

**OPTIMIZATION OF VARIABLES FOR THE DEGRADATION  
OF PROGESTERONE FROM WATER USING PHOTO  
ELECTRO-CATALYTIC OXIDATION PROCESS**

*Submitted to the Central University of Kerala in partial fulfilment of the  
requirement for the award of the degree of*

**MASTER OF SCIENCE**

**In**

**Environmental Science**

*Submitted by*

**UTUKURI GOPI**

Reg. No. EES025131

*Under the guidance  
of*

**Prof. (Dr). Muthukumar Muthuchamy**



**DEPARTMENT OF ENVIRONMENTAL SCIENCE**

**SCHOOL OF EARTH SCIENCE SYSTEMS**

**CENTRAL UNIVERSITY OF KERALA**

**KASARAGOD**

**AUGUST 2023**

## **CERTIFICATE**

This is to certify that the dissertation entitled "**Optimization of variables for the degradation of progesterone from water using photoelectrocatalytic oxidation process**" submitted by **UTUKURI GOPI** is a bonafide record of research work accomplished under my supervision, towards the partial fulfilment of the Master of Science degree in Environmental Science of the Central University of Kerala, and no part thereof has been presented for the award of any other degree, diploma or similar titles of any university.

Place: Kasaragod

( MUTHUKUMAR MUTHUCHAMY)

Date:

## **DECLARATION**

**I, UTUKURI GOPI**, hereby declare that the project entitled “**Optimization of variables for the degradation of progesterone from water using photoelectriocatalytic oxidation process**” was submitted to the Central University of Kerala in partial fulfilment of the requirements for the award of the degree of Master of Science in Environmental Science is a bonafide record of original research work done by me under the guidance and supervision of Prof. Muthukumar Muthuchamy, Department of Environmental Science, Central University of Kerala, Kasaragod. I also declare that the project has not been submitted partially or fully for the award of any other degree or diploma title or recognition.

Place: Kasaragod

**UTUKURI GOPI**

Date:

## **ACKNOWLEDGEMENT**

I wish to express my deep sense of gratitude and indebtedness to **Prof. Muthukumar Muthuchamy**, Department of Environmental Science, Central University of Kerala, for introducing the present topic and for his inspiring guidance, and constructive and valuable suggestions throughout this work. His able knowledge and expert supervision with unwavering patience fathered my work at every stage, for without her warm affection and encouragement, the fulfilment of the task would have been very difficult.

I extend my sincere gratitude to **Dr. Sudisha Jogaiah**, Associate Professor and Head, Department of Environmental Science, Central University of Kerala for his support and constant encouragement.

I extend my sincere thanks to **Dr Raja Naika. H**, Associate Professor, **Dr. K. Sowjanya Sree**, **Dr. J. Sangeetha** and **Dr. S. Anbazhagi** Assistant Professors, Department of Environmental Science, Central University of Kerala for their support and constant encouragement.

I express my heartfelt thanks to **Salman Farissi, Kavya Jeevan, Manjusha, and Prashanthi**, Ph.D scholars of Central University of Kerala, for their active cooperation and sincere help. I am genuinely appreciative of all my colleagues; **Gara Ajith, Harikrishnan P, Jithudas P, Shilpa G and Fathima Dishna** for their suggestions and moral support during my work.

I wish to acknowledge the support of **Mr. Stebin Jose** and **Mr. P Shiva Prasad** Technical Assistants, Dept. of Environmental Science, Central University of Kerala, for providing the facilities required during the course.

Last but not least, I express my gratitude to my parents and friends who stood with me in all circumstances and for their support and encouragement in all areas of my work.

**UTUKURI GOPI**

## TABLE OF CONTENTS

<b>CHAPTER NO</b>	<b>TITLE</b>	<b>PAGE NO</b>
	<b>CERTIFICATE</b>	i
	<b>DECLARATION</b>	ii
	<b>ACKNOWLEDGEMENT</b>	iii
	<b>ABSTRACT</b>	1
<b>CHAPTER 1</b>	<b>INTRODUCTION</b>	
1.1	Emerging pollutants	3
1.2	Emerging pollutants in Aquatic environment	4
1.3	Classification of emerging pollutants	8
1.3.1	Endocrine disruptors	8
1.3.2	Pharmaceuticals	10
1.3.3	Pesticides	10
1.4	Environmental and health risks associated with Emerging Pollutants	11
<b>CHAPTER 2</b>	<b>REVIEW OF LITERATURE</b>	
2.1	Waste and surface water concentrations of Progesterones	17
2.2	Sources of Progesterone occurrence in Environment	19
2.3	Concentration of Progesterone	21
2.4	Treatment process for Emerging Pollutants removal	23
2.4.1	Advanced Oxidation Process	25
<b>CHAPTER 3</b>	<b>SCOPE AND OBJECTIVES</b>	33
3.1	Scope of the study	33
3.2	Objective of the study	33
<b>CHAPTER 4</b>	<b>MATERIALS AND METHODS</b>	
4.1	Sample under the study	34
4.2	Photo electrocatalytic degradation	34
4.3	Estimation of pH	35

<b>CHAPTER NO</b>	<b>TITLE</b>	<b>PAGE NO</b>
4.4	Characterization studies	35
4.4.1	FTIR	35
4.4.2	XRD	35
4.5	Spectrophotometric analysis	36
4.6	Assessment of Chemical oxygen demand	36
<b>CHAPTER 5</b>	<b>RESULT AND DISCUSSION</b>	37
5.1	Photo electrocatalytic degradation of Progesterone	37
5.2	Characterization studies of V <sub>2</sub> O <sub>5</sub>	37
5.2.1	XRD studies on V <sub>2</sub> O <sub>5</sub>	37
5.2.2	FTIR Studies on V <sub>2</sub> O <sub>5</sub>	38
5.3	UV visible spectral analysis	40
5.3.1	Effect of pH	40
5.3.2	Effect of current density	40
5.3.3	Effect of treatment time	41
5.4	Analysis of COD during Photo electrocatalytic oxidation of Progesterone	44
5.4.1	Effect of treatment time	44
5.4.2	Effect of current density	45
5.4.3	Effect of pH	45
5.4.4	Effect of reusability of catalyst on COD removal efficiency	46
5.4.5	Reaction Mechanism of Photo Electrocatalytic Oxidation of Progesterone	49
<b>CHAPTER 6</b>	<b>CONCLUSION AND FUTURE RECOMMENDATIONS</b>	
6.1	Conclusion	50
6.2	Future recommendations	51
	<b>REFERENCES</b>	52

## **LIST OF TABLES**

SERIAL NO	TABLE NO	TITLE	PAGE. NO.
1	1.1	The Toxic Effects of Typical Emerging pollutants in The Environment	13
2	2.1	Important Physio-Chemical Properties of Progesterone	16
3	2.2	Progesterone Concentration in Different Waters	22
4	2.3	Different Advanced Oxidation Processes for the Degradation of Emerging Pollutants Present in Water	22
5	2.4	Removal Of Progesterone and Its Water-Soluble Form is Achieved by Various Advanced Oxidation Processes.	32

## LIST OF FIGURES

<b>FIGURE NO.</b>	<b>TITLE</b>	<b>PAGE. NO.</b>
1.1	Categories of emerging pollutants that impact soil, air, water, animals, plants, microorganisms, and humans	5
1.2	Pathways of EPs from the source to the aquatic environment.	7
1.3	General categories of Emerging Contaminants	9
1.4	environmental and health effects of Emerging pollutants	12
2.1	Chemical structure of progesterone	15
2.2	Locations in which studies on the levels of the synthetic Progesterone considered in this article were conducted in the aquatic environment from 2015 to 2021	18
2.3	Sources and pathways for the occurrence of progestagens in the environment	20
2.4	Different removal techniques for emerging pollutants	24
2.5	Mechanism of the anode during the treatment	30

<b>FIGURE NO.</b>	<b>TITLE</b>	<b>PAGE. NO.</b>
4.1	Experimental setup and mechanism for the photocatalytic oxidation of progesterone	34
5.2	XRD and FTIR STUDIES ON V <sub>2</sub> O <sub>5</sub>	39
5.3	Effect of pH on photo electrocatalytic oxidation of progesterone	42
5.4	Effect of current density on photo electrocatalytic oxidation of progesterone	42
5.5	Effect of treatment time on photo electrocatalytic oxidation of progesterone	43
5.6	Effect of Treatment Time on COD removal Efficiency (%)	47
5.7	Effect of current on COD removal efficiency (%).	47
5.8	Effect of pH on COD removal efficiency (%).	48
5.9	COD removal efficiency of photo electrocatalytic oxidation after 5 cycles of treatment using V <sub>2</sub> O <sub>5</sub> .	48

## **ABSTRACT**

Emerging pollutants include synthetic progestogens, and they primarily affect the hormonal behavior of the aquatic environment. Water contamination is a global issue that requires immediate attention. Progesterone is a sexual hormone that is naturally produced by humans. The initiation of pharmaceuticals has given rise to the synthetic production of PGT as a medicine for various pregnancy-related issues. PGTs are a growing pollutant in water sources all around the world because of their synthetic manufacturing and high consumption rates. Steroid pollutants cannot be eliminated by conventional wastewater treatment methods. Hence, the current study attempted the degradation of 10 mg L<sup>-1</sup> of PGT in water using photocatalysis (PC) followed by electrocatalytic oxidation (EC) using Vanadium Pentoxide (V<sub>2</sub>O<sub>5</sub>), carbon-coated titanium (C/Ti) anode, titanium as cathode and 20mM of electrolyte concentration. Characterization involved XRD and FTIR spectral studies that showed the stability of the catalyst with the fact that no adsorptive removal of PGT had taken place. Optimization studies found UV-C irradiation, pH 5, 50 mg L<sup>-1</sup> catalyst, 180 min PC, 180 min EC, and 95.5 mA.cm<sup>-2</sup> 20 mM (Na<sub>2</sub>SO<sub>4</sub>) of electrolyte concentration managed to accomplish 95% COD and 81% of compound removal.

# **CHAPTER 1**

## **INTRODUCTION**

Water is a vital resource for life on Earth. Water contamination is a global issue that demands immediate attention and planned implementation. According to the (UN WWAP, 2008) 2 million metric tons of sewage, industrial, and agricultural waste are released into the world's water every day, which is equal to the weight of the total human population. According to the UN, the quantity of wastewater generated yearly is around 1500 km, which is six times the total volume of river water on the globe.

Water contamination is caused by a lack of effective sanitization; it is the most prominent source of water pollution. 2.5 billion people worldwide do not have access to decent sanitation (UNICEF,2009). More than half of freshwater fish species are threatened with extinction, as are one-third of the world's amphibians (Vie, Hilton-Taylor, and Stuart, 2009).

According to China and Asia statistics, over 70% (1.8 billion) of people face a lack of sanitation, resulting in a fast-rising economy for water shortages, therefore 8 percent of freshwater must be required for 22 percent of the world's population. However, 33% of industrial wastewater and 70% of household waste were discharged into rivers and lakes, while 80% of China's cities lacked sufficient sewage treatment facilities and 90% of the water supply was contaminated (Water Pollution in China, Facts and Details).

Pollutants, nutrients, microbial contaminants, heavy metals, and colors were often the subject of wastewater treatment experiments. Several pollutants have recently come to the attention of people all around the world. Furthermore, these toxins may damage both human health and the environment (Vargas-Berrones et al.,2020; Anastopoulos et al.,2020).

There have been very few studies finding contaminants in wastewater in many underdeveloped nations, particularly in Africa and other regions of the world. One of the primary causes for the lack of proper procedures for detecting these dangerous compounds. The study of these contaminants, which are difficult to degrade in water and may be detrimental to both humans and the environment, must be accelerated by scientists in these nations. We can better safeguard

human health and the environment by knowing where these contaminants come from and what happens to them in the ecosystem (Stefanakis et al., 2016).

The categories used to categorize pollutants in the aquatic environment change throughout time, according to published studies. Because persistent contaminants can infiltrate the food chain, it is critical to boost research efforts and identify all alternatives for decreasing the repercussions and dangers associated with water pollution that have an indirect impact on human health (Stefanakis et al., 2016).

Advances in detection technologies have resulted in the discovery of an expanding diversity of pollutants and the consequences of their transformation in aquatic ecosystems in recent decades. Understanding the risks that these substances pose to the environment and human health is dependent on this information (Zwiener, and Frimmel, 2004). These compounds have been identified as emerging water pollutants.

## **1.1 EMERGING POLLUTANTS**

Emerging pollutants (Eps) also known as emerging contaminants (ECs) or contaminants emerging concern (CECs) are newly identified natural or synthetic chemical compounds that are not monitored (Necibi et al., 2021; Egbuna et al., 2021). The Journal Emerging Contaminants has defined these compounds as “*chemicals that are not currently (or have been only recently) regulated and about which there exist concerns regarding their impact on human or ecological health.*” (Salthammer, “Emerging indoor pollutants, 2020).

Endocrine disruptors, insecticides, medicines, and their breakdown products are examples of emerging pollutants (EPs). They have the potential to harm both human and environmental health. Their presence in the environment, however, is often in the low concentration range (from g/ L<sup>-1</sup> to ng /L<sup>-1</sup>) (Jiang et al., 2013). As a result, various studies on the contamination of the aquatic environment by EPs have been done globally, and their existence in practically all aqueous media, including surface water, groundwater, ocean, drinking water, and wastewater, has been proven.

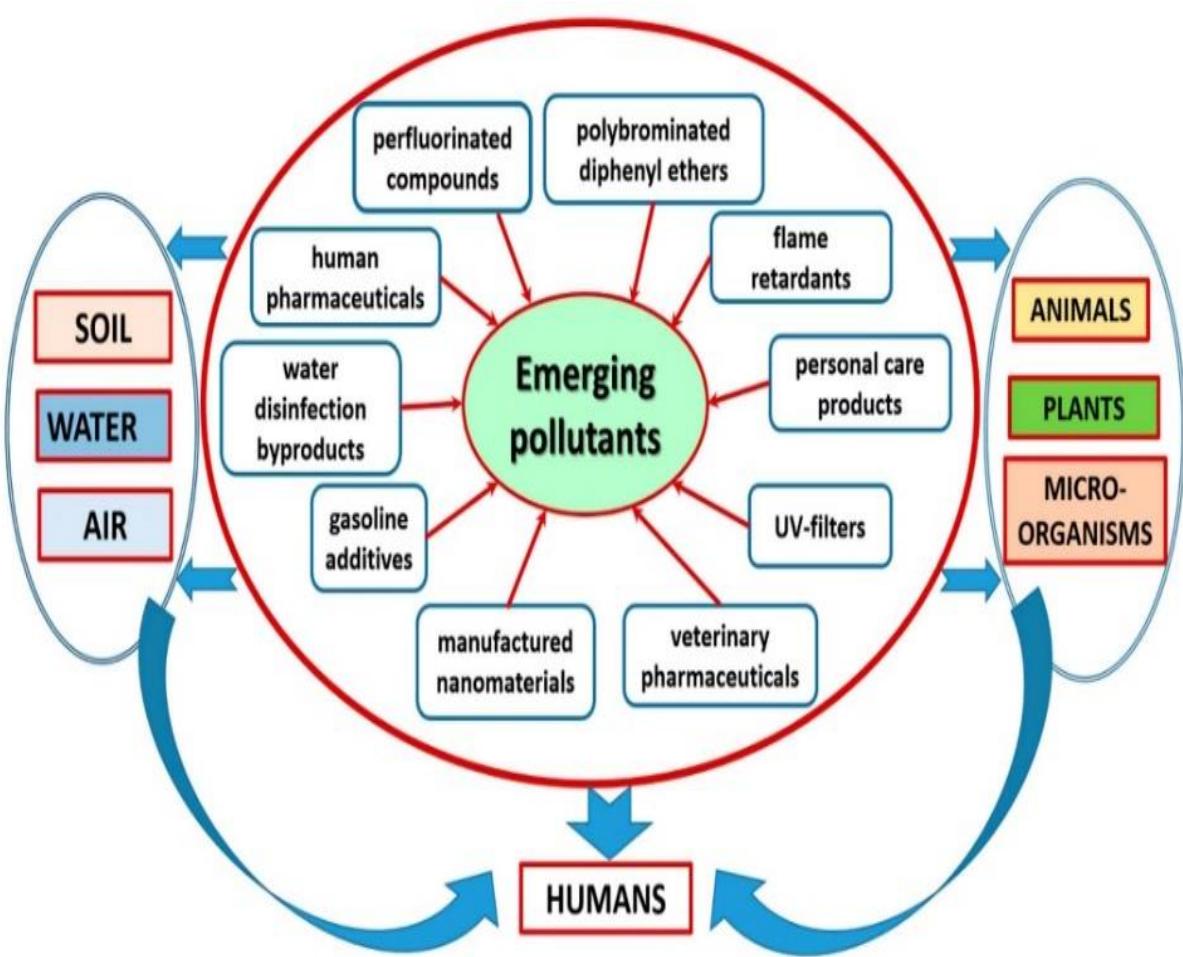
## **1.2 EMERGING POLLUTANTS IN THE AQUATIC ENVIRONMENT**

The production and use of chemicals referred to be "emerging pollutants" and/or "contaminants of emerging concerns" have risen because of the ongoing growth of human activities (industry, agriculture, and health). Early in the nineteenth century, the first EPs were found in aquatic settings (Du et al.,2015). Emerging pollutants come from a variety of human-made compounds that are vital for modern civilization, including a wide range of substances created by agriculture, unchecked urbanization, industry development, healthcare activities necessary to sustain human well-being, and transportation (Petrie et al.,2015).

EPs are synthetic persistent organic chemicals, which are not normally monitored in the environment but can create adverse effects on the environment and human health. According to the NORMAN database, ([www.norman-network.net](http://www.norman-network.net)), there are more than 700 compounds grouped into 20 classes of emerging pollutants: "surfactants, antibiotics and other pharmaceuticals, steroid hormones, and another endocrine-disrupting compounds (EDCs), fire retardants, sunscreens, disinfection byproducts, new pesticides, and pesticide metabolites, naturally-occurring algal toxins", etc (Geissen et al.,2015; Snow et al., 2017). Figure 1.1 shows the categories of emerging pollutants that impact soil, air, water, animals, plants, microorganisms, and humans.

Emerging contaminants are often chemicals having a newly known source/alternative route to people (Olatunde, Kuvarega, and Onwudiwe, 2020). They may enter the environment from a variety of sources, including industrial effluents, agricultural runoff, leaky home wastewater, and municipal wastewater treatment facilities (Gao et al.,2020).

Figure 1.1 displays the routes of EPs into the aquatic environment. Earlier research has found that existing conventional wastewater treatment plants are poor at removing/degrading many of these toxins, causing them to be discharged into the environment and endangering living species and human health (Necib et al.,2021, Zhao et al.,2018).

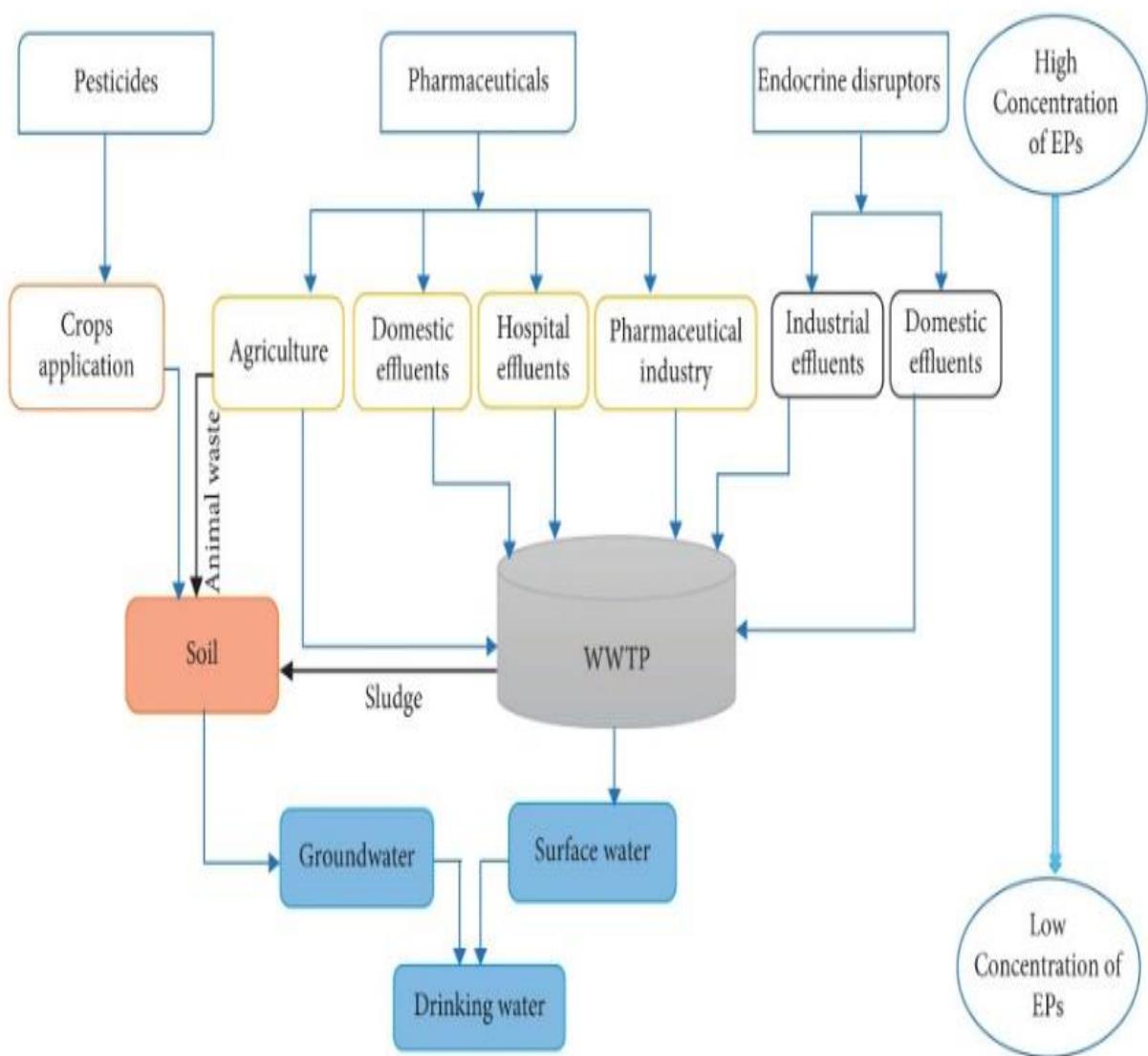


**Figure 1.1** Categories of emerging pollutants that impact soil, air, water, animals, plants, microorganisms, and humans (adopted from Le et al., 2015)

Emerging pollutants pose environmental problems due to their specific physicochemical properties. Treatment of surface water and wastewater containing these pollutants should consider interactions with various environmental conditions, such as seasonal changes, solar radiation intensity, temperature, and hydraulic resistances. These contaminants can be found in areas previously unutilized due to persistence during transport and bioaccumulation. They can reach soil, atmosphere, or water bodies through various mechanisms, depending on their properties and environmental compartments.

EPs can become pollutants in river ecosystems when treated wastewater from WWTPs is discharged. They accumulate in sediments and flora and fauna due to their biodegradation, chemical degradation, and photodegradation at low rates. Some microbial populations can alter EPs, increasing their degradation rate. However, few studies investigate the natural biodegradation of EPs, such as hormones, detergents, or pharmaceuticals. The development of microbial populations tailored for different EP categories is a challenging task for researchers.

Figure 1.2 depicts the pathways of EPs into the aquatic environment. According to earlier studies, existing conventional wastewater treatment plants are ineffective in removing/degrading many of these contaminants, allowing them to be released into the environment and threaten living organisms and human health.



**Figure 1.2** Pathways of EPs from the source to the aquatic environment. (Adopted from Tran et al., 2018)

## **1.3 CLASSIFICATION OF EMERGING CONTAMINANTS**

According to Tran et al. (2018) and Gogoi et al. (2018), emerging contaminants connections may be broadly classified into three categories:

### **1.3.1 Endocrine Disruptors**

Endocrine disruptors are natural or synthetic chemical substances that can interfere with the hormonal system (in which hormones act as chemical messengers to control and coordinate body functions) (Jiang et al., 2013; Darbar, 2015), by altering processes such as the synthesis and, storage, release, metabolism, and transport of the body's natural hormones (Gao et al., 2020). These are substances that can collect in the environment and affect the ecosystem as well as human health. Pesticides, flame retardants, natural and synthetic hormones, plasticizers, personal care items, detergents, and some medications are traditionally classified as EDs based on their usage (Calman and Gavrilescu, 2009; Laurenson et al., 2014).

The natural steroid hormone groups include progestogens, glucocorticoids, mineralocorticoids, androgens, and estrogens secreted by the hormonal systems of humans and animals. Synthetic steroid compounds are  $17\alpha$ -ethynodiol (EE2) and mestranol (MeEE2), commonly used in oral contraceptives and hormone replacement therapy. Natural steroid estrogen compounds are estrone (E1),  $17\beta$ -estradiol (E2), and estriol (E3). Synthetic androgens and progestins are also used as growth promoters in animal farms (Fent, 2015; Ting and Praveena, 2017).

Steroids with progestogenic activity are called gestagens, progestogens, or progestagens. In the case of gestagens present in the environment, the term “environmental gestagens” and the term progestin in the case of synthetic progestogens or gestagens are often used. In practice, synthetic progestins have endocrine activity, like  $17\alpha$ -ethynodiol. Together with synthetic estrogen steroids, progestins belong to the most important group of interest in environmental drugs, but unlike estrogens, progestins are not well studied and their environmental hazards are not fully known (Fent, 2015). They are found at varied levels in practically all aquatic systems, including surface water, groundwater, ocean, effluent from wastewater treatment facilities, and drinking water (Vieira et al., 2021). Because of their harmful influence on the ecology, these components are of major concern. It should be highlighted that these are only broad categories of EC; it is known what occurs in the environment and what happens to many different EC classes are shown in Figure 1.3

# EC

## Emerging contaminants

### Main classes

Pharmaceutically active compounds (PhACs)

Personal care products (PCP)

Endocrine disrupting compounds (EDC)

### Wider classification based on 4 criteria

High consumption all over the world

High detection frequency in sewage and sewage sludge

Potential risks for ecosystems and human health

Availability of analytical data

Antibiotics

Antifungal antimicrobial agents

Nonsteroidal antiinflammatory drugs

Anticonvulsants  
antidepressants

Beta-adrenoceptor blocking agents

Lipid-regulating drugs

Steroidal hormones

X-ray contrast media

UV filters

Stimulants

Antiitching drugs

Insect repellents

Plasticizers

Pesticides

Ilic drugs/abused substances

**Figure 1.3** General categories of Emerging contaminants (adopted from Tran et al., 2018; Gogoi et al., 2018).

### **1.3.2 Pharmaceuticals**

Pharmaceuticals are chemical molecules that are employed in medications to prevent and treat illness as well as to safeguard public health (Madikizela, et al.,2020). Human and veterinary medicines are becoming more common in daily life. They are classed therapeutically as analgesics, antibiotics, anti-inflammatories, antidepressants, lipid-lowering medicines, and beta-blockers (Rivera-Utrilla et al.,2013). Pharmaceuticals have been discovered in various amounts in wastewater effluents, surface water, groundwater, and saltwater. Pharmaceuticals have been discovered in various amounts in wastewater effluents, surface water, groundwater, and saltwater (de Oliveira et al.,2020).

They enter aquatic bodies from a variety of sources, including human excrement (which introduces them into the sewage system), drainage water, and industrial effluents. (Couto et al.,2020; Barra Caraccilo et al.,2015). Because certain compounds are very soluble in water, current wastewater treatment techniques are not intended to remove them, enabling them to reach surface water (Madikizela, et al.,2020). The ubiquitous presence of these pollutants in the environment has piqued the interest and attention of people all over the world.

### **1.3.3 Pesticides**

Pesticides are any substances that are designed to prevent, eradicate, repel, or minimize pests (Jurado et al.2012). Their applications range from agricultural land to individual gardens to public places (Hassaan and El Nemr, 2020). According to literary research, they are widely used in many regions of the world.

Pesticides are divided into four major groups based on their intended use: herbicides, insecticides, fungicides, and bactericides. Despite being sprayed into the soil, these compounds can be transferred off-field into water bodies by surface runoff and percolation via the soil, affecting water quality by posing a risk to aquatic compartments and human health (de Souza et al.,202; Foo and Hameed,2010).

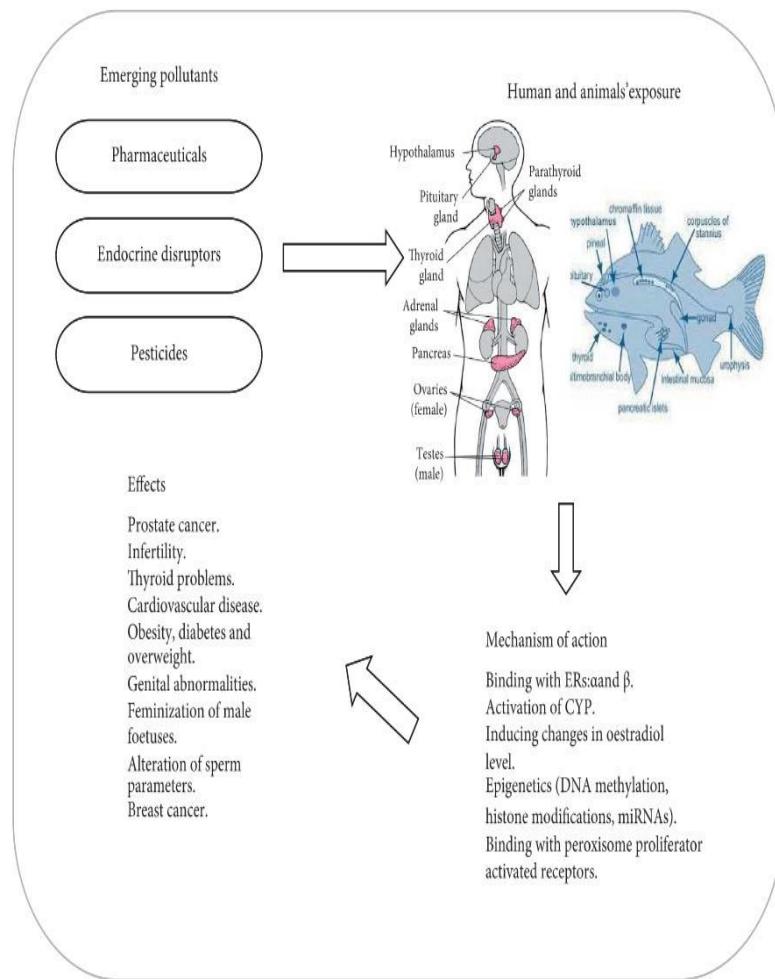
## **1.4 ENVIRONMENTAL AND HEALTH RISKS ASSOCIATED WITH EMERGING POLLUTANTS**

EPs pose environmental and human health risks due to their toxicity, with ng/L concentrations showing effects on humans and aquatic organisms. Estimating long-term impacts is difficult, and awareness of their behavior and hazard/ecological risks is insufficient. Tools like environmental risk assessment, quantitative analysis of the structure-activity relationship (QSAR), and the relationship between physicochemical properties and environmental behavior and fate (PPEF), assisted by software can help assess toxicity effects. (Carere et al., 2016; Sorlini et al., 2016). Studies on emerging pollutants' environmental risks, particularly in water, consider toxicity on aquatic flora and fauna, but also human health risks, particularly in water recovery and reuse systems.

The USEPA and WHO have developed guidelines for assessing EP risks to human health and determining exposure factors. The European Union has developed protocols and methodologies since 1980, including pharmaceutical products, and the REACH regulation is crucial for chemical authorization. The USEPA and WHO have developed guidelines for assessing EP risks to human health and determining exposure factors. The European Union has developed protocols and methodologies since 1980, including pharmaceutical products, and the REACH regulation is crucial for chemical authorization.

The literature on ecological and human health risks primarily focuses on contaminants in wastewater and surface water, as well as sediments as a sink for EPs and sources of contamination for aquatic flora and fauna. (Hang et al., 2016). Sediments can become a source of contamination if particles are remobilized and suspended in liquid flow. EPs associated with solid particles can become bioavailable to benthic organisms, generating acute and chronic exposure, and spreading to higher trophic levels (Dsikowitzky et al., 2020; Aukidy et al., 2015).

EPs can undergo transformations into less toxic products and be adsorbed on sediments, accumulating, or transported to other water bodies or groundwater sources. The environmental and health effects of emerging pollutants are shown in Figure 1.4 and Table 1.1. The toxic effects of EPs can cumulate and generate synergistic interactions, leading to the cocktail effect, increasing the difficulty of risk analysis. Stuart et al., (2020) give a clear-cut idea about the toxic effects of Eps in the environment.



**Figure 1.4** Environmental and health effects of Eps (adopted from Naidu et al., 2020)

**Table1.1** The toxic effects of typical EPs in the environment (adopted from Naidu et al.,2020)

<b>Emerging Pollutant</b>	<b>Ecology Effect</b>	<b>Human Health Effect</b>
Engineered nanoparticles	toxicity in plants, fish, earthworms, and bacteria (growth, mortality, reproduction, gene expression)	Cytotoxicity, oxidative stress, inflammatory effects, in lungs, genotoxicity, carcinogenic effects, granulomas, thickening of the alveolar wall, and augmented intestinal collagen staining
Endocrine disruptors	Toxic to wildlife, human	Alter reproductively relevant, sexually dimorphic neuroendocrine system, alter endogenous steroid levels, etc., diabetes, problems in the cardiovascular system, abnormal neural behaviors and linked to obesity
Ionic liquids	Inhibitory effects on a variety of bacteria and fungi, influencing the growth rate of algae, toxic to invertebrates, fish, and frogs	Adverse effects on neuronal process, cytotoxicity
<b>Perfluorinated compounds</b>	<b>Bioaccumulation in fish and fishery products</b>	<b>Accumulate primarily in the serum, kidney, and liver, potentially adverse effects on developmental, and reproductive systems and other damaging outcomes</b>

Consistent application of the precautionary principle is essential to ensure a clean and healthy environment for future generations. Further studies on the risks induced by EPs are essential to understand their specific environmental behavior, toxicity, and impact on the environment and human health (Naidu et al.,2020)

## CHAPTER 2

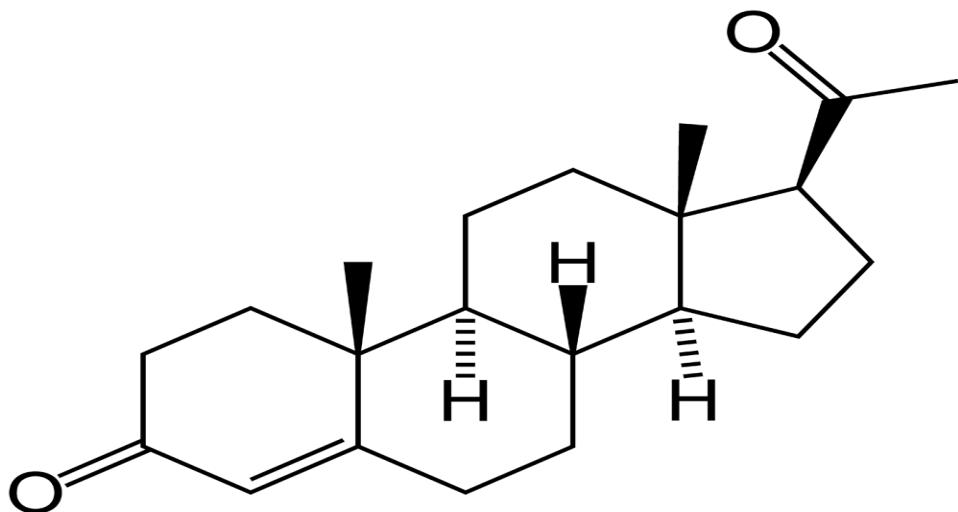
### REVIEW OF LITERATURE

The term ‘progestogens’ refers to natural and synthetic molecules having a pregestational activity that prepares the uterus for pregnancy. Synthetic compounds designed to bind progesterone receptors (PRs, also known as NR3C3: PR-A and PR-B) constitute classes of molecules that have different pharmacological properties and modes of action (Schumacher et al., 2007; Stanczyk et al., 2013)

Adolf Butenandt discovered and synthesized naturally occurring progesterone (P4), a 21-carbon sex steroid hormone, in the mid-1930s. He received the Nobel Prize in Chemistry for his work on sex hormones. In 1939, he was awarded the Nobel Prize in Chemistry (Butenandt and Westphal, 1974). Soon after that Progesterone and its synthetic analogs, known as progestins, were discovered. began to be used to prevent preterm birth and pregestational diabetes, Infertility, assisted reproduction, and threatening and routine abortion. Premenstrual syndrome, dysmenorrhea, endometriosis, osteoporosis, and other conditions Endometrial hyperplasia prevention with menopausal hormone treatment, as well as a variety of other illnesses (Henderson, 2018; Piette ,2018; and Sawyer 1960).

Progesterone (PG) is a C-21 structural steroid hormone that belongs to the family of prostaglandins, and it naturally occurs in the human body. Progesterone is widely applied in breast cancer therapy, endocrine regulation, drug contraception, and assisted reproduction. (Maria et.al., 2020).

Chemically progesterone is a highly hydrophobic sex steroid hormone ( $\log P = 3.9$ ) with exceptionally low solubility in water at room temperature (7-10  $\mu\text{g/mL}$ ) (Nandi et.al 2004). It dissolves slowly in gastrointestinal fluids. It has low solubility in water and rapid liver metabolism. (Adrina et.al 2012). The structure of progesterone is given the in Figure.2.1



**Figure.2.1** Chemical structure of progesterone ( $C_{21}H_{30}O_2$ )

The structure of progesterone is ( $C_{21}H_{30}O_2$ ), generally, the structure name of progesterone contains three Hexa cyclic hydrocarbons connected to Penta cyclic hydrocarbons. According to the scientific name groups, rone consists of four interconnected cyclic hydrocarbons with ketone and oxygenated functional groups as two methyl branches

Progesterone can be used as birth control, treatment of infertility, and hormone replacement therapy. Progesterone is also used to treat other conditions, such as endometriosis, fibroids and premenstrual syndrome (PMS). Progesterone is white in color, and toxic to the environment. Important physio-chemical properties of progesterone are given below in Table 2.1

**Table 2.1** Important physio-chemical properties of progesterone

SI NO	PROPERTIES	VALUES	REFERENCE
1	Molecular weight	314.5g/ mol	Pub chem.org.in
2	CAS-NO	57-83-0	
3	Solubility	Less than 1mg/ ml/ <0.1g/100 ml at 19 ° C	Pub chem.org.in
4	Pka1	Acidic = 4.8	Pub chem.org.in
5	Pka2	Basic =18.92	Pub chem.org.in
6	Log kow	-3.87	Pub chem.org.in
7	Density	1.66 g/ cu cm	Pub chem.org.in
8	Vapor pressure	$3.59 \times 10^{-4}$ mm hg at 25°C.	Pub chem.org.in
95	Half-life in environment	Absorption of half-life approx. 25-30hours, elimination half-life 5-20 min	Pub chem.org.in
10	Boiling point	394.13°C.	Pub chem.org.in
11	Melting point	250-252° F.	Pub chem.org .in

## **2.1 WASTEWATER AND SURFACE WATER CONCENTRATIONS OF PROGESTOGENS**

Progesterogens are considered emerging pollutants in aquatic ecosystems, where they are usually present in concentrations in the order of ng/L. However, accurately knowing their concentrations in water is crucial since such tiny amounts are potentially harmful to (at least) fish (Kumar et.al., 2015).

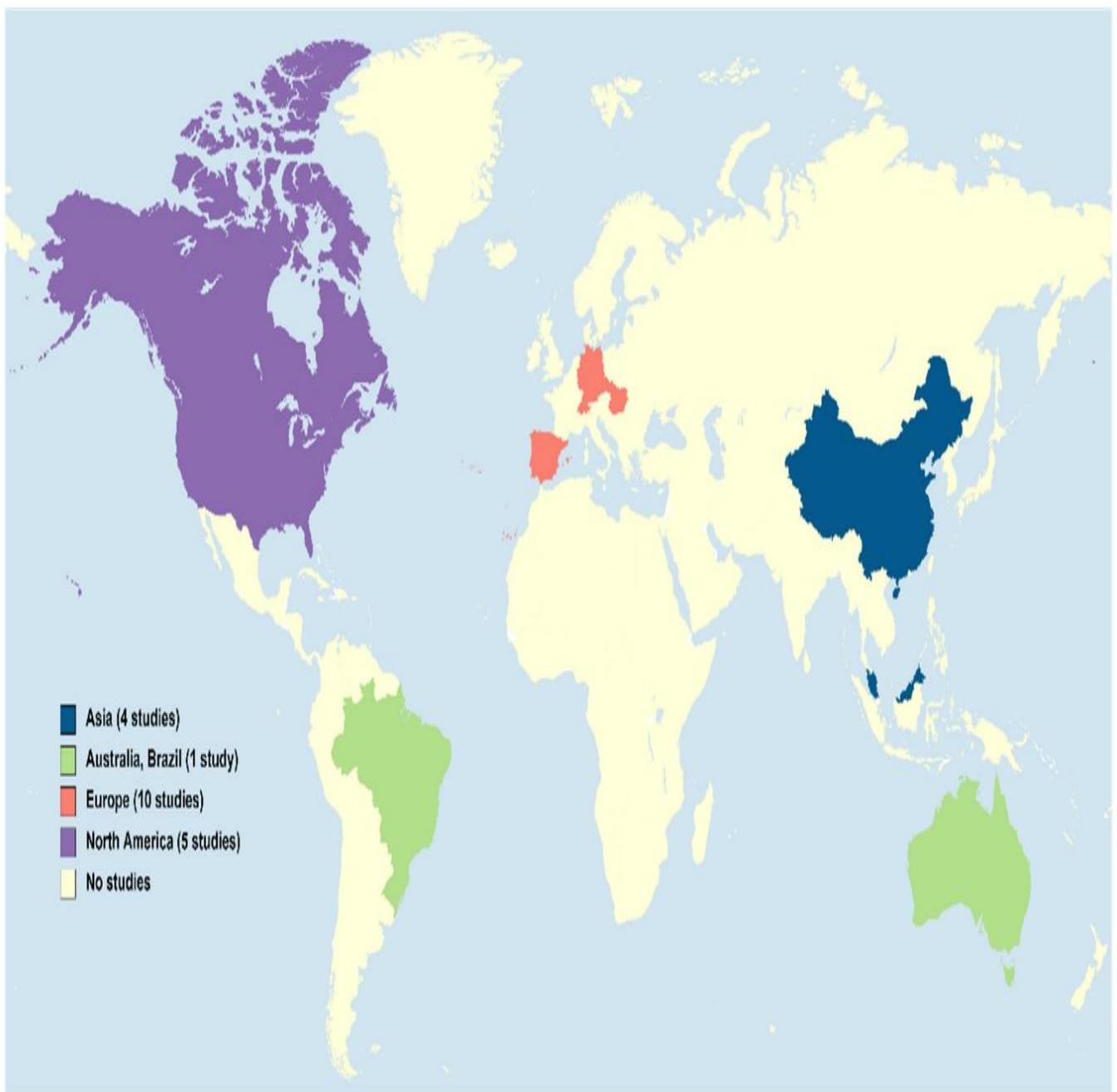
Because analyzing Progesterogens requires trace analytical methods for their extraction and quantification, the number of studies concerning the environmental levels of these compounds is still scarce. In most cases, focused on the concentrations of these hormones in influents and effluents from wastewater treatment plants (WWTPs).

In addition, the surveyed areas are limited in space. From 2015 to 2021, most research was performed in Europe (48%) and North America (24%). In Asia (19%), South America (5%), and Australia (5%), there are fewer details about the levels of synthetic Progesterogens in Africa. The following Figure 2.2 shows locations in which studies on the levels of synthetic Progesterogens (Adopted from Maria et al. (2022)).

Progesterone was detected in all samples with concentrations in the range of 0.82 to 1.1 ng/L in surface water and 0.11 to 110 ng/L in wastewater samples. Three synthetic progestogens, namely, megestrol acetate, medroxyprogesterone acetate, and dienogest, were detected most often in effluents; therefore, further attention should be paid to the monitoring of these compounds.

Progesterone levels in Them River samples ranged from undetectable to 439 nanograms per liter (ng/L), with an average of 120.3 ng/L. Progesterone levels were significantly higher in the midstream of the river than in the upstream and downstream sections. This was likely due to the combined effects of livestock, waste stabilization ponds (WSPs), household effluents, agricultural activities, and sewage infiltration.

While the progesterone levels in water were not extremely high, they were still high enough to cause harm to aquatic organisms in other studies. Samples collected from the WSPs showed that they released 215 ng of progesterone per liter of receiving waters. Although the WSPs were able to remove 75% of the progesterone, the amount that was released was still high enough to be harmful.



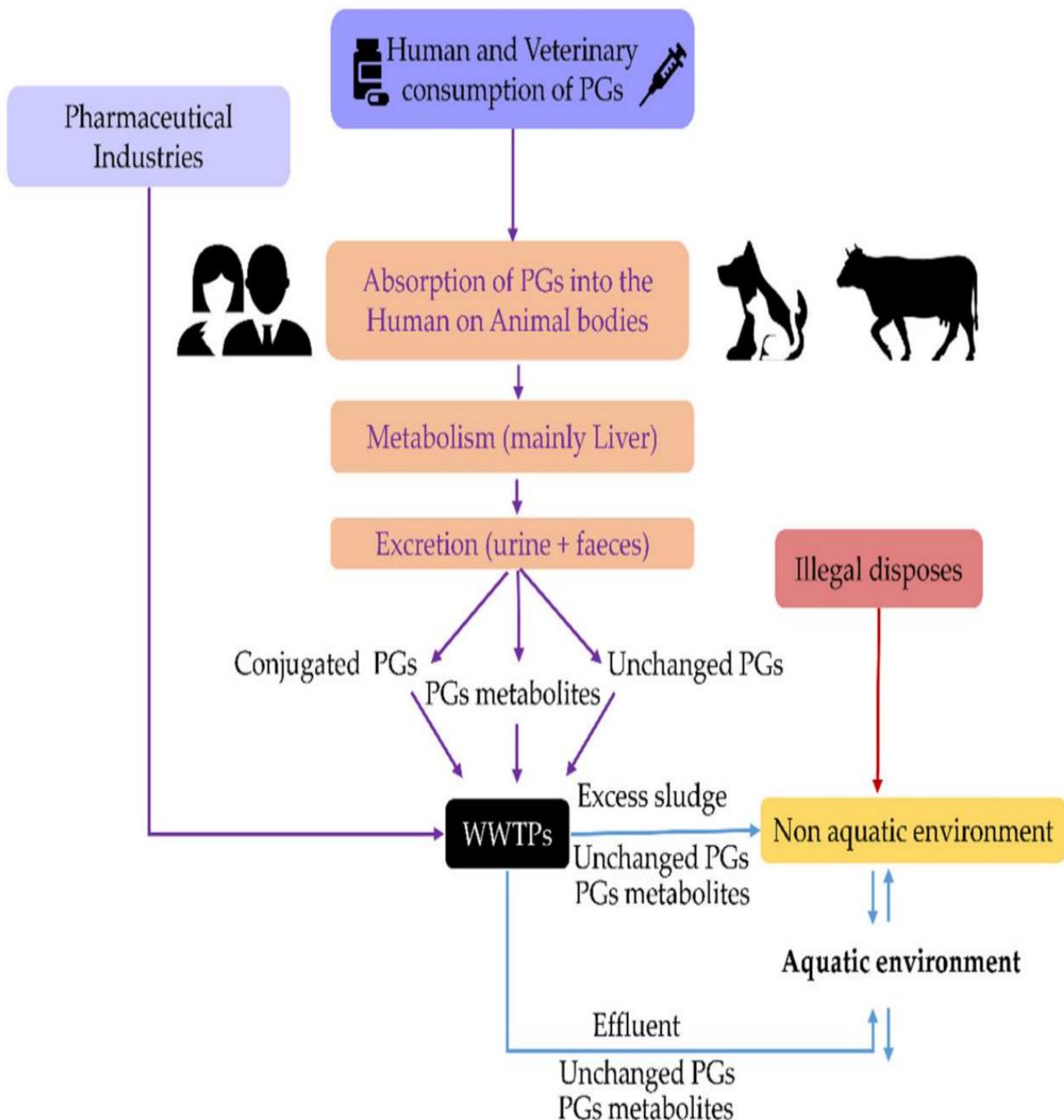
**Figure 2.2** Locations in which studies on the levels of the synthetic Progestogens (Adopted from Maria et al., 2022)

## **2.2 SOURCES OF PROGESTERONE OCCURRENCE IN THE ENVIRONMENT**

Naturally, excreted progesterone (P4) and its metabolites, as well as synthetic progestins that are widely used in human medicine and as growth promoters in livestock enter the aquatic environment through wastewater and agricultural run-offs. Consequently, P4 and synthetic progestins occur in surface and ground waters in the ng/L range. Of those, progestogen most widely detected in surface water, such as P4, levonorgestrel, norgestrel, and medroxyprogesterone acetate (MPA) at concentrations in the ng/L to up to over 100 ng/L.<sup>4-7</sup> In animal farm run-offs, concentrations were much higher. Besides aquatic wildlife, humans may also be exposed to natural and synthetic progestins via contaminated drinking water and seafood (in addition to the use of contraceptives). Figure 2.3 says the pathway that how progestins entered the environment.

Progesterone can be found in the environment from many different sources. The principal sources are Progesterone is excreted in human and animal feces and reaches the environment through septic systems and sewage treatment facilities. Industrial wastewater Progesterone is utilized in several industrial processes, and wastewater treatment facilities have the potential to discharge it into the environment. Progesterone can be found in cattle feed and can enter the environment because of agricultural runoff. Natural sources, the breakdown of plants and animals in the environment can naturally create progesterone.

Depending on the source and location, the amount of progesterone in the environment might change. For instance, progesterone levels are often greater in cities than they are in rural regions. Progesterone may affect the environment in a variety of ways, including Progesterone is an endocrine disruptor, which implies that it has the potential to interfere with wildlife's endocrine systems. Numerous issues, including issues with reproduction, growth, and behavior, may result from this. Progesterone may build up in the food chain, which means that animals at the top of the food chain may be exposed to larger quantities of the hormone than those at the bottom. For animals, this may have several detrimental effects. Progesterone's ability to taint drinking water and endanger human health is a concern. We still don't fully understand how progesterone affects the body.



**Figure 2.3** Sources and pathways for the occurrence of progestins in the environment.  
 (Adopted from Maria et.al.,(2022))

## 2.3 CONCENTRATION OF PROGESTERONE IN THE ENVIRONMENT

Progesterone concentrations in wastewater and surface water range between a few to tens ng/L (Fent, 2015). Considerably higher concentrations are reported in 1999–2000 by the US Geological Survey from 30 states in US rivers (Kolpin et al.,2002). In France (Besse and Garric, 2009) and Switzerland (Fent, 2015), progesterone and its synthetic analogs are consumed in larger amounts than other sex hormones: estrogens and androgens.

In China and the US, androgenic progestins are routinely applied as growth promoters in livestock and are discharged into the environment from wastewater. Consequently, high concentrations of progestins are found in livestock manure, soil, and runoff from farms. The largest contamination comes from sows and cows; up to 11,900 ng/L of progesterone were found in animal farm waste and 350 ng/L were detected in the associated runoffs (Liu et al.,2012).

The waste produced by farm animals is a major source of progestins in waters adjacent to farms and cattle feeding operations (Liu et al.,2012; Stavreva et al.,2021). In addition, other steroid hormones, including progestins, have been found in paper mill effluents which accumulate in river sediments (Chatterjee et al.,2007; Jenkins et al.,2003).

These may arise from processing pine pulp or microbial degradation of abundant phytosterols present in the waste from processing pine trees (Brockmeier et al.,2014). Only recently have analytical methods for the detection of progestins been fully developed and less than half of the 20 synthetic progestins have been documented in aquatic systems. Furthermore, methods to detect antagonists in the environment are lacking (Leusch et al.,2017; Viswanath et al.,2008) and need further development.

The progestins Norethindrone and Levonorgestrel in combination with other steroids were identified by liquid or gas chromatography-tandem mass spectrometry (LC-MS/MS and GC-MS/MS) in wastewater treatment plant effluents at concentrations up to 50 ng/L (Fernandez et al.,2007; Vulliet et al.,2007, 2008).

Medroxyprogesterone, well-known for its association with cancer of female organs, androgenic and spermatogenesis in the progeny (Liang et al.,1983; Shi et al.,2019) was detected in municipal wastewater plants effluents and surface water samples at the levels up to 15 ng/L and 1 ng/L, C (Kolodziej et al.,2003).

This is an unexpected outcome because progestins are presumed to be degraded in wastewater plants, mostly by biodegradation, with a removal efficiency of over 90% (Chang et al.,2011; Muz et al.,2014). Inefficient removal of progestins has been reported in Europe (Sauer et al.,2018) and high levels of norethindrone (up to 188 ng/L) were detected in effluent from a wastewater plant in Malaysia (Al-Odaini et al.,2010). Furthermore, due to the hydrophobic nature of progestins and other steroid hormones, they accumulate in aquatic organisms (Fick et al.,2010; Kroupova et al.,2014; Kumar et al.,2015).

For example, Levonorgestrel was measured by liquid and gas chromatography-mass spectrometry and found to accumulate in rainbow trout plasma at levels as high as 8.5–12 ng/mL (from the effluent wastewater with 1 ng/L) (Fick et al.,2010).

Deleterious effects of progestins specifically on male aquatic organisms and their reproduction are well documented (Kumar et al.,2015; Raghavan et al.,2018). Table 2.2 shows progesterone concentration in different water sources.

**Table 2.2:** Progesterone concentration in different waters.

Sl. No.	Location	Type of water, wastewater, and products	Concentration	Reference
1.	Helsinki, Finland	Wastewater	0.2 to 0.7 $\mu\text{g L}^{-1}$	Siren et al. 2017
2.	Czech Republic	Municipal wastewater	0.08 $\mu\text{g L}^{-1}$	Sauer et al. 2018
3.	China	Hospital wastewater (1) Livestock farm wastewater (2)	$\approx 1 \mu\text{g L}^{-1}$ (1) $\approx 3 \mu\text{g L}^{-1}$ (2)	Liang et al. 2022
4.	China	Swine wastewater	$\approx 1 \text{ mg L}^{-1}$	Liu et al. 2020
5.	USA	Wastewater effluent	0.4 $\mu\text{g L}^{-1}$	Yazdan et al. 2022

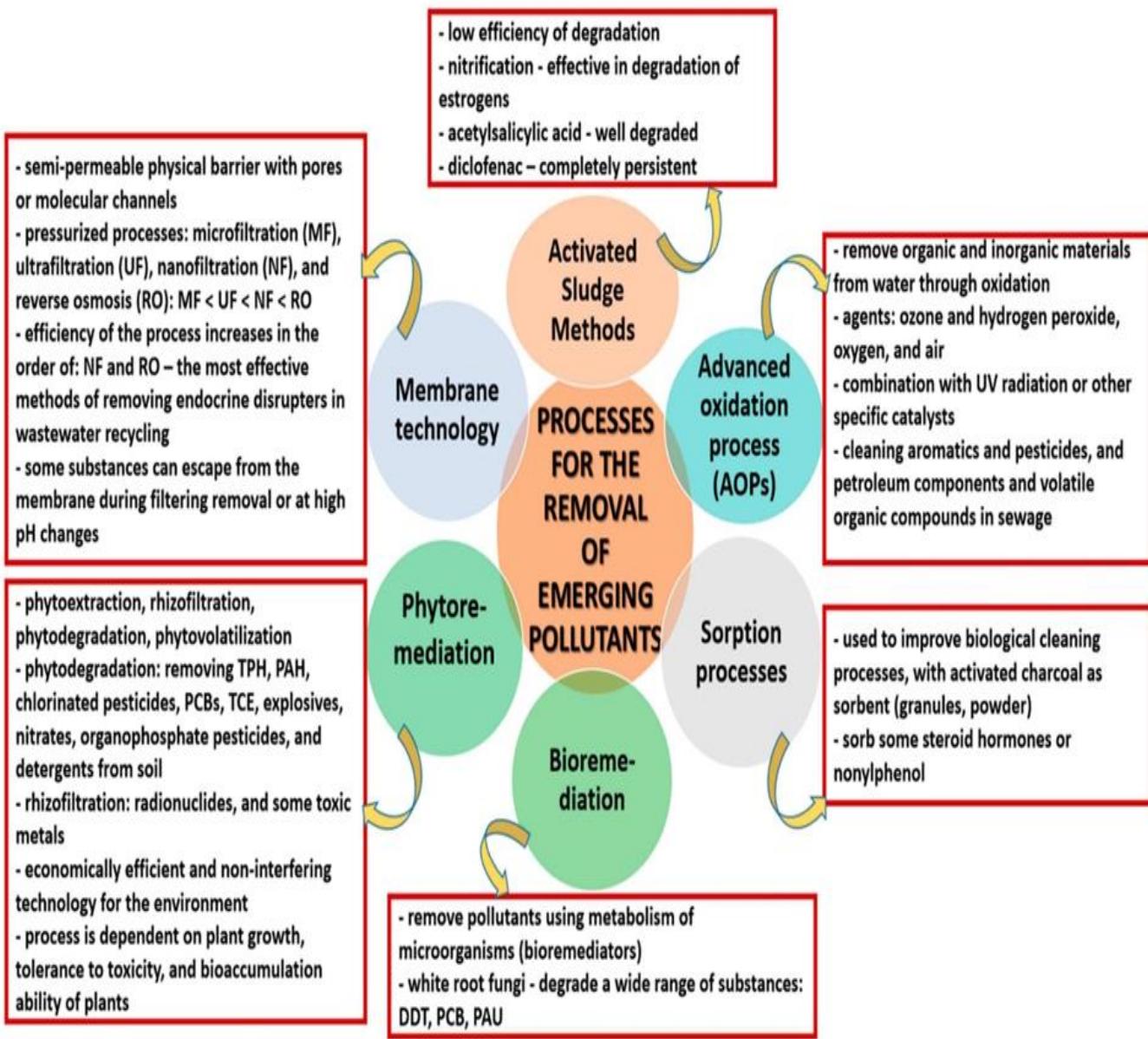
## **2.4 THE TREATMENT PROCESS FOR EMERGING POLLUTANTS REMOVAL**

Due to their various levels and concentrations, emerging pollutants in water have drawn the attention of experts all around the world. As a result, it's critical to safeguard our ecosystem against these chemicals and their consequences. Emerging pollutants in the water can be removed by employing hybrid, chemical, physical, biological, and other techniques.

Figure 2.4. shows different techniques used for the removal of merging contaminants. chemical process based on the many pollutants removal techniques that are expanding. Chemical treatment, also known as the use of chemicals in a series of reactions to using for the process of disinfecting wastewater, refers to the use of chemicals in a reaction to change toxins into a harmless form (Ahmed et.al.,2021).

Membrane filtration uses a semi-permeable membrane to remove contaminants from water. The pore size of the membrane can be selected to target specific contaminants. Membrane filtration is a very effective process for removing small molecules, such as pharmaceuticals and personal care products. Adsorption is a process in which contaminants are attracted to and removed from water by a solid surface.

Activated carbon is a common adsorbent for emerging contaminants. Adsorption can be effective for removing a wide range of contaminants, but it is not always as effective as other treatment processes. Biological treatment uses microorganisms to break down contaminants into harmless byproducts. Biological treatment is not as effective for removing emerging contaminants as other treatment processes, but it can be a cost-effective option for treating large volumes of water (Ahmed et al., 2021).



**Figure 2.4** Different removal techniques for emerging pollutants. (Adopted from Oliveira et al 2020)

#### **2.4.1 Advanced Oxidation Process**

AOPs are the family of technologies based on the production of hydroxyl radicles ( $\text{OH}^*$ ), which are stronger oxidants (oxidation potential of 2.8V) and capable of reacting rapidly with most organic compounds present in the water (HOU et al., 2017; LI et al., 2019). The generation of these reactive radicles is used by many processes including, homogeneous and heterogenous phases of the photocatalytic process ( $\text{H}_2\text{O}_2/\text{UV}$ ,  $\text{O}_3/\text{UV}$ ,  $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ , and  $\text{TiO}_3/\text{UV}$ ), homogeneous phase chemical oxidation processes ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2/\text{O}_3$ ), electrochemical oxidation processes, and Sono chemical oxidation processes (Zaviska et al., 2009).

Advanced oxidation processes (AOPs), such as Fenton reactions, photocatalytic oxidation, ozonation, and electrochemical oxidation, are highly effective in removing emerging pollutants that are challenging to treat with conventional physicochemical and biological techniques.

These AOPs offer high efficiency in degrading and eliminating recalcitrant contaminants, making them valuable solutions for tackling complex and persistent pollutants in various wastewater and environmental treatment applications. Different Advanced oxidation processes for the degradation of the emerging pollutants presenting in the wastewater are given in Table 2.3.

Hydroxyl radicals are produced in Fenton and Fenton-type reactions by the breakdown of hydrogen peroxide in the presence of a catalyst ( $\text{Fe}_3\text{O}_4$ , etc.).

According to Ma et al., (2021), the hydrogen peroxide utilized in the catalytic process typically derives from in situ production and external addition. However, the oxidation potential of  $(\text{H}_2\text{O}_2)$  rises when combined with an iron (II) ( $\text{Fe}^{2+}$ ) catalyst to generate the Fenton reagent. The wastewater is immediately mixed with  $(\text{H}_2\text{O}_2)$  and  $\text{Fe}^{2+}$  salts ( Elkacmi and Bennajah-2019) according to the following reaction:



**Table 2.3** Different Advanced oxidation processes for the degradation of emerging pollutants present in water (adapted from Yassine Jari et al., 2021)

Process	Target compound	Materials	Degradation (%)	Conditions	Additional information	References
Fenton/Fe nton-like processes	Bisphenol A	BaFe <sub>12</sub> O <sub>19</sub> -Ag <sub>3</sub> PO <sub>4</sub>	79.9	BPA] 20 mg/L; [catalyst] 1 g/L 300 W; Xe arc lamp ( $\lambda > 420$ nm); T 30°C; t=30 min	The reactive oxygen species are produced by the timely decomposition of H <sub>2</sub> O <sub>2</sub> generated on the surface of Ag <sub>3</sub> PO <sub>4</sub> via the BaFe <sub>12</sub> O <sub>19</sub>	Xu et al.,2019
	Atrazine				Surface Fenton system constructed with hydroxylamine (NH <sub>2</sub> OH), goethite ( $\alpha$ -Fe OH <sup>-</sup> ), and H <sub>2</sub> O <sub>2</sub> ( $\alpha$ -Fe OH <sup>-</sup> HA/H <sub>2</sub> O <sub>2</sub> ) to degrade atrazine.	Hou e al., 2017
	Amoxicillin				+e combination of TiO <sub>2</sub> and Fe <sub>3</sub> O <sub>4</sub> nanoparticles on graphene oxide (GO) nanoplatelets (TiO <sub>2</sub> -GO18wt% Fe <sub>3</sub> O <sub>4</sub> ) shows excellent AMX degradation under visible irradiation and 90% TOC removal.	Li et al.,2019
	Paracetamol				the catalytic tests were carried out in a four-vial collared reactor equipped with a temperature-controlled heating mantle; paracetamol was almost completely degraded within 20 min.	Q.C. Do, KIM and KO., 2017
		TiO <sub>2</sub> - GOFe <sub>3</sub> O <sub>4</sub>	90	[AMX] =10 mg/L. [catalyst]= 0.5 g L <sup>-1</sup> ; t=120 min; pH =3; T= 25°C		
		Fe <sub>3</sub> O <sub>4</sub> -SiO <sub>2</sub> -Cu	100	[PCM]= 2.0 mg L <sup>-1</sup> ; [catalyst] = 0.2 g L <sup>-1</sup> ; [H <sub>2</sub> O <sub>2</sub> ] = 15 mM; t = 20 min pH =5.0; T= 25°C		

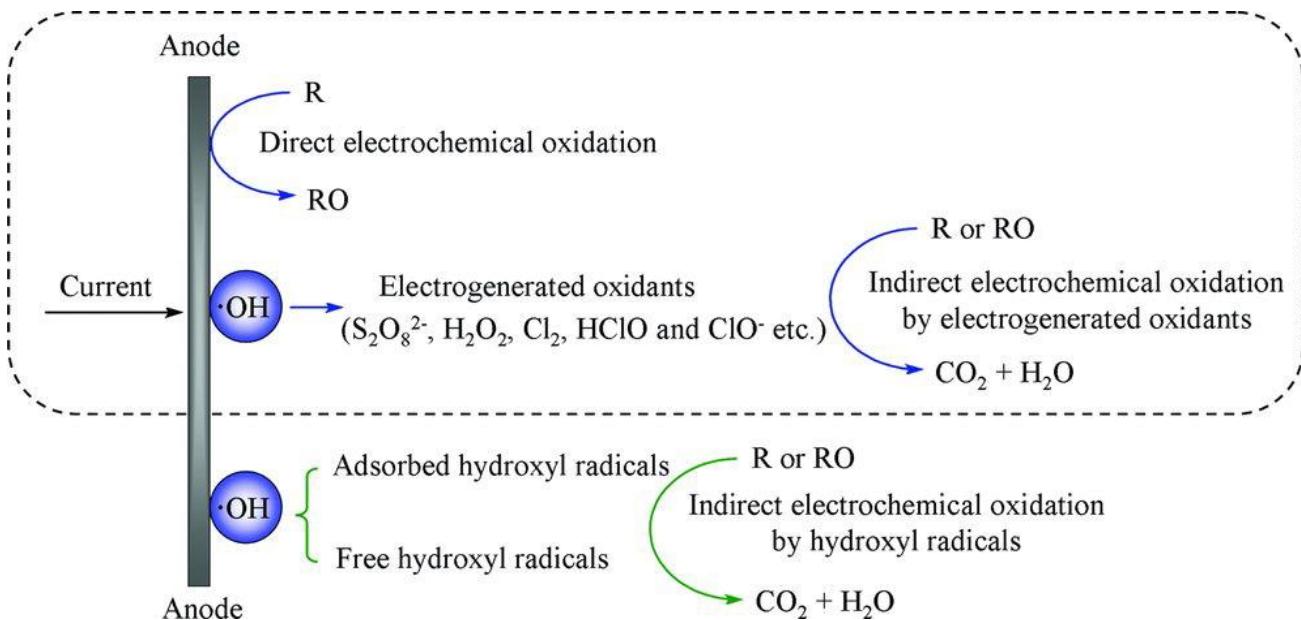
Photocatalysis	Bisphenol A	B-TiO <sub>2</sub> -graphene oxid	47.66	[Catalyst] = 1000 mg L <sup>-1</sup> ; [BPA] = 10 mg L <sup>-1</sup> ; t = 240 min; pH = 5; T = 25°C; K1 = 0.0023 min <sup>-1</sup>	Hydrothermal preparation of the photocatalyst, 300 W xenon lamp (1000 W/m <sup>2</sup> light intensity) with solar irradiation	Altin et., 2021
	Atrazine	Bi <sub>2</sub> MO <sub>6</sub> /PMS	99	[Bi <sub>2</sub> MoO <sub>6</sub> ] = 0.6 g/L; [PMS] = 0.8 mM; [ATZ] = 2.5 mg/L; t = 60 min; T = 25° C; visible light irradiation	Bismuth molybdate (Bi <sub>2</sub> MoO <sub>6</sub> ) prepared via the hydrothermal method and applied to activate peroxyomonosulfate (PMS)	Shen et al.,2020
	Amoxicillin	Ag/TiO <sub>2</sub> /mesoporous gC <sub>3</sub> N <sub>4</sub>	71	[Catalyst] = 1000 mg L <sup>-1</sup> ; [AMX] = 5 mg L <sup>-1</sup> ; t = 60 min	Hospital wastewater, 300 W xenon lamp ( $\lambda > 420$ nm) with visible light irradiation	Gao et al.,2019
	Paracetamol	Fe <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub>	95.85	Catalyst] = 1.25 g L <sup>-1</sup> ; [PCM] = 30 mg L <sup>-1</sup> ; pH = 11; solar irradiation	Fe <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub> is synthesized by the sol-gel method for the degradation of paracetamol in synthetic wastewater	Khasawneh et al.,2021
Ozonation	Bisphenol A	Ni-Fe LDHs/O <sub>3</sub>	100	[BPA] = 10 mg L <sup>-1</sup> ; [catalyst] = 0.3 g L <sup>-1</sup> ; [ozone] = 9.0 mg L <sup>-1</sup> ; [TOC] = 9 mg L <sup>-1</sup> ; [COD] = 32 mg L <sup>-1</sup> ; t = 120 min	Ni-Fe LDH showed effective catalytic performance in the catalytic ozonation of BPA in secondary effluent wastewater. BPA could be completely removed, and the final removal of TOC and COD was 56% and 68%.	Huang et al.,2019
	Atrazine	O <sub>3</sub> (microbubble )	95..3	ATZ] = 1.16 umol L <sup>-1</sup> ; [ozone] = 1 mg L <sup>-1</sup> ; gas flow: 0.5 L min <sup>-1</sup> ; t = 120 min; T = 20°C	Microbubble ozonation enhanced	Liu et al.,2020

	Amoxicillin	$O_3$	70	$[AMX] = 20 \text{ uM}$ ; $[\text{ozone}] = 75 \text{ mg L}^{-1}$ ; gas flow: $1 \text{ L min}^{-1}$ ; $T = 23^\circ\text{C}$ ; $\text{PH} = 6.8$	the degradation of atrazine at different pH levels in a semi-batch experiment. The degradation of amoxicillin by ozonation resulted in 70% removal with an ozone dose of $75 \text{ mg L}^{-1}$	Alsager et al.,2018
	Paracetamol	$MgO/O_3$	100	Ozone dose: $1.8 \text{ mg/min}$ ; $[\text{MgO}] = 0.1 \text{ g L}^{-1}$ ; $[\text{PCM}] = 50 \text{ mg L}^{-1}$ ; $t = 15 \text{ min}$ ; $\text{PH} = 5.4$	$MgO$ powder was used as a catalyst for the ozonation of paracetamol; total degradation and 94% mineralization were achieved at reaction times of 15 min	Mashayekh-Salehi et al.,2017
Electrochemical	Bisphenol A	Nb/BDD	90	$[\text{BPA}] = 5.0 \text{ mM}$ ; flow rate = $384 \text{ mL/min}^{-1}$ ; $j = 42.7 \text{ mA cm}^{-2}$ ; $t = 4 \text{ h}$ ; $\text{pH} = [7–10]$ ; $T = [6–20^\circ\text{C}]$	The application of electrochemical oxidation has shown high removal efficiency of BPA.	Ambauen et al.,2020
	Atrazine	Nb/BDD	99	$1.5 \text{ L of } 100 \text{ ug L}^{-1}$ atrazine $0.03 \text{ M Na}_2\text{SO}_4$ ; $j = 2 \text{ mA cm}^{-2}$ ; $\text{pH} = 3$ ; $T = 23^\circ\text{C}$ ; $t = 45 \text{ min}$ ; batch mode with undivided cylindrical cell	More than 99% of ATZ was removed by anodic oxidation; the atrazinedesethyl-desisopropyl (DEDIA) was the most important by-product recorded.	Komtchou et ai., 2017
	Amoxicillin	Ti/Cu-PbO <sub>2</sub>	99.4	$250 \text{ mL of } 100 \text{ mg L}^{-1}$ amoxicillin; $0.1 \text{ M Na}_2\text{SO}_4$ ; $j = 30 \text{ mA cm}^{-2}$ ; $\text{pH } 3.5$ ; room	Copper-doped PbO <sub>2</sub> electrode was prepared and used as an anode to degrade amoxicillin in a laboratory-scale experiment. The	Bain et al.,2019

	Paracetamol	Pt/Ag-AgCl	90	temperature; $t = 150$ min;  pseudo-firstorder reaction 250 mL of 20 mg L <sup>-1</sup> paracetamol; 0.1 M Na <sub>2</sub> SO <sub>4</sub> ; $j = 5.1$ mA cm <sup>-2</sup> ; pH = 4; $t = 240$ min	optimum removal of AMX and COD was 99.4% and 46.3% after 150 minutes of electrolysis.  The maximum removal of PCM, COD, and TOC reached 90%, 82%, and 65% after 240 min, with the formation of by-products (hydroquinone, benzoquinone, and carboxylic acid) during the electrolysis process	Periyasamy and Muthuchamy , 2018
--	-------------	------------	----	-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------	----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------	----------------------------------

Effluent in Morocco, including landfill leachates, emerging pollutants in aqueous solutions, and textile wastewater, was treated using a Fenton-based method (Ouhammou et al., 2019; El Mrabet et al., 2020; Marbet et al., 2018). The electro-Fenton technique was used to remove moxifloxacin in an acidic solution with a pH of 3.0. Moxifloxacin was mineralized by several OH attacks, and many intermediates were produced during the therapeutic process (Yahya et al., 2017). Rachidi looked at a similar process for the removal of the antidepressant sertraline hydrochloride (Rachidi et al., 2021). The optimal concentration of Fe<sup>2+</sup> was 0.1 mM, and the maximum degradation occurred at 400 mA.

According to H.K. Paumo et al. (2021), photocatalysis is a method for eliminating organic pollutants from wastewater that uses photocatalysts that can be activated by light irradiation. The interaction between organic pollutants and powerful oxidizing and reducing agents ( $h^+$  and  $e^-$ ) created by a light source on the surface of photocatalysts is the foundation of the photocatalysis technique, according to Zhou (2019). The standard photocatalytic process that removes pollutants from aqueous phases is shown.



**Figure 2.5** Mechanism of the anode during the treatment. (Adopted from Zho et al., (2019))

Due to its various benefits in the breakdown of pollutants, titanium dioxide ( $\text{TiO}_2$ ) is the most used photocatalyst.  $\text{TiO}_2$  has a lower capacity to absorb solar energy. Therefore, to improve its capacity to absorb visible light, most research focuses on its modification by doping with metals (such as  $\text{Ag}^+$ ,  $\text{Fe}^{3+}$ , and  $\text{Co}^{3+}$ ) and nonmetals (including N, S, F, C, B, and P).

Other photocatalytic materials for wastewater treatment applications have also drawn the attention of researchers, including oxides and perovskites (such as  $\text{ZnO}$ ,  $\text{WO}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{BiVO}_4$ ,  $\text{Ag}_3\text{VO}_4$ , and  $\text{TiO}_3$ ), bismuth oxyhalides (such as  $\text{BiOCl}$ ,  $\text{BiOBr}$ , and  $\text{BiOI}$ ), sulfides (such as  $\text{CdS}$ ,  $\text{ZnS}$ , and  $\text{MoS}_2$ ), as well as various composite materials (Antonopoulou et al., 2021). For the treatment of harmful pollutants in wastewater, a variety of photocatalytic materials have been used (Saher et al., 2021; Shahab-ud-Din et al., 2018).

Tabasum explored the metal ferrites doped with graphene oxide's photocatalytic potentials for breaking down acetamiprid (GO- $\text{Fe}_3\text{O}_4$  and GO- $\text{CoFe}_2\text{O}_4$ ). 90 and 97 percent of the material was degraded during the first hour of UV light exposure, respectively. Additionally, it investigated how well metal ferrites based on graphene oxide remove pesticide pollutants (Tabasum et al., 2020). The composites were proved to be highly biodegradable after 60 minutes of UV breakdown (90 percent). 2019 (Qureshi et al., 2016). To make graphene oxide-adorned  $\text{ZnWO}_4$  (GO- $\text{ZnWO}_4$ ) nanocomposites, Qureshi used a hydrothermal approach. These nanocomposites were then used to break down a pharmaceutical compound (cetirizine hydrochloride) when exposed to UV light.

The contaminant in the water was broken down by the photocatalyst to up to 89 percent. To combat emerging contaminants like zinc oxide-hydroxyapatite (HAP), another semiconducting photocatalyst has been developed and is now being deployed (Bekkali et al., 2018) looked at the use of ZnO-HAp in the UV irradiation-based antibiotic removal from polluted water (Bekkali et al., 2018). The nanocomposites outperformed the photocatalytic particles alone in terms of photodegradation efficiency. Additionally, colored titania nanoparticles made of activated carbon that was subjected to visible light showed excellent performance in removing developing medicines like amoxicillin and paracetamol from wastewater (Benjedim et al., 2021).

Additionally, Bougdour et al., (2020) investigated the treatment and mineralization of actual wastewater from the Moroccan textile industry using the  $\text{S}_2\text{O}_2^{-8}/\text{Fe}^{2+}/\text{UV}$  method. According to the findings, 87 percent of pollutants are mineralized. (Bougdour et al., 2020)

Ozone is a strong oxidizer that is used in ozonation procedures. After interacting with pollutants, ozone changes into oxygen (Gogi et al., 2018). This strategy has shown some effectiveness in tackling emerging pollutants; real secondary wastewater effluents showed 100% removal of bisphenol A (Huang et al., 2019).

Like this, paracetamol underwent full breakdown and 94 percent mineralization during reaction times of 15 minutes (Mashayekh-Salehi et al., 2017). Similar to this, microbubble ozonation boosted atrazine breakdown (by 90%) in a semi-batch experiment at various pH levels (Liu et al., 2020).

Electron transport is crucial for electrochemical oxidation. To accelerate the generation of hydroxyl radicals and enable the complete oxidation of several organic compounds in wastewater, insoluble electrodes (Nb/BDD, Ti/Cu-PbO<sub>2</sub>, and Pt/Ag-AgCl) are often used (Ambauen et al., 2020; Komtchou et al., 2017; Periyasamy and Muthuchamy 2018).

AOPs can be employed as a final treatment to mineralize the organic compounds or as a pretreatment to transform refractory chemicals into biodegradable products to treat aqueous solutions that contain organic materials (Zaviska et al., 2009). So, the following Table 2.4 lists various advanced oxidation processes for removing progesterone and its water-soluble form.

**Table 2.4** Removal of Progesterone and its water-soluble form is achieved by various advanced oxidation processes.

Sl. No.	Target compound concentration	Specific technique	Optimal conditions	PRO removal (%)	COD and orTOC removal (%)	Reference
1.	2 mg L <sup>-1</sup>	UV Photo assisted Fenton-like degradation	30 mg/L Ferrid, pH 3, 60 min, UV-A	95%	-	Ifelebueger et al. 2016
2.	100 mg L <sup>-1</sup> ( $\alpha$ - hydroxy progesterone)	Conductive diamond photoelectrochemical oxidation	30 mA.cm- 2, 0.035 M N <sub>2</sub> SO <sub>4</sub> , UV-C, Acidic pH	99%	99% TOC	Vidales et al. 2014
3.	1 mg L <sup>-1</sup>	Photocatalytic oxidation	8 g L <sup>-1</sup> TiO <sub>2</sub> (Degussa), 120 min, UV-A, pH- 5	95	-	AlAani et al. 2017
4.	0.35 mg L <sup>-1</sup>	Photocatalytic oxidation with Pt/WO <sub>3</sub>	UV-A, 180 min, 0.1 Na <sub>2</sub> SO <sub>4</sub> mol L <sup>-1</sup>	27% (UV Vis spectra)	-	Costa et al. 2018

# **CHAPTER 3**

## **SCOPE AND OBJECTIVES OF THE STUDY**

### **3.1 SCOPE OF THE STUDY**

Wastewater contains a wide range of pollutants, including contaminants of emerging concern (CECs) such as medicines, personal care products, surfactants, flame retardants, and other chemicals. CECs, which are present in trace concentrations, are discharged into the environment even after the water treatment process.

Therefore, this study aims to increase the efficacy of the water and wastewater treatment process by degrading a model CEC. Progesterone is a steroid hormone that was degraded using a low-cost manner that employs photo electrocatalytic oxidation using a catalyst with electrodes of carbon-coated titanium and titanium for finding out a process-efficient advanced oxidation water treatment technique.

### **3.2 OBJECTIVES OF THE STUDY**

- i. To study the effect of photo electrocatalytic oxidation on the degradation of progesterone
- ii. To analyze the effectiveness of a metal oxide catalyst (vanadium pentoxide) for the degradation of progesterone.
- iii. To analyze the structural capability of the catalyst for the combined process.
- iv. To optimize the degradation with various variables (Photo catalysis time, current density, pH, Electrocatalytic oxidation time).

## CHAPTER 4

### MATERIALS AND METHODS

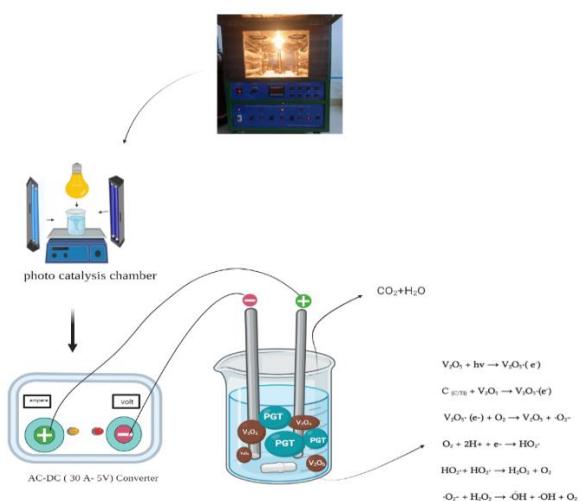
#### 4.1 SAMPLE PREPARATION

Progesterone ( $C_{21}H_{30}O_2$ ), [CAS No. 57-83-0] was obtained from HI Media Laboratories Pvt. Ltd. Vanadium Pentoxide  $V_2O_5$  [CAS No. 1314-62-1] (98% Extra pure powder) was obtained from Loba Chemie Pvt. Ltd. Progesterone samples and other solutions were made using deionized Milli-Q water [Millipore (Merck) Direct Q3]. For the preparation progesterone of 10 mg/L sample solution weighing about 0.025mg of the sample was taken in 250 mL of the Milli-Q water. The samples were weighted using the weighing balance (Shimadzu ATX/ATY Japan).

Sodium sulphate anhydrous 99% extra pure powdered compound obtained from Loba Chemi Pvt, ltd. 2.84g of  $Na_2SO_4$  was taken for preparing 20mM sodium sulphate solutions. The pH of the solution was adjusted by adding concentrated  $H_2SO_4$  (concentration of 1.87M) and NaOH solutions. (1.87M). Vanadium Penta oxide 98% extra pure powered compound obtained from Loba Chemi. Pvt. Ltd was used as the catalyst in the Photo catalysis process.

#### 4.2 PHOTO ELECTROCATALYTIC DEGRADATION

Figure 4.1 shows the experimental setup for the Photo electrocatalytic degradation studies.



**Figure 4.1** Experimental setup and mechanism of photo electrocatalytic oxidation of progesterone.

The sample was placed in a 250 mL quartz beaker with a magnetic attachment and kept in a photocatalysis chamber instrument with a UV-C source for processing. After processing in the Photocatalysis, the beaker was kept for electrocatalytic oxidation using titanium as the cathode and carbon-coated titanium (C/Ti) as the anode. The anode's surface area was 44 cm<sup>2</sup>. We need to use Milli-Q water to clean the electrodes before setting up the experiment. The degradation was conducted in a batch-mode reactor. AC-DC regulated power supply (Saba Electronics; DC Regulated Power Supply 0-30V/0-5A) was used to supply current. The distance between rods was kept at 1 cm. The degradation study was conducted at different sample concentrations, pH of the solution, current densities, and treatment time. The electrochemical degradation was conducted for an hour and samples were collected at every 60 min interval.

### **4.3 ESTIMATION of pH**

The pH scale determines how acidic or basic water or other liquid solutions are. It refers to the quantity of hydroxide (OH<sup>-</sup>) and free hydrogen (H<sup>+</sup>) ions in the water. Using a pH meter, the pH of the sample solution was determined. Accurate pH testing is crucial for determining the water's true state. And for the elevated pH in water as well as to reduce the pH utilizing conc, which was made by dissolving NaOH tablets in distilled water. To lower the pH, H<sub>2</sub>SO<sub>4</sub> (100 mM) was dissolved in water. HANNA instruments' pH and ORP Tester (HI98121) were used to test pH for the investigations.

### **4.4 CHARACTERIZATION STUDIES**

#### **4.4.1 FT-IR (Fourier-Transform Infrared Spectroscopy)**

FT-IR spectra of the catalyst were assessed in the mid-IR region using attenuated total reflection (ATR) mode by Jasco FT-IR spectrometer. The spectra were analyzed from wavenumber 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. After completing the treatment of photocatalytic degradation of progesterone, the remaining catalyst was sent to the FTIR along with the raw catalyst.

#### **4.4.2 X-Ray Diffraction (XRD)**

XRD analysis was employed utilizing Bruker D-8 Advance Twin-Twin diffractometer with Ni-filtered Cu-K $\alpha$  radiation ( $\lambda = 1.54$ ). The residual catalyst was submitted to the XRD together

with the raw catalyst without treatment after the photo electrocatalytic treatment for the degradation of progesterone was finished.

#### **4.5 SPECTROPHOTOMETRIC ANALYSIS**

A UV-Visible Spectrophotometer (Evolution 260 Bio, UV-Visible Spectrophotometer) was employed to measure the absorbance of the solution from the range 200-400 nm. The absorbance was carried out by using the quartz cuvette in the UV-Vis spectrophotometer. The dimensions of the cuvette containing the volume:3.5ml/3500μl, path-length10mm(45×12.5×12.5mm) the cuvettes are supplied by Lark Scientifico.

#### **4.6 ASSESSMENT OF CHEMICAL OXYGEN DEMAND**

According to Boyles (1997), chemical oxygen demand (COD) is "a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant" In other terms, the quantity of a certain oxidant that interacts with the sample under controlled circumstances is the chemical oxygen demand (COD). Oxygen equivalency is used to represent the amount of oxidant consumed. The Chemical Oxygen Demand (COD) test uses a strong chemical oxidant in an acid solution and heat to oxidize organic carbon to CO<sub>2</sub> and H<sub>2</sub>O. Oxygen demand is decided by measuring the amount of oxidant consumed using titrimetric or photometric methods. (Boyles., 1997)

The samples' COD was determined using the open reflux titrimetric technique developed by APHA in 2017.

$$COD \text{ of the sample (as mg/L)} = \frac{(A - B) \times N \times 8000}{mL \text{ of sample}}$$

where:

A= mL of FAS used for blank,

B= mL of FAS used for the sample,

N = Normality of FAS, and

8000 = milliequivalent weight of oxygen ×1000

## CHAPTER 5

### RESULTS AND DISCUSSION

#### 5.1 PHOTO ELECTROCATALYTIC DEGRADATION OF PROGESTERONE

Progesterone was administered at a concentration of 0.025 mg/250mL, while vanadium pentoxide, the catalyst, was administered at a concentration of 0.500 mg/250mL, and (sodium sulfate), the electrolyte at a concentration of 1.42 mg/250mL. Each of these was put into a 250 mL quartz beaker for photocatalysis (PC) and after PC samples were taken for electrocatalytic oxidation (EC). For Photocatalysis, we use a UV-C source with the magnetic stirrer at various treatment intervals (3, 6, 9, 12, 15, and 18).

Following PC treatment, the samples were examined at 248 nm in a UV-vis spectrophotometer. Using titanium (Ti) as the cathode and carbon-coated titanium (C/Ti) as the anode with various current densities (31.84 mA/cm<sup>2</sup>, 63.7 mA/cm<sup>2</sup>, 95.5 mA/cm<sup>2</sup>, 127.38 mA/cm<sup>2</sup>) and initial pH levels of 3, 5, 7 and 9, photo electrocatalytic oxidation was performed. The duration of the treatment was set at 180 minutes, and these samples were studied under the UV-Visible Spectrophotometer at the range of 200-400nm.

#### 5.2 CHARACTERIZATION STUDIES OF VANADIUM PENTOXIDE

##### 5.2.1 XRD Studies On V<sub>2</sub>O<sub>5</sub>

By examining the peak intensity, width, full-width half maximum (FWHM), and location, XRD investigations are often used to investigate the composition of solids and their structural integrity (Cullity and Freda., 1958). Figure 5.1 shows the XRD peaks of V<sub>2</sub>O<sub>5</sub> obtained before and after Photo electro-catalytic using a light source of (UV-C). Figure 5.1. Shows the XRD peaks of V<sub>2</sub>O<sub>5</sub> obtained before and after Photoelectrocatalytic oxidation of progesterone using light source (UV-C).

To establish the kind of catalyst and its structural stability, the current study additionally concentrated on XRD spectra. Showing diffraction peaks at 15.33<sup>0</sup>, 20.24<sup>0</sup>, 21.67<sup>0</sup>, 25.49<sup>0</sup>, 26.09<sup>0</sup>, and 30.96<sup>0</sup> belong to V<sub>2</sub>O<sub>5</sub> (Wang et al., 2017; Iordanova et al., 1996). The diameter was calculated by the Debye-Scherrer formula using Eq.1 (Cullity, B.D. and Freda, A., 1958.)

$$D = 0.94\lambda / (\beta_{\text{sample}} - \beta_{\text{ref}})1/2 \cos\theta \quad \dots \text{Eq.5.1}$$

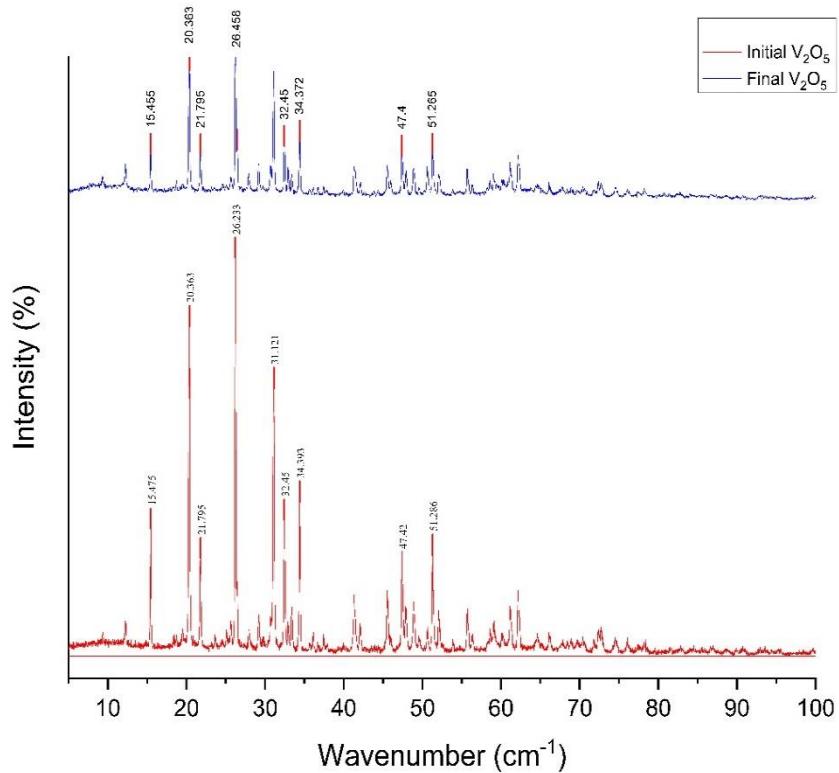
where,  $D$  is the crystallite size diameter (nm),  $\lambda = 1.54\text{\AA}$ ,  $\beta$  is the full width at half maximum (FWHM) of a diffraction peak and  $\beta_{\text{ref}}$  is the instrumental FWHM.

The average particle size of the  $\text{V}_2\text{O}_5$  catalyst was 46.91 nm. According to Figure 5.1, the catalyst structure is still intact after treatment since the XRD diagram of the catalyst still contains all of the peaks of virgin  $\text{V}_2\text{O}_5$  although with decreased intensity.

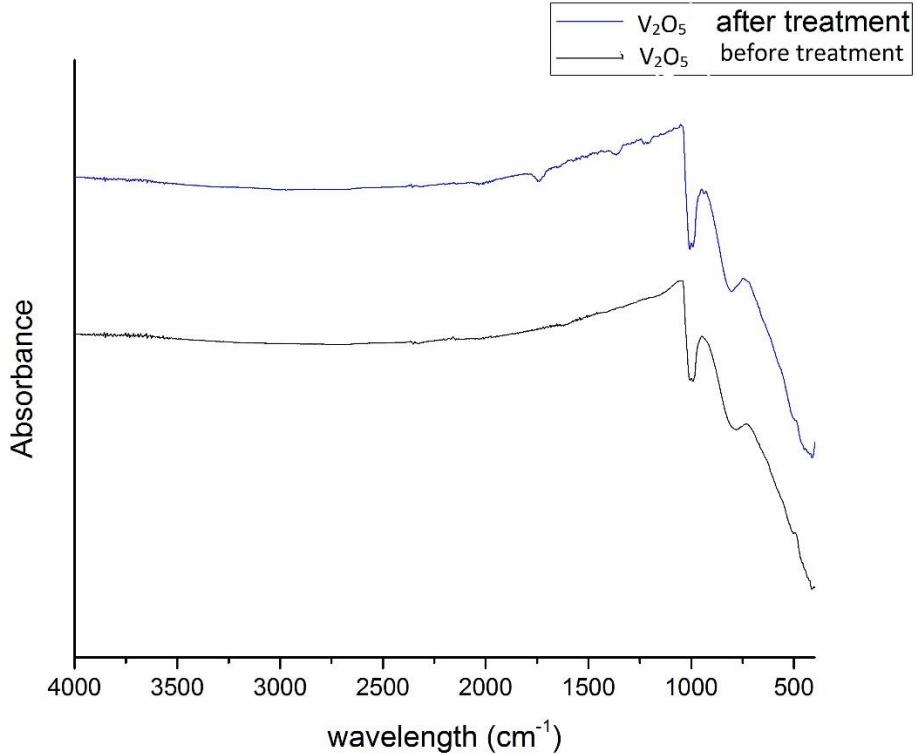
### 5.2.2 FTIR Studies on $\text{V}_2\text{O}_5$

Vanadium in  $\text{V}_2\text{O}_5$  has been examined using FTIR spectroscopy to determine its oxidation state. Understanding these facts is crucial for understanding the electrical characteristics of  $\text{V}_2\text{O}_5$ . The structural alterations that take place when it is subjected to various circumstances, such as temperature, pressure, and light, have been studied using FTIR spectroscopy. Understanding the stability and characteristics of  $\text{V}_2\text{O}_5$  under various circumstances requires knowledge of this information. The surface characteristics of  $\text{V}_2\text{O}_5$  have been investigated using FTIR spectroscopy. Understanding how  $\text{V}_2\text{O}_5$  interacts with different substances, such as metals and polymers, is crucial.

Fourier transform infrared spectroscopy (FTIR) has been used in the past to examine the chemical makeup and functional groups of several materials (Wang et al., 2017; Iordanova et al., 1996). To determine the alterations in the functional group of the catalyst before and after treatment, the current study used FTIR investigations. Figure 5.2 shows the FTIR spectra of  $\text{V}_2\text{O}_5$  taken before and after PC+EC (UV-C). The Small stretching bands belong to carboxylic acid groups ( $\text{C}=\text{O}$ :  $1700\text{-}1725\text{ cm}^{-1}$ ,  $\text{C}-\text{O}$ :  $1100\text{-}1300\text{cm}^{-1}$ ) which implies the creation of degradation byproducts (Uddin, J. ed., 2012)



**Figure 5.1** The XRD peaks of  $V_2O_5$  obtained before and after Photo electrocatalytic oxidation of progesterone in (UV-C).



**Figure 5.2** The FTIR spectra of  $V_2O_5$  taken before and after Photo electrocatalytic oxidation of progesterone in (UV-C).

## **5.3 UV -VISIBLE SPECTRAL ANALYSIS**

### **5.3.1 Effect of Initial pH**

The photocatalytic oxidation of progesterone in four sample solutions at pH 3,5,7 and 9 with 20mM Na<sub>2</sub>SO<sub>4</sub> electrolyte concentration was performed for a Photocatalysis treatment time of 180 min followed by Electrocatalysis treatment time of 180 minutes at a constant current intensity of 95.5 mA/cm<sup>2</sup>. Progesterone was measured using a UV-visible spectrophotometer at four different pH levels and wavelengths ranging from 200 to 400nm. Figure 5.3 shows how the initial pH affects the breakdown of progesterone in the presence of 20 mM Na<sub>2</sub>SO<sub>4</sub> as the supporting electrolyte.

Progesterone was degraded more at pH 5, which is slightly acidic in nature. Even though pH 3, pH 7, and pH 9 show compound removal, pH 5 had the maximum compound removal of 81 percent. Progesterone has limited solubility and degrades quickly in an acidic environment (Gengec et al., 2012). During the electrocatalysis oxidation process, hydroxyl radicals were responsible for greater efficiency at pH, near neutral indicating that pH 5 was favorable for progesterone breakdown.

### **5.3.2 Effect of Current Density**

Current density, which is measured in terms of current per unit area and affects response rate, is one of the significant factors driving photo electrochemical deterioration (Gengec et al. 2012).

To find their effects on the photoelectrochemical degradation of PGT at a concentration of 10 mg/L, current densities ranging from 31.84 mA/cm<sup>2</sup> to 127.38 mA/cm<sup>2</sup> were applied to the photoelectrochemical cell. After a 180-minute PC and 180-minute EC treatment, the photo electrochemically damaged samples were collected and examined under a UV-Visible Spectrophotometer at a wavelength of 248 nm. Figure 5.4 shows the effect of current density photo electrocatalytic oxidation of progesterone.

The percentage change in absorbance peak says that 95.5 mA/cm<sup>2</sup> is the efficient current density for the elimination of progesterone at a concentration of 10 mg/L with an efficiency of 81%. Even though 127.3 mA/cm<sup>2</sup> had 82 percent compound removal, considering the heavy use of energy for the treatment process, it is preferable and more efficient to use 95.5 mA/cm<sup>2</sup>

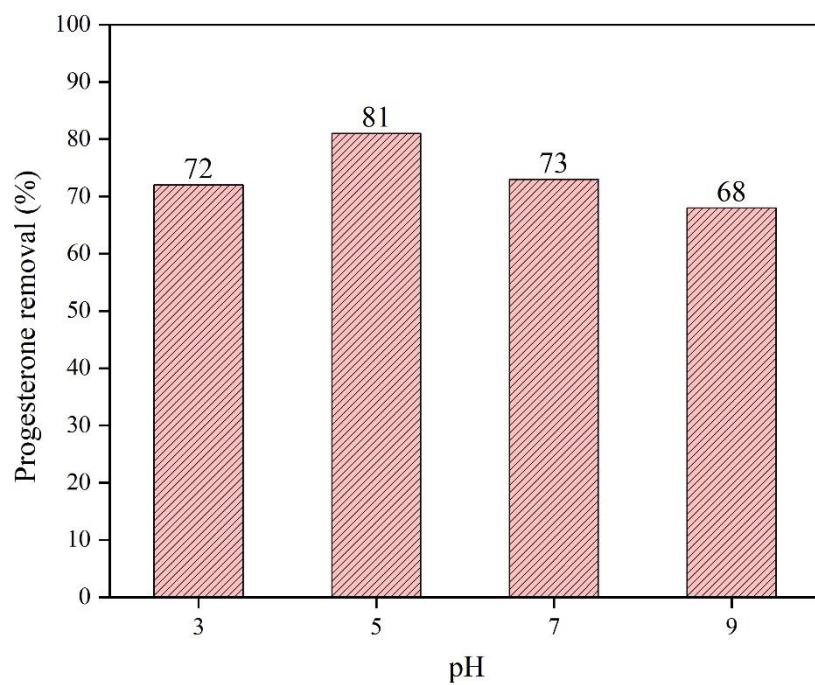
as the optimal current density. The current density is an important aspect of the degradation process. However, the amount of energy used, and the energy efficiency should be considered.

### 5.3.3 Effect of Treatment Time

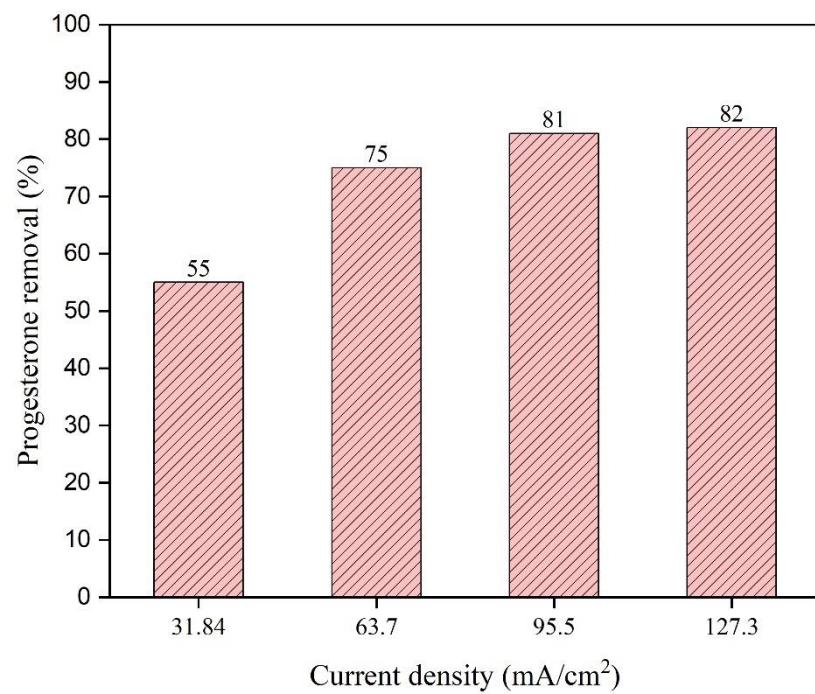
It has been shown that operational elements such as treatment duration and the current employed during electrochemical deterioration have a considerable impact on treatment efficiency (Periyasamy and Muthuchamy.,2018). The impact of treatment duration on the photoelectrochemical oxidation of progesterone is investigated under constant conditions of pH 5, 95.5 mA/cm<sup>2</sup>, and 20 mM Na<sub>2</sub>SO<sub>4</sub> as the electrolyte.

The degraded sample was collected and studied under the UV-Visible spectrophotometer after an electrocatalytic treatment time of 60, 120, and 180 minutes, while the PC time remained constant at 180 minutes. Figure 5.5 depicts the outcomes of the treatment time.

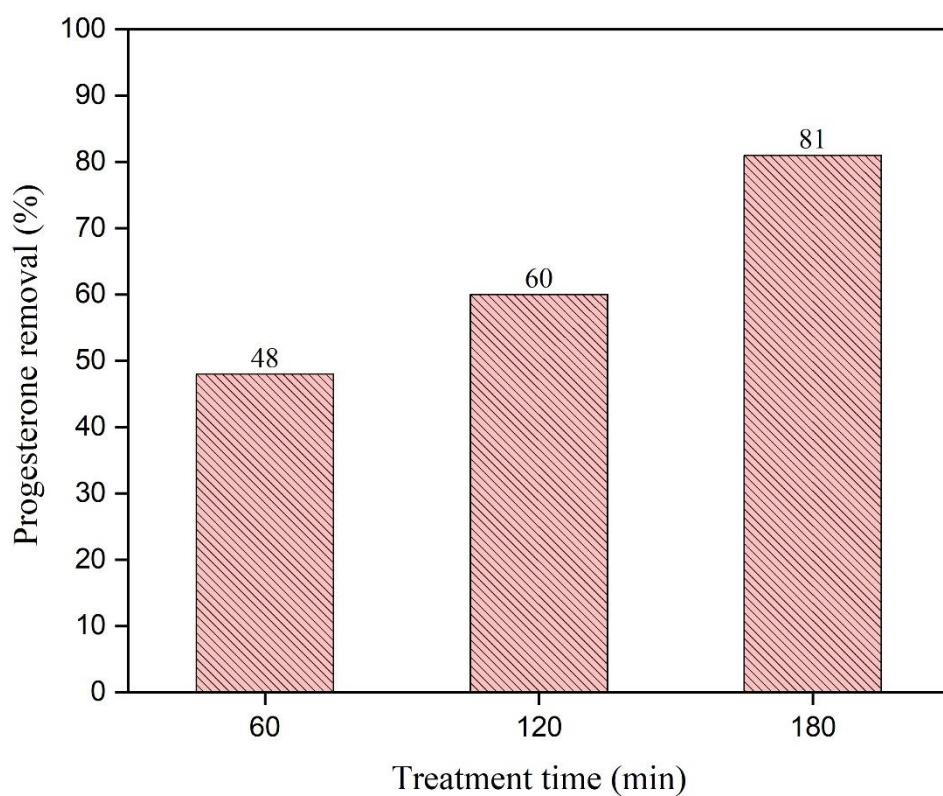
The UV-Vis spectrophotometer optimization shows that a continuous PC duration of 180 minutes paired with an EC treatment period of 180 minutes, pH 5, 20 mM Na<sub>2</sub>SO<sub>4</sub> electrolyte concentration, and 95.5 mA/cm<sup>2</sup> current density can achieve 81 percent of progesterone elimination. After 60 minutes, progesterone removal was 48 percent, and after 120 minutes, it was 60 percent. The best condition was determined to be 180 minutes with a compound elimination efficiency of 81 percent since energy consumption increases with time.



**Figure 5.3** Effect of pH on photo electrocatalytic oxidation of progesterone



**Figure 5.4** Effect of current density on photo electrocatalytic oxidation of progesterone.



**Figure 5.5** Effect of treatment time on photo electrocatalytic oxidation of progesterone.

## **5.4 ANALYSIS OF COD DURING THE PHOTO ELECTROCATALYTIC OXIDATION OF PROGESTERONE**

The qualitative evaluation of UV-Visible spectroscopic data offers a glimpse of information in understanding whether photo-electrochemical oxidation or photo-electrocatalytic oxidation of progesterone is occurring or not. Quantitative investigations that offer a promising direction for the scientific study being considered must be used to validate the data gained from experiments (Ge et al.,2016).

Chemical Oxygen Demand (COD) serves as a crucial criterion for assessing the quantity of organic pollutants present in wastewater. It stands as the most vital metric in managing effluent quality, monitoring water quality, and mitigating water pollution levels (Ge et al. 2016).

### **5.4.1 Effect of Treatment Time**

The concentration of progesterone with 10mg/L was conducted and with a treatment PC with variable PC 180 minutes, EC treatment time of 60 minutes. The COD removal rate was 48% at 60 minutes and maximum efficiency was seen at 180 minutes at 95%. It validates the hypothesis that when the PC treatment time of progesterone increases its photo electrocatalytic degradation increases from 60 minutes to 180 minutes. Figure 5.6 shows the effect of treatment time of photo electrocatalytic oxidation of progesterone on COD removal efficiency (%).

It has been shown that operational factors like treatment time and electrochemical degradation current have a significant impact on treatment effectiveness (Periyasamy and Muthuchamy.,2018). Under constant circumstances of pH 5, 95.5 mA/cm<sup>2</sup>, and 20 mM Na<sub>2</sub>SO<sub>4</sub> as the electrolyte, the effect of treatment time on the photoelectrochemical oxidation of progesterone is examined. According to the study o of COD removal efficiency of progesterone optimization, 95 percent of progesterone may be eliminated with a continuous Photo catalysis period of 180 minutes combined with an Electrocatalytic treatment time of 180 minutes, pH 5, 20 mM Na<sub>2</sub>SO<sub>4</sub> electrolyte concentration, and 95.5 mA/cm<sup>2</sup> current density. Progesterone elimination was 60 percent after 60 minutes and 80 percent after 120 minutes. Since energy consumption rises with time, 180 minutes with an elimination efficiency of 95 percent was found to be the ideal condition.

### **5.4.2 Effect of Current Density**

Current density is a relevant factor in EO as radical production depends on it (chen et al.,2002). At optimal conditions,  $95.5\text{mA/cm}^2$  current density was found to be optimal for progesterone. An increase in current from  $95.5$  to  $127.3\text{ mA/cm}^2$  resulted in a negligible increase in COD removal with higher energy consumption. Figure 5.7 shows the effect of the current density of photocatalytic oxidation of progesterone COD removal efficiency.

The current densities applied to the electrolytic cell varied widely. (Chen et al., 2002) According to the percentage change in the COD removal of progesterone, the effective current density of  $95.5\text{ mA/cm}^2$  for the 81 percent efficient elimination of progesterone at a concentration of  $10\text{ mg/L}$  is  $95.5\text{ mA/cm}^2$ . Even though  $127.3\text{ mA/cm}^2$  had a 95 percent compound removal rate, it is preferable and more effective to use  $95.5\text{ mA/cm}^2$  as the ideal current density because it uses less energy. An essential part of the deterioration process is the current density. However, it is important to consider the quantity of energy utilized and the energy efficiency.

### **5.4.3 Effect of Initial pH**

The removal efficiency was seen at pH 5 with a maximum COD removal efficiency of 95%, as shown in Figure 5.8 and gradually decreases from there to a minimum at pH 80 %. This is because the acidic nature of pH handles producing more hydroxy radicals with the assistance of electrolyte  $\text{Na}_2\text{SO}_4$ . This combination of producing sulphate and peroxy disulfate radicals was avoided.

However, the compound's dissolution was not uniform in those cases. In the case of COD removal, only pH 7,5 was observed with 91% and 95% effectiveness, as indicated in the figure. This shows that pH 3,9 was not that much of a suitable environment for progesterone degradation. Figure 5.8. shows the effect of pH on photo electrocatalytic oxidation of progesterone COD removal efficiency (%).

At pH 5, which is slightly acidic in nature, progesterone was destroyed more quickly. Although compound removal was evident at pH 3, pH 7, and pH 9, pH 5 had the highest compound removal rate of 95 percent.

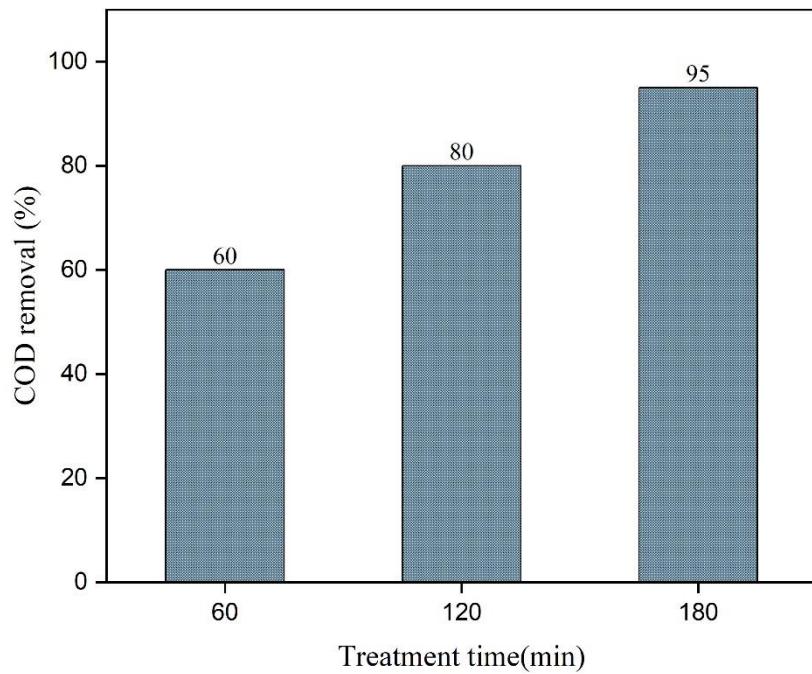
In a slightly acidic environment, progesterone has low solubility and degrades fast. Hydroxyl radicals were shown to be more effective during the electrocatalytic oxidation process at pH values close to neutral, indicating that pH 5 was advantageous for progesterone breakdown. So, the presence of V<sub>2</sub>O<sub>5</sub> resulted in the production of radicals promoting the optimal pH 5 for degradation to become near neutral or slightly acidic.

#### **5.4.4 EFFECT OF REUSABILITY OF THE CATALYST ON COD REMOVAL STUDIES**

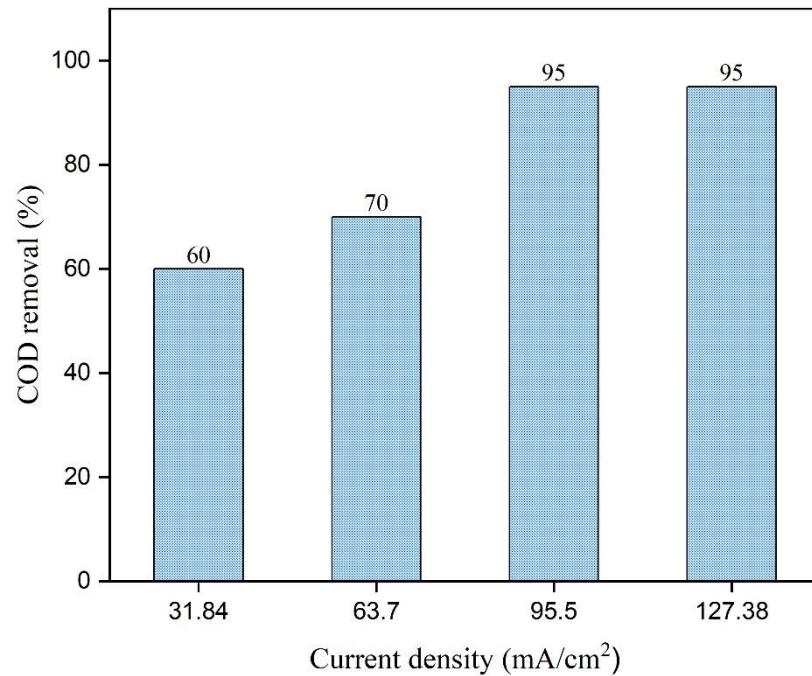
Since it considerably enhances the catalytic stability, the catalyst's ability to be employed again in the Photo electrocatalytic oxidation process is essential. Additionally, for applications to be practical and successful, a photocatalyst's stability during photocatalytic degradation is essential ( Oliverose et al., 2020).

To determine reusability, the present study used cod analysis. Figure 5.9 depicts the effectiveness of COD removal following five cycles of treatment with the same batch of V<sub>2</sub>O<sub>5</sub>.

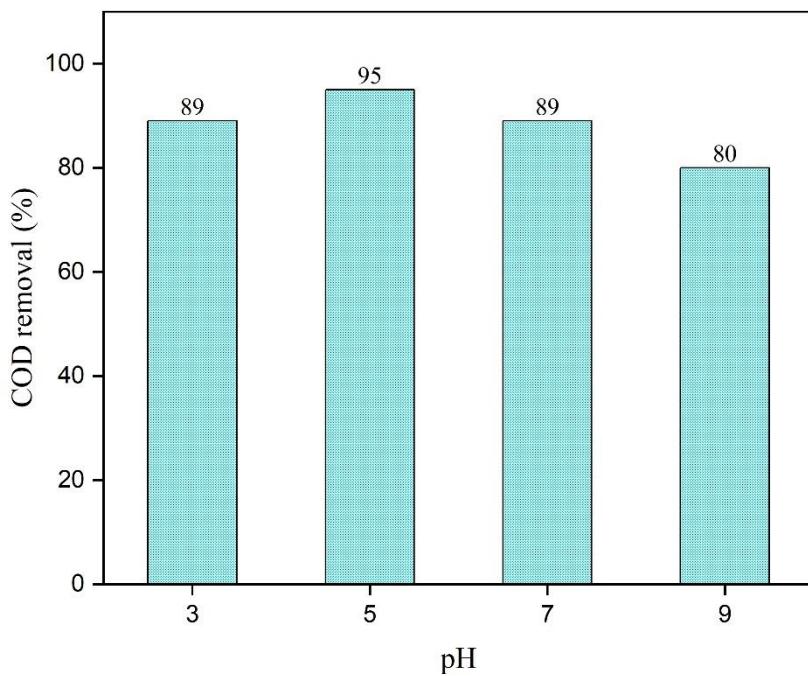
The first cycle achieved 89% followed by an efficiency of 78%. After 5 cycles the removal efficiency was 47%. Reusability studies show that V<sub>2</sub>O<sub>5</sub> can be used up to 1 or 2 times for adequate COD removal.



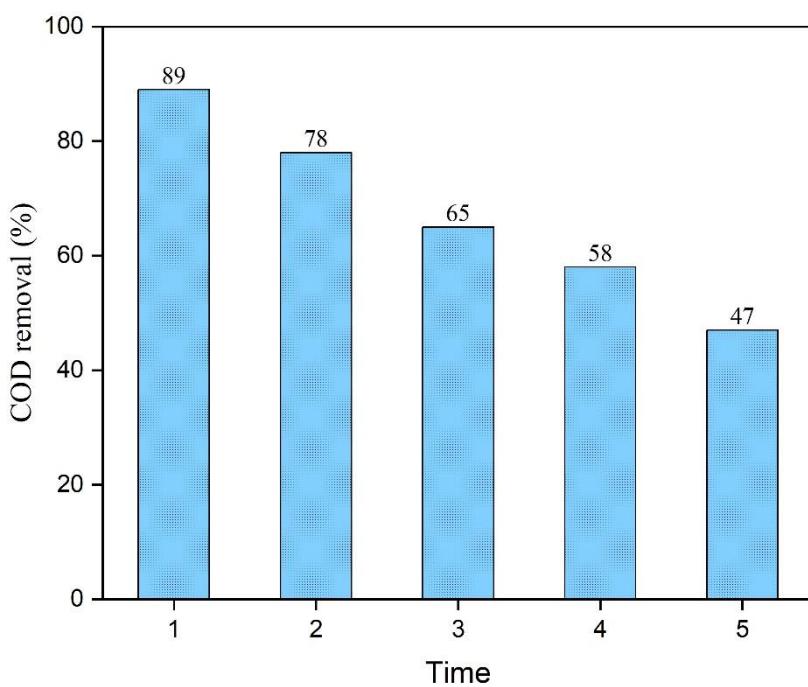
**Figure.5.6** Effect of treatment time on COD removal (%).



**Figure.5.7** Effect of the current density COD removal (%) .



**Figure 5.8** Effect of pH on COD removal (%).

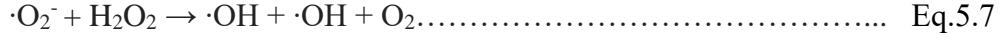


**Figure 5.9** COD removal efficiency of photo electrocatalytic oxidation after 5 cycles of treatment using  $\text{V}_2\text{O}_5$ .

## **5.4.5 REACTION MECHANISM OF PHOTO ELECTROCATALYTIC OXIDATION OF PROGESTERONE**

Mass transfer in electrochemistry refers to the movement of substances, such as electrons, radicals, etc., from one place to another. Electrons are produced by changes in the electric potential, chemical potential, or volume movement in a specific place. Convection, migration, and diffusion are the three basic mechanisms responsible for mass transfer. Diffusion is the spontaneous movement of any material from one place to another. Migration describes the movement of charged particles in an electric field. Convection is the term for the movement of material inside a volume element of a stirred (hydrodynamic) solution (Chen et al.,2002).

The significant improvement in the photoactivity of the V<sub>2</sub>O<sub>5</sub> sample compared to the pristine V<sub>2</sub>O<sub>5</sub> can be attributed to vacancies that are formed when oxygen atoms are removed from the lattice structure during the reaction process with NaBH<sub>4</sub>, initially leaving positively charged defects on the surface. The proposed mechanism for photocatalytic dye degradation using b V<sub>2</sub>O<sub>5</sub> is like that reported for its pristine counterpart. VO<sup>2+</sup> represents the positively charged surface oxygen vacancies at the time of induction (Badreldin et al., 2021). The mechanism of OH radical production is given from eq.5.2 to 5.7.



Eq. 5.2 says about photoactivation when  $V_2O_5$  reacts with light it gives  $V_2O_5$  radicle.

Eq.5.3 says about electron activation when Carbon reacts with  $V_2O_5$  gives the  $V_2O_5$  radicle.

Eq. 5.4 says  $V_2O_5$  radicles react with oxygen it gives  $V_2O_5$  and di oxygen radicles.

Eq. 5.5 says oxygen, react hydrogen ions again react with radicle give per hydroxy radicle.

Eq. 5.6 says two per hydroxy radicles combine to form hydrogen peroxide and oxygen.

Eq. 5.7 says di oxygen radicle reacts with hydrogen peroxide givies hydroxyl radicle and oxygen. ( deng et al., 2018)

# **CHAPTER 6**

## **CONCLUSION AND FUTURE RECOMMENDATIONS**

### **6.1 CONCLUSION**

Pharmaceutical compounds are synthetic organic compounds found among the most common classes of contaminants of emerging concern (CECs). These contaminants are major contributors to surface and groundwater contamination in the 21<sup>st</sup> century and pose a serious threat to society. Due to their possible biological activity, pharmaceuticals have caught the attention of the scientific community regarding their existence in the environment. Progesterone is a fat-soluble compound which is a hormone that is involved human mensuration cycle. Due to its high use, progesterone is also an emerging contaminant that requires strict monitoring and degradation methods to remove them from the environment.

In the current study, photo electrocatalytic oxidation of progesterone was carried out by analyzing the influence parameters such as the target compound concentration, initial pH, current density, and treatment time. Carbon-coated titanium with a surface area of 44 cm<sup>2</sup> was used as an anode and titanium was used as a cathode, and sodium sulfate (20 mM Na<sub>2</sub>SO<sub>4</sub>) was the supporting electrolyte. When photo electrocatalytic degradation was carried out under the optimal conditions of 10 mg/L progesterone solution with a pH of 5, a current density of 95.5mA/cm<sup>2</sup>, and a treatment time of Photo catalysis 180 minutes using UV-C light source after electrocatalytic oxidation treatment time of 180 minutes, the percentage reduction in the UV-Visible spectral absorbance of progesterone reached the highest value of 81% and COD removal of 95% at optimal conditions. The experimental studies showed that carbon-coated titanium and titanium are suitable electrode materials for the photo electrocatalytic oxidation of progesterone that can be reused multiple times.

Optimization studies found characterization studies using XRD & FTIR found that the catalyst is stable and reusable.

## **6.2 Future Works and Recommendations:**

- i. Photo electrocatalytic oxidation of progesterone in tap water and actual wastewater using carbon-coated titanium and titanium electrodes.
- ii. Comparison studies on photo electrocatalytic oxidation of progesterone using different electrode materials, (such as graphite rods and sheets, and various catalysts with different concentrations).
- iii. Comparison of different concentrations, by using various catalysts for photo electrocatalytic oxidation of progesterone.
- iv. Toxicological assessment of photo electrocatalytically degraded progesterone samples, with mass spectroscopy and liquid chromatography studies.

## REFERENCES

- A. Alsager, M. N. Alnajrani, H. A. Abuelizz, and I. A. Aldaghmani, “Removal of antibiotics from water and waste milk by ozonation: kinetics, byproducts, and antimicrobial activity,” Ecotoxicology and Environmental Safety, vol. 158, pp. 114–122, 2018.
- A. Caliman and M. Gavrilescu, “Pharmaceuticals, personal care products, and endocrine disrupting agents in the environment-a review,” CLEAN-Soil, Air, Water, vol. 37, no. 4- 5, pp. 277–303, 2009.
- A. Hassaan and A. El Nemr, “Pesticides pollution: classifications, human health impact, extraction and treatment techniques” Ie Egyptian Journal of Aquatic Research, vol. 46, no. 3, pp. 207–220, 2020.
- Ahmed, F. Saleem, A. Khan, et al., “Emerging pollutants and their removal using visible-light responsive photocatalysis—a comprehensive review,” Journal of Environmental Chemical Engineering, vol. 9, 2021.
- Al Aukidy, M.; Verlicchi, P.; Jelic, A.; Petrovic, M.; Barcelo, D. Monitoring release of pharmaceutical compounds: Occurrence and environmental risk assessment of two WWTP effluents and their receiving bodies in the Po Valley, Italy. *Sci. Total Environ.* 2012, 438, 15–25. [CrossRef]
- Altin, X. Ma, V. Boffa, E. Bacaksız, and G. Magnacca, “Hydrothermal preparation of B-TiO<sub>2</sub>-graphene oxide ternary nanocomposite, characterization and photocatalytic degradation of bisphenol A under simulated solar irradiation,” *Materials Science in Semiconductor Processing*, vol. 123, Article ID 105591, 2021.
- Ambauen, J. Muff, F. Tscheikner-Gratl, T. T. Trinh, C. Halle, and T. Meyn, “Application of electrochemical oxidation in cold climate regions-effect of temperature, pH and anode material on the degradation of bisphenol A and the formation of disinfection by-products,” *Journal of Environmental Chemical Engineering*, vol. 8, no. 5, Article ID 104183, 2020.
- Archer, E., et al., 2017. The fate of pharmaceuticals and personal care products (PPCPs), endocrine disrupting contaminants (EDCs), metabolites, and illicit drugs in a WWTW and environmental waters. *Chemosphere* 174, 437–446

Author links open overlay panel Anindita Gogoi<sup>a</sup> <sup>1</sup>, Payal Mazumder<sup>b</sup> <sup>1</sup>, Vinay Kumar Tyagi<sup>c</sup>, G.G. Tushara Chaminda<sup>d</sup>, Alicia Kyoungjin An<sup>e</sup>, Manish Kumar<sup>f</sup>

Barra Caracciolo, E. Topp, and P. Grenni, “Pharmaceuticals in the environment: biodegradation and effects on natural microbial communities. A review,” *Journal of Pharmaceutical and Biomedical Analysis*, vol. 106, pp. 25–36, 2015

Barron, E., Deborde, M., Rabouan, S., Mazellier, P., & Legube, B. (2006). Kinetic and mechanistic investigations of progesterone reaction with ozone. *Water Research*, 40(11), 2181–2189.

Bian, Y. Xia, T. Zhan et al., “Electrochemical removal of amoxicillin using a Cu doped PbO<sub>2</sub> electrode: electrode characterization, operational parameters optimization, and degradation mechanism,” *Chemosphere*, vol. 233, pp. 762– 770, 2019.

Butenandt, A., Westphal, U., 1974. Isolation of progesterone—forty years ago. *Am. J. Obstet. Gynecol.* 120, 137–141.

C. Do, D.-G. Kim, and S.-O. Ko, “Nonsacrificial template synthesis of magnetic-based yolk-shell nanostructures for the removal of acetaminophen in Fenton-like systems,” *ACS Applied Materials & Interfaces*, vol. 9, no. 34, pp. 28508–28518, 2017. position [Cullity, B.D. and Freda, A., 1958. A quantitative method for the determination of fiber texture. *Journal of Applied Physics*, 29(1), pp.25-3.

D. Darbre, “What are endocrine disrupters and where are they found?” *Endocrine Disruption and Human Health*, vol. 24, pp. 3–26, 2015.

Dsikowitzky, L.; Crawford, S.E.; Nordhaus, I.; Lindner, F.; Dwiyitno; Irianto, H.E.; Ariyani, F.; Schwarzbauer, J. Analysis and environmental risk assessment of priority and emerging organic pollutants in sediments from the tropical coastal megacity Jakarta, Indonesia. *Reg. Stud. Mar. Sci.* 2020, 34, 101021. [CrossRef]

Du, B.; Haddad, S.P.; Scott, W.C.; Chambliss, C.K.; Brooks, B.W. Pharmaceutical bioaccumulation by periphyton and snails in an effluent-dependent stream during an extreme drought. *Chemosphere* 2015, 119, 927–934. [CrossRef]

E. Bekkali, H. Bouyarmane, M. E. Karbane et al., “Zinc oxide-hydroxyapatite nanocomposite photocatalysts for the degradation of ciprofloxacin and ofloxacin antibiotics,” *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 539, pp. 364–370, 2018.

E. Mrabet, M. Kachabi, M. Nawdali et al., “Treatment of landfill leachate from Fez city (Morocco) using Fenton and photo-fenton processes,” IOP Conference Series: Earth and Environmental Science, vol. 161, Article ID 012025, 2018.

Egbuna, C. N. Amadi, K. C. Patrick-Iwuanyanwu et al., “Emerging pollutants in Nigeria: a systematic review,” Environmental Toxicology and Pharmacology, vol. 85, Article ID 103638, 2021

Mrabet, M. Benzina, H. Valdes, and H. Zaitan, ‘Treatment of landfill leachates from Fez city (Morocco) using a sequence of aerobic and Fenton processes,’ Scientific African, vol. 8, Article ID e00434, 2020.

Elkacmi and M. Bennajah, “Advanced oxidation technologies for the treatment and detoxification of olive mill wastewater: a general review,” Journal of Water Reuse and Desalination, vol. 9, no. 4, pp. 463–505, 2019.

F. Ahmed, M. Mofijur, S. Nuzhat et al., “Recent developments in physical, biological, chemical, and hybrid treatment techniques for removing emerging contaminants from wastewater,” Journal of Hazardous Materials, vol. 416, Article ID 125912, 2021.

F. Couto, L. C. Lange, and M. C. S. Amaral, “Occurrence, fate and removal of pharmaceutically active compounds (PhACs) in water and wastewater treatment plants—a review,” Journal of Water Process Engineering, vol. 32, Article ID 100927, 2019.

F. Zaviska, P. Drogui, G. Mercier, and J.-F. Blais, “Advanced oxidation processes for waters and wastewaters treatment: application to degradation of refractory pollutants. Proced’ es d’oxydation avancee dans le traitement des eaux et des ef- fluents industriels: application à la d’egradation des polluants refr,” Revue Des Sciences de l’Eau, vol. 22, 2009.

Gao, J. Wang, M. Dou, C. Xu, and X. Huang, “Enhanced photocatalytic removal of amoxicillin with Ag/TiO<sub>2</sub>/mesoporous g-C<sub>3</sub>N<sub>4</sub> under visible light: property and mechanistic studies,” Environmental Science and Pollution Research, vol. 27, 2019.

Ge, Y., Zhai, Y., Niu, D., Wang, Y., Fernandez, C., Ramakrishnappa, T., ... & Wang, L. (2016). Electrochemical determination of chemical oxygen demand using Ti/TiO<sub>2</sub> electrode. *International journal of electrochemical science*, 11(12).

Gao, S. Kang, R. Xiong, and M. Chen, “Environment-friendly removal methods for endocrine disrupting chemicals,” *Sustainability* (Switzerland), vol. 12, p. 7615, 2020

Geissen, V.; Mol, H.; Klumpp, E.; Umlauf, G.; Nadal, M.; van der Ploeg, M.; van de Zee, S.E.A.T.M.; Ritsema, C.J. Emerging pollutants in the environment: A challenge for water resource management. *Int. Soil Water Conserv. Res.* 2015, 3, 57–65. [CrossRef]

Gogoi, P. Mazumder, V. K. Tyagi, G. G. Tushara Chaminda, A. K. An, and M. Kumar, “Occurrence and the fate of emerging contaminants in the water environment: a review,” *Groundwater for Sustainable Development*, vol. 6, pp. 169– 180, 2018

Henderson, V.W., 2018. Progesterone and human cognition. *Climacteric* 21, 333–340.

Hou, X. Huang, F. Jia, Z. Ai, J. Zhao, and L. Zhang, “Hydroxylamine promoted goethite surface Fenton degradation of organic pollutants,” *Environmental Science & Technology*, vol. 51, no. 9, pp. 5118–5126, 2017. [105] Q.

Huang, T. Yang, M. Liang et al., “Ni-Fe layered double hydroxides catalized ozonation of synthetic wastewater containing bisphenol A and municipal secondary effluent,” *Chemosphere*, vol. 235, pp. 143–152, 2019.

Huang, Z., Lin, Q., Luo, H., Guo, P., Weng, Q., Lei, Y., Cheng, S., & Liu, S.-S. (2020). Degradation of progesterone by coexisting free radical and nonradical pathways in the CuO/hnts-PS system. *Chemical Engineering Journal*, 398, 125458. <https://doi.org/10.1016/j.cej.2020.125458>

Iordanova, R., Dimitriev, Y., Dimitrov, V., Kassabov, S. and Klissurski, D., 1996. Glass formation and structure in the V<sub>2</sub>O<sub>5</sub>– Bi<sub>2</sub>O<sub>3</sub>– Fe<sub>2</sub>O<sub>3</sub> glasses. *Journal of Non-Crystalline Solids*, 204(2), pp.141-150.

J. Rivera-Utrilla, M. Sa'nchez-Polo, M. A' . Ferro-Garc'ia, G. Prados-Joya, and R. Ocampo-P'erez, “Pharmaceuticals as emerging contaminants and their removal from water. A review,” *Chemosphere*, vol. 93, no. 7, pp. 1268–1287, 2013.

J.-Q. Jiang, Z. Zhou, and V. K. Sharma, “Occurrence, transportation, monitoring and treatment of emerging micro-pollutants in wastewater-a review from global views,” *Microchemical Journal*, vol. 110, pp. 292–300, 2013.

Joseita dos Santos Costa, M., dos Santos Costa, G., Estefany Brandão Lima, A., Eduardo da Luz Júnior, G., Longo, E., Santos Cavalcante, L., & da Silva Santos, R. (2018a). Photocurrent response and progesterone degradation by employing  $\text{WO}_3$  films changed with platinum and silver nanoparticles. *ChemPlusChem*, 83(12), 1153–1161. <https://doi.org/10.1002/cplu.201800534>

Joseita dos Santos Costa, M., dos Santos Costa, G., Estefany Brandão Lima, A., Eduardo da Luz Júnior, G., Longo, E., Santos Cavalcante, L., & da Silva Santos, R. (2018b). Photocurrent response and progesterone degradation by employing  $\text{WO}_3$  films modified with platinum and silver nanoparticles. *ChemPlusChem*, 83(12), 1153–1161. <https://doi.org/10.1002/cplu.201800534>

Jurado, E. Vazquez-Suñé, J. Carrera, M. López de Alda, E. Pujades, and D. Barceló, “Emerging organic contaminants in groundwater in Spain: a review of sources, recent occurrence and fate in a European context,” *Science of the Total Environment*, vol. 440, pp. 82–94, 2012.

K. Paumo, S. Dalhatou, L. M. Katata-Seru, et al., “TiO<sub>2</sub> assisted photocatalysts for degradation of emerging organic pollutants in water and wastewater,” *Journal of Molecular Liquids*, vol. 331, Article ID 115458, 2021.

K. Y. Foo and B. H. Hameed, “Detoxification of pesticide waste via activated carbon adsorption process,” *Journal of Hazardous Materials*, vol. 175, pp. 1–11, 2010.

Klamerth, N., Rizzo, L., Malato, S., Maldonado, M. I., Agüera, A., & Fernández-Alba, A. R. (2010). Degradation of fifteen emerging contaminants at  $\mu\text{g L}^{-1}$  initial concentration by mild solar photo-fenton in MWTP effluents. *Water Research*, 44(2), 545–554. <https://doi.org/10.1016/j.watres.2009.09.059>

L. Rachidi, G. Kaichouh, M. Khachani, et al., “Optimization and modeling of the electro-Fenton process for treatment of sertraline hydrochloride: mineralization efficiency, energy cost and biodegradability enhancement,” *Chemical Data Collections*, vol. 35, Article ID 100764, 2021.

L. Zhao, J. Deng, P. Sun et al., “Nanomaterials for treating emerging contaminants in water by adsorption and photocatalysis: a systematic review and bibliometric analysis,” *Science of the Total Environment*, vol. 627, pp. 1253–1263, 2018.

Lei, M.; Zhang, L.; Lei, J.; Zong, L.; Li, J.; Wu, Z.; Wang, Z. Overview of emerging contaminants and associated human health effects. *BioMed Res. Int.* 2015, 404796. [CrossRef]

Li, H. Kong, P. Li, J. Shao, and Y. He, “Photo-fenton degradation of amoxicillin via magnetic TiO<sub>2</sub>-graphene oxide-Fe<sub>3</sub>O<sub>4</sub> composite with a submerged magnetic separation membrane photocatalytic reactor (SMSMPR),” *Journal of Hazardous Materials*, vol. 373, pp. 437–446, 2019

M. Antonopoulou, C. Kosma, T. Albanis, and I. Konstantinou, “An overview of homogeneous and heterogeneous photocatalysis applications for the removal of pharmaceutical compounds from real or synthetic hospital wastewaters under lab or pilot scale,” *Science of the Total Environment*, vol. 765, Article ID 144163, 2021.

M. C. Necibi, D. Dhiba, and S. El Hajjaji, “Contaminants of emerging concern in African wastewater effluents: occurrence, impact and removal technologies,” *Sustainability*, vol. 13, no. 3, p. 1125, 2021

M. C. Necibi, D. Dhiba, and S. El Hajjaji, “Contaminants of emerging concern in African wastewater effluents: occurrence, impact and removal technologies,” *Sustainability*, vol. 13, no. 3, p. 1125, 2021

M. de Oliveira, B. E. F. Frihling, J. Velasques, F. J. C. M. Filho, P. S. Cavalieri, and L. Migliolo, “Pharmaceuticals residues and xenobiotics contaminants: occurrence, analytical techniques and sustainable alternatives for wastewater treatment,” *Science of the Total Environment*, vol. 705, Article ID 135568, 2020.

M. Madikizela, S. Ncube, and L. Chimuka, “Analysis, occurrence and removal of pharmaceuticals in African water resources: a current status,” *Journal of Environmental Management*, vol. 253, Article ID 109741, 2020.

M. Ouhammou, M. Bouchdoug, A. Jaouad, R. Ouaabou, B. Nabil, and M. Mahrouz, “Textile wastewater discoloration by Fenton oxidation process,” Moroccan Journal of Chemistry, vol. 7, pp. 516–527, 2019.

M. S. Yahya, N. Beqqal, A. Guessous, M. R. Arhoutane, and K. El Kacemi, “Degradation and mineralization of moxifloxacin antibiotic in aqueous medium by electro-Fenton process: kinetic assessment and oxidation products,” Cogent Chemistry, vol. 3, no. 1, Article ID 1290021, 2017.

Ma, H. Yi, C. Lai et al., “Critical review of advanced oxidation processes in organic wastewater treatment,” Chemosphere, vol. 275, Article ID 130104, 2021.

Marson, E. O., Paniagua, C. E. S., Gomes Júnior, O., Gonçalves, B. R., Silva, V. M., Ricardo, I. A., V. M. Starling, M. C., Amorim, C. C., & Trovó, A. G. (2022). A review toward contaminants of emerging concern in Brazil: Occurrence, impact and their degradation by advanced oxidation process in aquatic matrices. *Science of The Total Environment*, 836, 155605. <https://doi.org/10.1016/j.scitotenv.2022.155605>

Mashayekh-Salehi, G. Moussavi, and K. Yaghmaeian, “Preparation, characterization and catalytic activity of a novel mesoporous nanocrystalline MgO nanoparticle for ozonation of acetaminophen as an emerging water contaminant,” Chemical Engineering Journal, vol. 310, pp. 157–169, 2017.

Meng Lei, Lun Zhang, Jianjun Lei, Liang Zong, Jiahui Li, Zheng Wu, Zheng Wang, "Overview of Emerging Contaminants and Associated Human Health Effects", *BioMed Research International*, vol. 2015, Article ID 404796, 12 pages, 2015.

N. Bougdour, R. Tiskatine, I. Bakas, and A. Assabbane, “Photocatalytic degradation of industrial textile wastewater using S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/Fe<sup>2+</sup> process,” Materials Today: Proceedings, vol. 22, pp. 69–72, 2020.

O. C. Olatunde, A. T. Kuvarega, and D. C. Onwudiwe, “Photo enhanced degradation of contaminants of emerging concern in wastewater,” Emerging Contaminants, vol. 6, pp. 283–302, 2020.

O. F. S. Khasawneh, P. Palaniandy, P. Palaniandy, M. Ahmadipour, H. Mohammadi, and M. R. Bin Hamdan, “Removal of acetaminophen using Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> nanocomposites by photocatalysis under simulated solar irradiation: optimization study,” *Journal of Environmental Chemical Engineering*, vol. 9, no. 1, Article ID 104921, 2021.

Occurrence and fate of emerging contaminants in water environment: A review

Laurenson, R. A. Bloom, S. Page, and N. Sadrieh, “Ethinyl estradiol and other human pharmaceutical estrogens in the aquatic environment: a review of recent risk assessment data,” *Ie AAPS Journal*, vol. 16, no. 2, pp. 299–310, 2014.

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 Res.* 2015, 72, 3–27. [CrossRef]

Piette, P., 2018. The history of natural progesterone, the never-ending story. *Climacteric* 21, 308–314.

Q. Li, H. Kong, P. Li, J. Shao, and Y. He, “Photo-fenton degradation of amoxicillin vimagnetic TiO<sub>2</sub>-graphene oxide-Fe<sub>3</sub>O<sub>4</sub> composite with a submerged magnetic separation membrane photocatalytic reactor (SMSMPR),” *Journal of Hazardous Materials*, vol. 373, pp. 437–446, 2019.

Qureshi, M. Z. Ahmad, I. A. Bhatti, M. Zahid, J. Nisar, and M. Iqbal, “Graphene oxide decorated ZnWO<sub>4</sub> architecture synthesis, characterization and photocatalytic activity evaluation,” *Journal of Molecular Liquids*, vol. 285, pp. 778–789, 2019.

R. M. de Souza, D. Seibert, H. B. Quesada, F. de Jesus Bassetti, M. R. Fagundes-Klen, and R. Bergamasco, “Occurrence, impacts and general aspects of pesticides in surface water: a review,” *Process Safety and Environmental Protection*, vol. 135, pp. 22–37, 2020.

R. Saher, M. A. Hanif, A. Mansha, et al., “Sunlight-driven photocatalytic degradation of rhodamine B dye by Ag/FeWO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> composites,” *International Journal of Environmental Science and Technology*, vol. 18, no. 4, pp. 927–938, 2021.

Rocha, M., & Rocha, E. (2022). Synthetic progestins in waste and surface waters: Concentrations, impacts and ecological risk. *Toxics*, 10(4), 163.

S. Benjedim, J. Castelo-Quibén, E. Bailón-García et al., “Activated carbon-based colored titania nanoparticles with high visible radiation absorption and excellent photoactivity in the degradation of emerging drugs of wastewater,” *Carbon*, vol. 178, pp. 753–766, 2021.

. Komtchou, A. Dirany, P. Drogui, D. Robert, and P. Lafrance, “Removal of atrazine and its by-products from water using electrochemical advanced oxidation processes,” *Water Research*, vol. 125, pp. 91–103, 2017.

S. Periyasamy and M. Muthuchamy, “Electrochemical oxidation of paracetamol in water by graphite anode: effect of pH, electrolyte concentration and current density,” *Journal of Environmental Chemical Engineering*, vol. 6, no. 6, pp. 7358–7367, 2018.

Salthammer, “Emerging indoor pollutants,” *International Journal of Hygiene and Environmental Health*, vol. 224, Article ID 113423, 2020

Schumacher, M., Guennoun, R., Ghoumari, A., Massaad, C., Robert, F., El-Etr, M., Akwa, Y., Rajkowski, K., Baulieu, E.E., 2007. Novel perspectives for progesterone in hormone replacement therapy, with special reference to the nervous system. *Endocr. Rev.* 28, 387–439.

Shahab-ud-Din, M. Z. Ahmad, K. Qureshi, and I. A. Bhatti, M. Zahid, J. Nisar, M. Iqbal, and M. Abbas, Hydrothermal synthesis of molybdenum trioxide, characterization, and photocatalytic activity,” *Materials Research Bulletin*, vol. 100, pp. 120–130, 2018.

Shen, H. Zhou, Z. Pan et al., “Degradation of atrazine by Bi<sub>2</sub>MoO<sub>6</sub> activated peroxymonosulfate under visible light irradiation,” *Journal of Hazardous Materials*, vol. 400, Article ID 123187, 2020.

Snow, D.D.; Cassada, D.A.; Larsen, M.L.; Mware, N.A.; Li, X.; D’Alessio, M.; Zhang, Y.; Sallach, J.B. Detection, occurrence and fate of emerging contaminants in agricultural environments. *Water Environ. Res.* 2017, 89, 897–920. [CrossRef] [PubMed]

Stanczyk, F.Z., Hapgood, J.P., Winer, S., Mishell Jr., D.R., 2013. Progestogens used in postmenopausal hormone therapy: differences in their pharmacological properties, intracellular actions, and clinical effects. *Endocr. Rev.* 34, 171–208.

Stuart, M.; Lapworth, D.; Crane, E.; Hart, A. Review of risk from potential emerging contaminants in UK groundwater. *Sci. Total Environ.* 2012, 416, 1–21. [CrossRef]

Swyer, G.I., 1960. Progestogens and their clinical uses: Part II. *Br. Med. J.* 1, 121–122

T. Vieira, M. B. De Farias, M. P. Spaolonzi, M. G. C. Da Silva, and M. G. Adeodato Vieira, “Endocrine-disrupting compounds: occurrence, detection methods, effects and promising treatment pathways-a critical review,” *Journal of Environmental Chemical Engineering*, vol. 9, no. 1, Article ID 104558, 2021.

Tabasum, I. A. Bhatti, N. Nadeem, et al., “Degradation of acetamiprid using graphene-oxide-based metal (Mn and Ni) ferrites as fenton-like photocatalysts,” *Water Science and Technology*, vol. 81, no. 1, pp. 178–189, 2020.

Tabasum, M. Alghuthaymi, U. Y. Qazi et al., “Uvaccelerated photocatalytic degradation of pesticide over magnetite and cobalt ferrite decorated graphene oxide composite,” *Plants*, vol. 10, pp. 1–18, 2021.

Ting, Y. F., & Praveena, S. M. (2017). Sources, mechanisms, and fate of steroid estrogens in wastewater treatment plants: a mini-review. *Environmental monitoring and assessment*, 189(4), 178.

Ting, Y.F. and Praveena, S.M., 2017. Sources, mechanisms, and fate of steroid estrogens in wastewater treatment plants: a mini review. *Environmental monitoring and assessment*, 189(4), p.178

[ Uddin, J. ed., 2012. *Macro to nano spectroscopy*. BoD–Books on Demand]

[Wang, Q., Zhang, Y., Zheng, J., Hu, T. and Meng, C., 2017. Synthesis, structure, optical and magnetic properties of interlamellar decoration of magadiite using vanadium oxide species. *Microporous and Mesoporous Materials*, 244, pp.264-277.

X. Hou, X. Huang, F. Jia, Z. Ai, J. Zhao, and L. Zhang, “Hydroxylamine promoted goethite surface Fenton degradation of organic pollutants,” Environmental Science & Technology, vol. 51, no. 9, pp. 5118–5126, 2017.

Y. Liu, S. Wang, L. Shi, W. Lu, and P. Li, “Enhanced degradation of atrazine by microbubble ozonation,” Environmental Science: Water Research & Technology, vol. 6, no. 6, pp. 1681–1687, 2020.

Y. Xu, F. Ge, M. Xie et al., “Fabrication of magnetic BaFe<sub>12</sub>O<sub>19</sub>/Ag<sub>3</sub>PO<sub>4</sub> composites with an in situ photo-Fenton-like reaction for enhancing reactive oxygen species under visible light irradiation,” Catalysis Science & Technology, vol. 9, no. 10, pp. 2563–2570, 2019.

Zaviska, P. Drogui, G. Mercier, and J.-F. Blais, “Advanced oxidation processes for waters and wastewaters treatment: application to degradation of refractory pollutants. Proced’ es d’oxydation avancee dans le traitement des eaux et des ef- fluents industriels: application à la d’egradation des polluants refr,” Revue Des Sciences de l’Eau, vol. 22, 2009.

Zhu and Q. Zhou, “Action and mechanism of semiconductor photocatalysis on the degradation of organic pollutants in water treatment: a review,” Environmental 22 Journal of Chemistry Nanotechnology, Monitoring & Management, vol. 12, Article ID 100255, 2019.

Zwiener, C., Frimmel, F.H. LC-MS analysis in the aquatic environment and in water treatment technology – a critical review. *Anal Bioanal Chem* **378**, 862–874 (2004).