxidation Techniques for wastewater treatment (Rayaroth et al., 2022)

5.2.1. Direct Photolysis (UV/Solar)

Photo driven oxidation is expected to play an important role in degradation of emerging organic contaminants (Wang et al., 2017). Photolysis is a phenomenon that can lead to the destruction of organic compounds in intermediate or inert end products by the interaction of light (natural/artificial) either visible or ultraviolet. There are two possible photolysis processes in water: direct and indirect photolysis. In the process of direct photolysis, organic contaminant directly absorbs light energy, turn into unstable compound and then decomposes, while indirect mechanism of photolysis contributes to the decomposition of targeted organic contaminant when other light absorbing molecules present in water generates reactive chemical species mainly OH^- after absorption of light that attack and degrade the targeted contaminant.

The pharmaceutical compounds that can absorb light with wavelength of greater than 290 nm can easily photo-degrade under sunlight. But for the compounds which absorbs less than 290 nm, the process of indirect photolysis by the

production of oxidants such as hydroxyl radicals (OH•) or singlet oxygen (O_2) can be started naturally due to the presence of naturally occurring dissolved organic matter (DOM) and nitrates (Niu et al., 2016). In surface waters or wastewater treatment plant effluents, photolysis (either direct or indirect) is considered an important pathway to degrade persistent fluoroquinolone antibiotics (Niu et al., 2016). Many fluoroquinolone antibiotics exert substantial absorbance in the region of UV plus visible light which make them ideal for direct photolysis or photo-sensitization (Niu et al., 2016).

5.2.2. Photo-catalysis

Photo-catalysis is the process of speeding up the photochemical oxidation reaction by using the radiations (UV, visible or infrared) in the presence of photo-catalysts (Lofrano et al., 2018). In previous studies variety of photo-catalysts (TiO_2, ZnO, Fe_2O_3, ZnS, CdS) have been used by the researchers globally but, the mostly employed catalyst for photo-degradation of antibiotic compounds is found to be titanium dioxide (TiO_2) (Lofrano et al., 2017). TiO_2 is frequently applied catalyst because of its chemical stability under a range of pH, high photo-reactivity, economically low cost and low toxicity (Lofrano et al., 2017).

5.2.3. Fenton based Oxidation

With the help of UV light and ferrous/ferric species, radicals, mostly HO•, are produced by the photo-Fenton process (pF), which are then used to breakdown organic contaminants. In a nutshell, the process begins with the combination of Fe^{2+} and peroxide (Eq. 1). Ferric aquo-complexes (like [Fe (OH)] $^{2+}$) are formed from the Fe^{3+} generated in the first stage. These complexes absorb a lot of light between 290 and 410 nm, which UV-light may use to their advantage by reducing them and releasing additional hydroxyl radicals (Eq. 2) in a photo catalytic reaction (Prada-Vásquez et al., 2020).

$Fe_2+ + H_2O_2 \rightarrow Fe_3+ + HO\bullet + HO-$ (1)

$Fe\ (OH)]\ ^{2}+ + hv\ (UV) \rightarrow Fe_2+ + HO\bullet, \lambda = 290\text{-}410\ nm$ (2)

$Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+ OH^{-}+HO^*$ (3)

$Fe^{3+}+H_2O_2 \rightarrow Fe^{2+}+ HO_2^*+ H^+$ (4)

$HO^*+H_2O_2 \rightarrow HO_2^*+H_2O$ (5)

$HO^*+Fe^{2+} \rightarrow Fe^{3+}+OH^-$ (6)

$Fe^{3+}+ HO_2^* \rightarrow Fe^{2+}+ O2+H^+$ (7)

$Fe^{2+}+ HO_2^*+ H^+ \rightarrow Fe^{3+}+ H_2O_2$ (8)

$HO_2^* + H_2O_2 \rightarrow HO^*+ H_2O+O_2$ (9)

$2HO_2^* \rightarrow O_2 +H_2O_2$ (10)

$HO_2^*+ HO^* \rightarrow H_2O + O_2$ (11)

$HO^* + HO^* \rightarrow H_2O_2$ (12)

$HO^* + RH \rightarrow H_2O + R^*$ (13)

$R^* + Fe^{3+} \rightarrow R^+ + Fe^{2+}$ (14)

5.2.4. Plasma based oxidation

Thermal plasmas are generally categorized by high mass of energetic electrons and thermal equilibrium in heavy particles and electrons (Samal, 2020), generated at high pressure > 10kPa through direct or alternative current, microwave sources or radio frequency with enough temperature (4000-20000 K) to ionize the gas. Whereas, the non-thermal/cold plasmas (typically glow discharges, corona discharges, gliding arc discharge, dielectric-barrier discharge, or spark discharges) are low pressure plasmas categorized by low mass of electrons having much of its energy. However due to little mass of electrons in this plasma, it can be readily enhanced to energies which are enough to ionize the gas molecules (at or near room temperature). In this type of plasma, temperature of the energetic electrons or other particles like molecules, ions or atoms are not in state of thermal equilibrium (Samal, 2022).

5.2.5. Ozonation Process

Ozone has a long history of praise as an efficient disinfectant and oxidant. Acidic environments favors ozone's oxidizing properties. However, it is dependent on reactions of free radicals when in a neutral or alkaline environment. Rapid oxidation and decomposition of most organic substances in the water by ozone makes it an excellent pollution remover. However, direct mineralization is challenging. On the other hand, a biodegradable product may be manufactured. It may also filter out harmful bacteria and dissolved solids from wastewater. Ozone chemical oxidation technology is created when ozone is mixed with other methods for treating wastewater. When it comes to reactants, this approach is less selective

and has a higher oxidation capacity. The combination of O_3 and H_2O_2, O_3 and UV, etc. (Niu et al., 2016).

The formation of superoxide radicals requires the addition of ozone to the hydroxyl group of water. Hydroxyl radical generation may be stimulated by adding hydrogen peroxide, as illustrated in the equation. Three moles of oxygen (O_3) plus two moles of hydrogen ions (H^+) yields four moles of oxygen (O_2). In water, ozone, an unstable gas composed of three oxygen atoms, undergoes a complicated breakdown reaction sequence that yields highly reactive species such as HO_2* and OH* and induces the indirect oxidation of organic compounds (Eq. 15-20).

$$O_3 + OH^- \rightarrow O_2 + HO_2^- \quad (16)$$

$$O_3 + HO_2^- \rightarrow HO_2^* + O_3^{*-} \quad (17)$$

$$HO_2^* \rightarrow H^+ + O_2^{*-} \quad (18)$$

$$O_2^{*-} + O_3 \rightarrow O_2 + O_3^{*-} \quad (19)$$

$$O_3^{*-} + H^+ \rightarrow HO^* + O_2 \quad (20)$$

When compared to other AOPs, ozonation through H_2O_2/O_3 networks seems to be the most crucial in remediation. Contact time, water alkalinity, and ozone dosage all have a role in the efficiency of the procedure. Use of a homogeneous or heterogeneous catalyst is another method for accelerating the ozonation process. At higher pH levels, the combined use of ozone plus a catalyst seems to be more successful than using ozone alone in reducing COD and TOC. Decomposition of ozone by absorption of UV light yields H_2O_2 as an intermediate, which subsequently decomposes to hydroxyl radical, hence increasing ozonation (Srivastav et al., 2018).

6. Effect of various parameters on AOPs

Ozonation uses less energy in treated wastewater than other treatments. Nonetheless, ozone dosage is a major factor in these prices (Mousel et al., 2017). Furthermore, it allows for almost 100% water recovery with zero byproducts. When there are changes in the parameters of the incoming wastewater, ozonation is more flexible. A potential downside of the poor mineralization attained is the potential for the creation of hazardous intermediates. However, if required, this may be remedied by including a bio filtering phase with minimal running costs. However, owing to its toxicity, it is important to follow the necessary safety protocols while working with ozone. Actually, an ozonation factory cannot function without its dedicated staff. The fact that ozone destroys impurities rather than concentrating or transferring them to another phase gives it an edge over competing technologies like osmosis and AC sorption, both of which need more energy to run (Mousel et al., 2017). The chemical structures of PPCPs matter for their elimination by ozonation. Reasons for this include reactivity of hydroxyl radical and selective interaction of ozone with particular functional groups (Papageorgiou et al., 2016).

6.1. Effect of H_2O_2 Concentration

There is much evidence and research to support the idea that H_2O_2 enhances the ozonation process. When hydrogen peroxide (H_2O_2) is present, ozone breaks down more quickly. Higher H_2O_2 concentrations can scavenge hydroxyl radicals, according to previous research. At high concentrations, H_2O_2 may slow the breakdown of ozone by activating free radical processes, whereas at optimal concentrations, it speeds up the creation of hydroxyl radicals (Patel et al., 2020).

The pattern of behavior by showing that the elimination of COD drops from 85% to 75% when the H_2O_2 concentration is 0.264 mol/dm_3, compared to 85% when the concentration is 0.176 mol/dm^3. It was determined that a 50% increase in H_2O_2 dosage resulted in an 11.8% decrease in COD elimination. However, hydroxyl radical scavenging might be inhibited by the production of superoxide ion. The highest elimination (85%) was seen at an H_2O_2 concentration of 0.176 mol/dm^3, hence this value was taken as the optimal value. The results demonstrated that raising the concentration of H_2O_2 improved the efficiency with which COD was removed (Patel et al., 2020).

6.2. Effect of Ozone Dose

Studies have shown that the concentration of ozone in the air has a significant role in determining how well pollutants are broken down. For this purpose, we used ozone at concentrations spanning between 2.85 to 11.0 gO_3/h, delivered at a pH of 8, and left on for a total of 180 min. A rise in ozone dose from 2.85 through 9.2 gO_3/h was accompanied by a rise in the efficiency with which TOC, DOC, or CODT were removed. Total organic carbon (TOC), chlorofluorocarbons (COD), and dissolved organic carbon (DOC) residual concentrations were 182, 530, and 134.3 mg/L, respectively, while the ozone dose was held constant at 2.85 gO_3/h, equating to elimination efficiencies of 10.34%, 19.72%, and 13.33%, respectively. After 180 min of treatment time and 9.2 gO_3/h, the removal efficiencies of TOC, CODT, and DOC were 34, 43.64, and 41.86 percent, correspondingly (Daghrir et al., 2016)

6.3. Effect of Contact Time

The adsorption process benefits greatly from the contact time of the contaminants with various clay adsorbents. The adsorption capability of Fe(III) or Zn(II) from the effluent at a pH at 6, adsorbent dosage of 0.05 g, heat of 303 K (kelvin), quantity of 25 mL, and concentrations of 88.52 milligrams and 3.26 mg/L, respectively. Uptake capacity showed increase with increasing contact time, reaching an equilibrium value of 13.145 mg/g, 16.37 mg/g, and 17.4624 mg/g when incubated with Fe (III), and 0.555 mg/g, 0.461mg/g, as well as 0.460 mg/g when incubated with Zn (II). Because more adsorb ate molecules are able to cross the mass transfer barriers (flow separation effect) at the strong interphase with longer contact durations, the adsorption process. (Abdullah et al., 2020).

6.4. Combined processes with Ozone

Patel et al. (2019) indicated that by using ozonation and adsorption together, they were able to remove 90% of the imidazole and mineralize the remaining 10%. With an adsorbent present, the already reduced toxicity is reduced by another 30%. Removing drugs may be achieved using catalytic ozonation in conjunction with adsorption. In reality, the medicinal products were degraded by the ozonation process, and the adsorbent may collect any leftover pharmaceuticals or degradation byproducts. In addition, Mojiri et al. (2019) demonstrated that acetaminophen and amoxicillin were efficiently removed by 84.8% and 82.7%, respectively, when treated with a combination of ozone as well as adsorption (cross-linked chitosan/bentonite). The initial concentrations of ozone were 0.17 and 0.16 mg/L, respectively. Over 95% efficacy was achieved by combining the sun photochemical process of photo-Fenton with biological therapy. Both catalytic deals with the process and adsorption on altered activated carbon (Fe_2O_3/CeO_2-loaded activated charcoal) at 2 g/L, applied for just 50 min, were also effective in removing Sulfamethoxazole. Since then, numerous researchers have recommended combining AOP and adsorption to address the problems that arise when using them alone (Knopp et al., 2016).

Catalytic ozonation has been shown to be an efficient method for the removal of prescription antibiotics from wastewater. Synthetic and actual pharmaceutical wastewater containing ciprofloxacin were treated utilizing an alumina particles catalytic ozonation technique, as described by Sani et al. (2019). Studies have shown that the efficacy of catalytic ozonation is substantially increased when combined with electrochemical processes, since this combination creates new channels for the fast creation of OH radicals, which easily demolish the organics (Jin, 2020; Gomes at al., 2017).

When comparing the ozonation and EC procedures alone to one another, Asaithambi et al., (2016a) found that the combination of the two was the most successful method, removing 100% of the color and 97.50% of the COD from the distillery industrial effluent as illustrated in Figure-2.1. Particularly, at beginning pH 5, the E-HOC process's average DOC % removal achieved 58.6% for 1.5 mg O_3/mg DOC, whereas at pH values 7 and 9, the corresponding values are 45.2% and 42.2%, respectively. As the solution's pH rose, more hydroxide ions were present. Al-based coagulants may potentially serve as catalysts to increase OH formation during ozonation, as suggested in prior work (Jin et al., 2017, 2020).

Hybrid or synergistic methods are also more realistic and sustainable since they improve treatment efficiency, call for smaller, less expensive reactors, and use less energy. Electro flocculation and the catalytic ozonation process both play crucial roles in the synergic process. Electrocoagulation is a powerful tool for removing suspended solids, and catalytic ozonation is effective in removing COD. However, the standalone process may not function well under high turbidity circumstances, thus the synergic process, assuming both processes concurrently, may be advantageous for the treatment of actual wastewater. In the present study and

analysis, turbidity may inhibit catalytic performance in a single process, therefore catalyst packaging in the buckets assembly might improve efficiency levels (Gomes at al., 2017; Asaithambi et al., 2020).

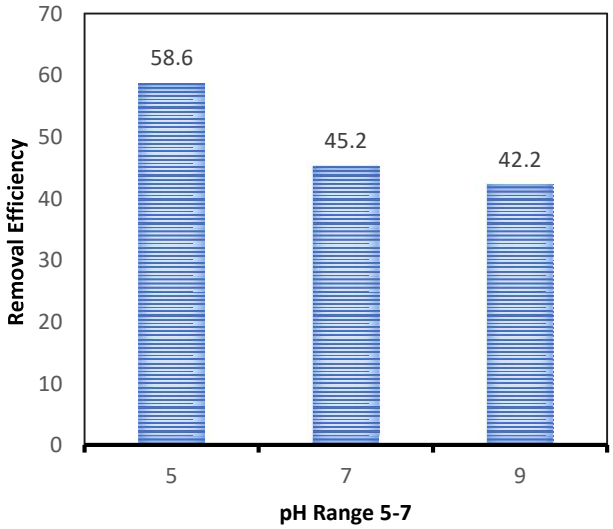


Figure-4: Removal Efficiencies at various pH after ozone-assisted Electrocoagulation

Conclusion

Combining ozonation with coagulation offers significant advantages in the treatment of pharmaceutical wastewater over conventional treatment processes. Ozonation is an advanced oxidation process that generates highly reactive ozone molecules, which effectively break down complex pharmaceutical compounds that are often resistant to conventional biological and chemical treatments. When paired with coagulation, which aggregates and removes suspended particles, the process enhances the removal of dissolved organic pollutants and micropollutants. This synergy not only improves the overall efficiency of contaminant degradation but also reduces the formation of potentially harmful by-products compared to conventional methods. Additionally, the combination of these processes can lead to lower operational costs and energy consumption, making it a more sustainable and economically viable option for treating pharmaceutical wastewater.

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