# ADVANCED ENVIRONMENTAL CHEMISTRY APPLICATIONS

<u>Editors</u> Dr. M. R. Jayapal Dr. P. Sudheer Paul

Kripa Drishti Publications, Pune.

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# **PREFACE**

With great vision and passion we initiated the book Advanced Environmental Chemistry applications. Environmental science is multidisciplinary area for great research and Environmental chemistry was an emerging field, aiming at a inclusive explanation of the Earth's environment, encircling the bio–geo, physical, chemical, and transformations of chemical substances occurring on a local as well as a global. Environmental chemistry became the promising area to combat the global warming b and climate change through green approaches.

Contributions are written by leading scientists, academicians and experts with practical experiments in their fields. The book Advanced Environmental Chemistry applications grows with the increase in our scientific understanding, leads into great interest and provides a sound full of knowledge, a great source not only researchers, academicians, students, but also for environmental managers and policy makers.

This book covers a wide range of environmental chemistry topics like Global warming, Climate Change, Water resources management, Bioremediation, Green Synthesis and green technologies.

Chapter 1 serves as an introduction to the green synthesis, as it is a simple, singlestep bio reduction method that requires relatively low energy to initiate the reaction. Different methods used for the synthesis of Nanoparticles discussed and a comparison of bio-mediated synthesised NPs with other chemically synthesised. Green synthesis of NPs found to be simple, single step and low energy initiator and Biologically synthesised NPs are non toxic, eco-friendly and environmentally acceptable.

Chapter 2 discusses about the Global warming, atmospheric implications, atmospheric lifetime, Global Warming Potential, Chlorofluorocarbon (CFC) Substitutes and their potential impact on Climate Change.

Chapter 3 covers the natural healing of Environmental pollutants in the Environment through Bio-remediation, and also discusses the role play of white Rot fungi Enzymes , Remediation of polluted water ,removal of pollutants ,filtration of Farm Runoff water, Toxic wildfire ash removal, remediating polluted soil ,diesel contaminated land with fungi.

Chapter 4 deals a novel green solvent –Based Gel Type Adsorbent materials for waste water treatment and describes Multifunctional self healing Eutecto gels induced by supra molecular assembly for smart conductive materials, interface lubrication and dye adsorption, Environmentally friendly eutectogels for waste water treatment were discussed.

Chapter 5 deals with water pollution: unravelling the genesis, consequences and resolutions, effects of water pollutions, water pollution control measures.

Chapter 6 deals with Water resources Management, recent trends in Resources Development and management, sustainable development and discusses Soil resources through its distribution, soil degradation and conservation, water resources, ground water quality, management of water resources, protection of water from pollution.

The book advanced Environmental Chemistry applications provides a solid basis from which scientists and academicians can share their knowledge on the different aspects of environmental problems, presenting a wide spectrum of viewpoints and approaches.

The book will also be useful to those appearing in various competitive examinations, entrance examinations and also to researchers, educationists.

The Editors thank contributors and kripa drishti (P) Ltd publishers and their team for bringing out this informative book.

Dr. M. R. Jayapal (Stephen Stanley Jayapal) and Dr. P. Sudheer Paul

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# 1. A Review on Bio-Mediated Nanoparticles and their Applications

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#### Abstract:

Studies showed that chemically produced nanoparticles are more expensive to produce and have limited applications due to the use of hazardous chemical reagents and toxic solvents. Exposure to these nanoparticles may have harmful impacts on living creatures and the environment. Therefore, a green and non-toxic approach to the synthesis of eco-friendly and environmentally acceptable metal oxide nanoparticles is required. Biological approaches for the preparation of metal oxide nanoparticles are an environmentally safe and green alternative because they do not require harmful chemicals or toxic solvents. Biological methods employ microorganisms (bacteria, fungi, and algae) and plant extracts for the synthesis of metal oxide nanoparticles. Green synthesis is a simple, single-step bio reduction method that requires relatively low energy to initiate the reaction. Therefore, biosynthesis is a cost-effective method for the production of metal oxide nanoparticles.

#### Keywords:

Green Synthesis, Nanoparticles, Biological methods, Non-toxic.

# **1.1 Introduction:**

Nanoparticles (NPs) have gained significant attention in photocatalysis due to their unique properties such as chemical, optical, electrical and mechanical properties because of the quantum confinement effect (Pande et al., 2008; Trinh et al., 2020). Instead of bulk material as a catalyst, nano particles such as TiO2, ZnO, Fe2O3, WO3, SnO2, ZrO2, CdS, SrTiO3 and Cu2O can be used to improve the efficiency of photocatalytic reactions (Abbas et al., 2018; Falah & Mackenzie, 2020; Rani & Shanker, 2019, 2021). The surface to volume ratio property of nanoparticles especially as a catalyst increases efficiency hundred percent as compared to bulk materials (Dewangan et al., 2012). Studies showed that chemically produced NPs were costlier in production and have limited application due to the use of hazardous chemical reagents and toxic solvents. Furthermore, environmental exposure to these NPs may have harmful impacts on living creatures and the environment.

Therefore, a green and non-toxic approach for the manufacture of ecologically acceptable metal oxide nanoparticles is required. Biological approaches for the manufacture of metal oxide NPs are an environmentally safe and green alternative because they do not require dangerous chemicals or toxic solvents.

Biological methods employ microorganisms (bacteria, fungi and algae) and plant extracts for the synthesis of metal oxide NPs (Singh et al., 2018). The NPs synthesised using these methods are known as bio-mediated NPs. Green synthesis is a simple and single step bio-reduction method that requires relatively low energy to initiate the reaction (Kalpana & Devi Rajeswari, 2018). Therefore, biosynthesis is a cost-effective method for the production of metal oxide NPs.

#### 1.2 Different types of Bio-mediated nanoparticles:

The distinct properties of nanoparticles depend upon the different method used for synthesis (Figure 1.1). Bio-mediated synthesised NPs have numerous applications in different fields such as photocatalysts, electrode active materials, solar cells and antibacterial activity. Due to presence of natural surfactants and stabilizing agents which are rich biological activity.



#### Figure 1.1: Different methods used for the synthesis of nanoparticles

#### **1.3 Silver nanoparticles (Ag NPs):**

Ag NPs have been prepared by various methods including spark discharging, electrochemical reduction, solution irradiation and cryo chemical synthesis. The size of synthesized nanoparticles was smaller than 100 nm and consisted of about 20-15,000 silver atoms (Chen & Schluesener, 2008). Ag NPs have been widely used as antimicrobial agents in commercial medical and consumer products (Rai et al., 2009; Ravindra et al., 2010). Ag

NPs preparation using plants (inactivated plant tissue, plant extracts and living plant) is an important branch of biosynthesis processes. It was reported that different plant leaves have the potential to reduce metal ions to zero valent metal nanoparticles (Makarov et al., 2014). Bio-mediated Ag NPs showed their applications in industries such as photocatalysts, in hospitals it was used for treating burns, and medical bandages because of its nano size and antimicrobial properties (Kirubaharan et al., 2012; Muthu & Priya, 2017; Pang et al., 2021; Vigneshwaran et al., 2007).

(Bankar et al., 2010) synthesised Ag NPs using banana peel extract. It was reported that Ag NPs have antimicrobial activity against fungal as well as bacterial cultures. Tabernaemontana divaricate leaf extract was used for the reduction of silver ions to Ag NPs by (Arun et al., 2014). The synthesised Ag NPs exhibited size of 22 nm with excellent stability for six months and cytotoxic activity against human breast cancer cell line (MCF-7). In a similar study (Ramesh et al., 2015) fabricated Ag NPs in an aqueous medium using Emblica officinalis fruit extract as a stabilizer and reducing agent. It was examined that the synthesized Ag NPs were spherical in shape (78 nm) and showed inhibition against both gram-positive and gram-negative bacterial strains.

Furthermore, bio-synthesis of Ag NPs using aqueous extract of Neem (Azadirachta indica) leaves was done by (Verma & Mehata, 2016). Synthesized Ag NPs were crystalline in nature, and poly dispersed because of which they exhibited high energy surface plasmon resonance band at around 400 nm and a strong photoluminescence band at 450 nm. Bio-mediated Ag NPs showed enhanced antibacterial activity against the bacterial colony and were used in the field of medicine, food and cosmetic industries.

The synthesis of Ag NPs using Azadirachta indica (neem) was done by (Nagar & Devra, 2019). Prepared Ag NPs were applied as the catalyst for the degradation of methyl orange (MO) in an aqueous solution and real wastewater. The degradation of MO followed pseudofirst order kinetics and maximum degradation of MO reached 88% in 40 min in aqueous solution and 80 min in real wastewater. (Küp et al., 2020) prepared Ag NPs from aqueous extract leaf of Aesculus hippocastanum (horse chestnut). It was observed that horse chestnut leaves have reduction potential as well as being a capping agent to produce well-defined nanoscale silver particles. Bio-mediated Ag NPs using Aesculus hippocastanum exhibited strong antibacterial activity against tested bacterial species but have no effect against fungal strains. Bio fabricated Ag NPs (25 nm) were prepared using Nepeta leucophylla extract by (Singh & Dhaliwal, 2020). Synthesised Ag NPs exhibited Surface Plasmon Resonance band at 430 nm in the ultraviolet-visible spectrum and showed 82.8 % phototcatalytic degradation of methylene blue dye from the aqueous solution in the presence of light and 61.2 % in dark in 180 min.

Ag NPs were prepared through in-situ reduction by aminated alkaline lignin by (Pang et al., 2021). Results showed that Ag NPs has a good catalytic performance for the reduction of 4-nitrophenol after recycling eight times. Ag NPs/aminated alkaline lignin composite exhibited cyclic catalytic activity due to the strong binding force between the amine groups of lignin and Ag NPs. Photocatalytic activity and spectral properties of Ag NPs fabricated using Ferula assafoetida were evaluated by (Subramaniam et al., 2022). Using halogen lamp, studies explored that the photocatalytic activity of Ag NPs against the methylene blue dye was 96 % in 90 min.

(Hashemi et al., 2022) synthesized bio based Ag NPs using Sambucus ebulus extract as a stabilizing, capping and reducing agents for the evaluation of efficient antibacterial, anticancer, and photocatalyst activities. TEM and FE-SEM analysis showed that Ag NPs were spherical in shape with a size range of 35–50 nm. The biosynthesized Ag NPs showed anti-cancer activity against breast (MCF-7) and gastric (AGS) cancer cell lines. The biogenic Ag NPs showed high catalytic activity with 95 % degradation of methyl orange dye under sun-light irradiation in 11 min.

#### 1.4 Cu2O NPs:

Cu2O NPs have attracted the attention of researchers due to their tuneable direct bandgap, p-type conductivity, non-toxicity, abundance and low-cost productivity (Minami et al., 2016; Nandy et al., 2013). The p-type behaviour of cuprous oxide nanoparticles is due to the special configuration of the valence band, formed by 3d10 levels of the Cu+ cation. The existence of these different levels contributes to a less localized population of holes, which improves the mobility of these charges (Matsuzaki et al., 2008). Cu2O NPs have shown unique properties in different fields such as solar energy, gas sensing, photocatalysis and magnetic storage devices because of their capacity to absorb visible light (Huang et al., 2009; Kumar et al., 2018; Li et al., 2021).

A comparison of previous studies with present study is shown in Table 1.1 (Jassal et al., 2016) synthesised  $\alpha$ -Fe2O3 nanoparticles using Sapindus mukorossi and showed the 81 % degradation efficiency for 4-Aminopyridine in 1440 min. (Kerour et al., 2018a) showed the 70 % degradation of methylene blue in 10 min using Cu2O nanoparticles prepared using Aloe Vera extract. Results demonstrated that the performance and catalytic activity of Cu2O NPs towards the degradation of various toxic dyes using different source of light was very effective. In the present study 80 % degradation of 4-Aminopyridine has been achieved using Cu2O NPs with 82 % COD and 65 % of TOC removal.

Reference	Methods		Degradation Efficiency and Mineralization		Time	
	Nanoparticles And Reaction conditions	Plant Extract	Pollutant	Removal Efficiency	COD Removal	(min)
(Behera & Giri, 2016)	Cu <sub>2</sub> O 500 W Xenon lamp	Calotropis Giganetea	Methylene blue (20 ppm)	90 %	-	120
(Borah et al., 2016)	Cu <sub>2</sub> O	Syzygium jambos (L.) Alston plant	Ary boronic acid (0.041 mmol / 5ml)	95%	-	300

Table 1.1: Comparison of Bio- mediated synthesised Cu2O NPs with other
chemically synthesized

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Reference	Methods			Degradation Efficiency and Mineralization		Time
	Nanoparticles And Reaction conditions	Plant Extract	Pollutant	Removal Efficiency	COD Removal	(min)
(Jassal et al., 2016)	α-Fe <sub>2</sub> O <sub>3</sub> nanoparticles	Sapindus mukorossi	4- Aminopyridine (25 mg/L)	81%	_	1440
(Mousavi- Kamazani et al., 2017)	Cu/Cu <sub>2</sub> O 250W Mercury lamp	Pomegranate marc peels (PMP)	Methylene blue (25 mg/L)	99%	-	150

# **1.5 Conclusion:**

Studies showed that bio-mediated NPs are cheaper to produce and have wide applications in various fields due to the use natural surfactants. Biologically synthesized NPs are nontoxic, eco-friendly and environmentally acceptable. Green synthesis of nanoparticles was found to be simple, single-step and low energy initiator. Bio-mediated prepared NPs were found to comparatively more effective as compare to chemically synthesize. Therefore, biosynthesis is a cost-effective method for the production of NPs.

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# 2. Chlorofluorocarbon (CFC) Substitutes and Their Potential Impact on Climate Change

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#### Abstract:

Hydrofluoroethers (HFEs) are promising next-generation climate-friendly compounds that can substitute ozone-depleting substances like ((chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs))and other potent greenhouse gases ((Hydrofluorocarbon (HFC)) compounds. These alternative compounds, used in various industrial applications (e.g. detergents, propellants, solvents, lubricants, etc.) have shorter atmospheric lifetime due to bond activation by the presence of ether oxygen. However, these compounds have  $-CF_3$ - and  $-CF_2$ - groups, making it a very active fluorinated greenhouse gas (GHG) in the atmosphere. In this chapter, we present kinetic data for few selected  $(CF_3CF_2OCH_3,$  $CHF_2CF_2OCHF_2$ , hydrofluoroethers  $CF_3CF_2CF_2OCH_3$ ,  $CF_3CF_2CF_2CF_2OCH_3$ ,  $CF_3CH_2OCH_2CF_3$ , and  $CHF_2CF_2OCH_2CF_3$ ) calculated using computational quantum chemistry and transition state theory. Our study discusses factors affecting climate change, include atmospheric lifetime, radiative efficiency, and global warming potential of these compounds. Therefore, the information presented here will expand the database for future applications and assess the suitability of HFE as a CFC replacement.

# Keywords:

Chlorofluorocarbon; Greenhouse Gases; Hydrofluoroether; Global warming Potential.

# 2.1 Introduction:

Global warming is not a myth but a well-accepted environmental problem caused by the cumulative accumulation of greenhouse gases observed in the stratosphere over the past

four decades. Back in the 1970s, M. J. Molina and F. S. Roland discovered the loss of stratospheric ozone and recognized that man-made gases, fully halogenated chlorofluorocarbons (CFCs), posed a serious threat to the ozone layer.<sup>1</sup> They postulated a theory that unusually stable chlorofluorocarbons may migrate up the atmosphere over time and be destroyed by intense radiation, releasing chlorine atoms that catalyze ozone depletion and cause the Antarctic "ozone hole", as shown in Figure 2.1.



# Figure 2.1: Stratospheric photodissociation of CFCl3 and Cl atom-catalyzed ozone destruction process

This breakthrough insight brought global attention to the scientific community, led to widespread awareness of the need to limit CFC production, and inspired a collective determination to find better alternative compounds for industrial and commercial appliances, such as refrigerants, detergents, propellants, solvents, lubricants, etc.



Figure 2.2: Progress of CFC alternatives and their negative effects and one of their representative compounds GWP and ODP indicate global warming potential and ozone depletion potential

In 1987, the Montreal Protocol, an international treaty designed to protect ozone layer, which stipulated the phasing out CFCs, HCFCs and other ozone-depleting substances (ODS) globally, while replacing them by hydrofluorocarbons (HCFCs) which have zero ozone-depleting potential (ODP) due to the absence of chlorine atoms.<sup>2</sup> However, due to the early focus on protecting the ozone layer, the scientific community and policy makers have paid little attention to the enormous global warming potential (GWP) of HFCs.<sup>3</sup> Recent disclosures of this potential climate impact have have sparked debate over the Montreal Protocol.

This led to further amendment of Montreal Protocol<sup>4,5</sup> and various other amendments such as the Kyoto protocol,<sup>6</sup> the 2016 Kigali Amendment,<sup>7</sup> the Paris agreement<sup>8</sup> etc. The further revised critique calls for developed countries and the rest of the world to phase out 85% of high-GWP HFCs by 2036.<sup>9,10</sup> In addition, there has been an unexpected and sustained increase in global emissions of the ozone-depleting substance CFC-11 recently showing: Unreported new production is on the rise.<sup>11,12</sup> This is inconsistent with the Montreal Protocol's agreement to phase out global CFC production by 2010, causing delays in the recovery of the ozone hole.<sup>13,14</sup> To this end, the global scientific community has made every effort to replace these compounds with low-GWP candidates.

In recent years, oxygenated hydrofluorocarbons (HFOCs) such as hydrofluoroethers (HFE), hydrofluoroalcohols (HFA), and hydrofluoroolefins (HFO) have emerged as a promising next-generation CFC replacement for various applications.<sup>15-36</sup> These compounds do not contain chlorine, therefore not harmful to the ozone layer, and ODP.

In this regard, the relative applicability of HFOCs to CFCs will be determined primarily by measuring their GWP indices.<sup>37,38</sup> However, these compounds have -CF<sub>3</sub>- and -CF<sub>2</sub>- groups, and the presence of C-F bonds in these compounds can effectively absorb the infrared radiation emitted by the earth, enhancing their role as effective greenhouse gases (GHG). These gases contribute to the GWP. Therefore, before large-scale commercialization and industrialization, it is necessary to understand their lifetime in the atmosphere to assess their impact on the environment, especially their GWP, which needs to be thoroughly evaluated to determine their suitability as a CFCs substitute.

In general, tropospheric oxidation of volatile organic compounds (VOCs) is initiated by short-lived radicals such as OH, HO<sub>2</sub>•, and RO<sub>2</sub>• (peroxy) radicals, mainly OH radicals via hydrogen abstraction reactions. Although the reaction with OH radicals is the main removal pathway for HFOCs in the troposphere, the reaction with Cl atoms may also make an important contribution to the removal process in coastal or oceanic boundary layers or in polluted urban area. The computational research focus of tropospheric chemistry has grown rapidly in recent years, allowing advanced quantum chemical theory to be applied to solutions with near-experimental precision.<sup>27-36,39</sup>

In this chapter, we have chosen to discuss the kinetic data and climatic implications of the reactions of some selected hydrofluoroethers  $(HFEs)^{15-36}$  such as non-segregated HFEs  $(CF_3OCH_3, CF_3CF_2OCH_3, CHF_2CF_2OCHF_2, CF_3CF_2OCH_3 and n-CF_3CF_2CF_2OCH_3)$  and segregated HFEs  $(CF_3CH_2OCH_2CF_3 and CHF_2CF_2OCH_2CF_3)$  with OH radicals and Cl atoms using computational quantum chemistry.

#### **2.2 Computational Methods:**

Electronic structure calculations on the gas-phase reaction of HFE with OH radicals and Cl atoms were carried out employing the Gaussian 09 program suite.<sup>40</sup> All the stationary points on the potential energy surface (PES) i.e. the reactants, products, transition states and reaction complexes were optimized using the DFT-based M06-2X<sup>41,42</sup> and MPWB1K<sup>43</sup> methods and *ab initio* MP2 method,<sup>44</sup> which has been shown to produce reliable results for kinetic studies of atmospheric molecular-radical reactions. Rate coefficient have calculated using BIRATE, GAUSSRATE,<sup>45</sup> and POLYRATE<sup>46</sup> was employed to carry out the kinetic calculations for the HFEs gas-phase reaction with OH radicals and Cl atoms using conventional transition state TST with Eckarts<sup>47</sup> tunneling and canonical variational transition state theory (CVT) with small curvature tunneling (SCT) corrections.<sup>48</sup>

#### 2.3 Results and Discussions:

Table 2.1: Experimental and theoretical rate coefficients (cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>) at 298 K of hydrofluoroethers and theoretical methods.

Compound	Calculated	Experimental	Method
CF <sub>3</sub> OCH <sub>3</sub>	$k_{OH}$ =6.9×10 <sup>-14</sup> Ponnusamy et al. <sup>27</sup>	$(1.28\pm0.19)\times10^{-14}$ Østerstrøm et al. <sup>15</sup>	CCSD(T)/aug-cc- pVTZ//M06-2X/6- 311+G(d,p)
		$(1.4\pm0.2)\times10^{-13}$ Christensen et al. <sup>16</sup>	
CF <sub>3</sub> CF <sub>2</sub> OCH <sub>3</sub>	$k_{\rm OH} = 1.09 \times 10^{-14}$ Lily et al. <sup>28</sup>	$(1.28\pm0.19) \times 10^{-14}$ Østerstrøm et al. <sup>15</sup>	M06-2X/6-31+G(d,p)
		$(1.09\pm0.16) \times 10^{-13}$ Østerstrøm et al. <sup>16</sup>	
CHF <sub>2</sub> CF <sub>2</sub> OCHF <sub>2</sub>	$k_{\rm OH} = 1.01 \times 10^{-15}$	2.36×10 <sup>-15</sup>	G2(MP2)//
	Lily et al. <sup>29</sup>	Chen et al. <sup>17</sup>	MPWB1K
	$k_{\rm Cl}$ =4.55×10 <sup>-16</sup>	$5.5 \times 10^{-16}$	M06-2X/
	Baidya et al. <sup>30</sup>	Andersen et al. <sup>18,19</sup>	6-311++G(d,p)
CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> OCH <sub>3</sub>	$k_{\rm OH}$ =0.77×10 <sup>-14</sup>	$(1.18\pm0.05)\times10^{-14}$	M06-2X/
	Mishra et al. <sup>31</sup>	Tokuhashi et al. <sup>20</sup>	6-31+G(d,p)
	$k_{\rm Cl}$ =4.6×10 <sup>-14</sup>	$(9.1\pm1.3)\times10^{-13}$	M06-2X/
	Mishra et al. <sup>31</sup>	Bravo et al. <sup>21</sup>	6-31+G(d,p)
n-CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> OCH <sub>3</sub>	$k_{\rm OH} = 1.11 \times 10^{-14}$	$(1.49\pm0.13)\times10^{-14}$	M06-2X/
	Mishra et al. <sup>32</sup>	Bravo et al. <sup>21</sup>	6-31+G(d,p)
	$k_{\rm Cl}=0.17\times10^{-13}$	$(0.97\pm1.4)\times10^{-13}$	M06-2X/
	Mishra et al. <sup>32</sup>	Wallington et al. <sup>22</sup>	6-31+G(d,p)
CF <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CF <sub>3</sub>	$k_{\rm OH} = 1.32 \times 10^{-13}$	$1.30 \times 10^{-13}$	M06-2X/
	Lily et al. <sup>33</sup>	Wilson et al. <sup>23</sup>	6-31+G(d,p)

Compound	Calculated	Experimental	Method
	$k_{\rm Cl} = 1.95 \times 10^{-13}$	$(7.1\pm0.9)\times10^{-13}$	CCSD(T)//BHandHLY/6-
	Lily et al. <sup>34</sup>	Wallington et al. <sup>24</sup>	311++G(d,p)
CHF <sub>2</sub> CF <sub>2</sub> OCH <sub>2</sub> CF <sub>3</sub>	$k_{\rm OH} = 1.01 \times 10^{-14}$	9.08×10 <sup>-15</sup>	G2(MP2)//M06-2X
	Lily et al. <sup>35</sup>	Tokuhashi et al. <sup>25</sup>	/6-31+G(d,p)
	$k_{\rm Cl} = 1.21 \times 10^{-14}$	$(8.63\pm6.66)\times10^{-15}$	M06-2X/
	Lily et al. <sup>36</sup>	Papadimitriou et al. <sup>26</sup>	6-311++G(d,p)

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Rate coefficient values  $k_{OH}$  and  $k_{Cl}$  calculated are listed in Table 1 along with the experimental values at 298K. The calculated  $k_{OH}$  values of ~10<sup>-14</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for non-segregated HFE (CF<sub>3</sub>OCH<sub>3</sub>, CF<sub>3</sub>CF<sub>2</sub>OCH<sub>3</sub>, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>OCH<sub>3</sub>, and n-CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>OCH<sub>3</sub>) with OH radicals at the M06-2X barrier height, which agreed well with the experimental values.

The calculated rate coefficients of  $CF_3CF_2CF_2OCH_3+Cl$  and  $CF_3CF_2CF_2CF_2OCH_3+Cl$  reactions are about  $10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, which are also in reasonable agreement with the experimental results. For the reaction of  $CHF_2CF_2OCHF_2$  with OH radicals and Cl atoms, using G2(MP2)//MPWB1K method, the rate coefficient of the reaction with OH radicals is reduced by an order of magnitude to  $\sim 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and by two orders of magnitude for reactions with Cl atoms by  $\sim 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. This suggests that the substitution of hydrogen atoms for fluorine atoms reduces the reaction rate.

For the segregated HFE reaction with OH radicals, according to M06-2X/6-31+G(d,p) barrier height of  $CF_3CH_2OCH_2CF_3 + OH$  reaction and CCSD(T)/BHandHLY/6-311++G(d, H)p) method for the  $CF_3CH_2OCH_2CF_3 + Cl$  reaction is close to the experimental results, however, our calculated  $k_{CI}$  is slightly higher than the experimental results by 3.64 times. For the CF<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CF<sub>3</sub> + OH reaction, our calculated G2(MP2)//M06-2X/6-31+G(d,p) rate coefficient values are in good agreement, and recent experimental results are available, allowing us to confirm our kinetic model quality using the G2(MP2)//M06-2X/6-31+G(d,p) method. In fact, the G2(MP2)//M06-2X/6-31+G(d,p) method combined with DFT-level geometry optimization produces reliable kinetic results. CHF<sub>2</sub>- sites ( $k_1$ =0.566×10<sup>-14</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) had slightly higher H-abstraction than  $-CH_2$ - sites ( $k_2=0.450\times10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>). Our analysis suggests that this is mainly due to the presence of a large Arrhenius pre-exponential factor at the CHF<sub>2</sub>-. For example, the Arrhenius pre-exponential factor of  $k_1$  is  $4.2 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K, and the Arrhenius pre-exponential factors of  $k_{2a}$  and  $k_{2b}$  are  $2.5 \times 10^{-13}$  and  $2.5 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively. To estimate the accuracy of the rate coefficient, we assume that there is an error of  $\pm 4$  kJmol<sup>-1</sup> in the barrier heights calculated from the G2(MP2) results. Based on this estimate, k<sub>OH</sub> at 298 K should be in the range of  $1.9 \times 10^{-15} - 5.5 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. For the CF<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CF<sub>3</sub>+Cl reaction, our calculated M06-2X/6-311++G(d,p) rate coefficient values are in good agreement with the existing experimental results. From the obtained rate coefficient values, it can be seen that the segregated HFE reacts slightly faster with Cl atoms than with OH radicals. The lifetime of VOCs is an important parameter that is used to predict their future abundances which will directly contribute towards GWPs. The obtained rate coefficients will be used to estimate radiative efficiency (RE) and GWP.

#### 2.4 Atmospheric Implications:

To determine the effectiveness of greenhouse gas of a compound over its atmospheric lifetime, RE one needs to calculate the GWP. The RE and GWP are useful metrics for assessing the relative impact of long-lived greenhouse gases, such as fluorinated ethers, on climate. These highly fluorinated compounds have vibrational stretching transitions associated with C-F bonds occurring in the atmospheric window 700-1250 cm<sup>-1</sup>.<sup>49,50</sup> These compounds are absorbed by the atmospheric window, hindering the escape of terrestrial radiation and warming the Earth's surface.

A. Atmospheric Lifetime: The tropospheric lifetime  $(\tau_{eff})$  of HFEs is calculated assuming that their removal from the atmosphere is decided by the reaction with OH radicals and Cl atoms alone.

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{OH}} + \frac{1}{\tau_{Cl}} \tag{1}$$

**B. Global Warming Potential (GWP:** Global-warming potential is a relative measure of how much heat greenhouse gas traps in the atmosphere. The GWP is generally predicted based on the time-integrated radiative efficiency from the instantaneous emission of 1 kg of a compound relative to that of 1 kg of a reference gas (CO<sub>2</sub>). It can be expressed as an absolute GWP for a gas i(AGWP<sub>i</sub>) by the AGWP of a reference gas (CO<sub>2</sub>). Here, GWPs for HFEs are estimated (relative to CO<sub>2</sub>) using the expression given by Hodnebrog et al.<sup>42</sup>

$$GWP_i(H) = \frac{\int_0^H RF_i(t)dt}{\int_0^H RF_{CO_2}(t)dt} = \frac{AGWP_i(H)}{AGWP_{CO_2}(H)}$$
(2)

The radiative efficiency of HFE molecules was calculated using the relationship RE

$$RE = \sum_{k} A_{\nu} F(\bar{\nu}_{k}) \tag{3}$$

where  $A_k$  is the absorption cross-section in cm<sup>2</sup> molecule<sup>-1</sup>averaged over a 10 cm<sup>-1</sup> interval around the wave number  $(\overline{\vartheta}_k)$  and  $F(\overline{\vartheta}_k)$  is the instantaneous, cloudy sky, radiative forcing per unitcross section per wave number ((W m<sup>-2</sup> cm (cm<sup>2</sup> molecule<sup>-1</sup>)<sup>-1</sup>) evaluated at the band scaled center wave number  $(\overline{\vartheta}_k)$ . The instantaneous RE is derived from a line-by-line model simulation in Oslo, and the adjusted Pinnock curve model is within 10% of the modelderived value.<sup>54</sup>

To understand the suitability of proposed HFEs replacements for ODS (CFCs and HCFCs) and high-GWP substances (HFCs), it is crucial to recognize the potential impact of this species on climate. When HFEs are released into the atmosphere from commercial and industrial sources, their primary fate is to react with OH radicals on a global scale and Cl atoms in the ocean boundary layer. HFE is estimated to have a significantly shorter atmospheric lifetime than CFCs and HFCs, resulting in less accumulation levels in the atmosphere. Although HFEs possess zero ODP when compared to CFCs and HCFCs, they still exhibit a considerable GWP and therefore can be classified as an active fluorinated gas.

<b>Table 2.2:</b> Atmospheric lifetime, radiative efficiency, and GWP-100-year time horizon
(calculated values are given in brackets) for HFE and CFC-11, HCFC-21, and HFC-
23 values obtained from WMO (2022). <sup>43</sup>

Reaction	Lifetime	Radiative	GWP- 100-
	(Years)	Efficiency	year
		$(W m^{-2} ppb^{-1})$	time horizon
CF <sub>3</sub> OCH <sub>3</sub>	$4.5 (4.82)^{27}$	0.189	660 (607) <sup>27</sup>
CF <sub>3</sub> CF <sub>2</sub> OCH <sub>3</sub>	$3.9(4.99)^{28}$	$0.296 (0.34)^{28}$	497 (754) <sup>28</sup>
CHF <sub>2</sub> CF <sub>2</sub> OCHF <sub>2</sub>	$35(18.9)^{30}$	$0.32 (0.638)^{30}$	4131 (4750) <sup>30</sup>
CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> OCH <sub>3</sub>	$4.4(5.1)^{31}$	0.343	579
n-CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> OCH <sub>3</sub>	$1.2(5.05)^{32}$	0.3	$132 (59)^{32}$
CF <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CF <sub>3</sub>	79-270 days (87	0.19	$21 (24)^{34}$
	days) <sup>34</sup>		
CHF <sub>2</sub> CF <sub>2</sub> OCH <sub>2</sub> CF <sub>3</sub>	$3.14(6.1)^{36}$	0.483	601 (964) <sup>36</sup>
CFC-11 (CCl <sub>3</sub> F)	1770	0.299	5910
HCFC-21 (CHCl <sub>2</sub> F)	1.82	0.145	161
HFC-23 (CHF <sub>3</sub> )	243	0.192	14,700

### 2.5 Conclusion:

A new generation of CFC, HFC and HCFC substitutes has been commercialized in the market for various industrial applications with serious environmental concerns. To assess the environmental impact of new CFC, HFC and HCFC alternatives, it is important to study the greenhouse gas effects of the compounds in terms of atmospheric lifetime, radiative efficiency and GWP. To achieve scientific goals, the kinetic data and climatic influence factors of non-segregated HFE (CF3OCH3, CF3CF2OCH3, CF3CF2CF2OCH3 and CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>OCH<sub>3</sub>) and segregated HFE (CF<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CF<sub>3</sub> and CHF<sub>2</sub>CF<sub>2</sub>OCH<sub>2</sub>CF<sub>3</sub>) with OH radicals and Cl atoms were investigated using computational quantum chemistry, as they are considered as a potential replacement for CFC, HFC, HCFC in various industrial applications. In the evaluation of the kinetic data, we observed that the DFT theory at the M06-2X level is one of the best tools for developing the atmospheric H-abstraction reaction potential energy profile, which leads to accurate kinetic parameters when compared with existing experiments and reliable result values. The same basis sets were then used for single-point CCSD(T) and G2(MP2) calculations on the M06-2X and MPW1K optimized structures to improve the accuracy of the results. Rate coefficients for simple bimolecular reactions of atmospheric importance are estimated by using conventional transition state theory (TST). However, significant variation effects were observed in many H-abstraction reactions. Such reactions were treated using variational transition state theory (VTST).

From these observations, we have reported that theoretical calculations, especially kinetics, may be as good as laboratory studies when experimental data for a specific reaction are not available. Therefore, this knowledge should be useful in understanding future laboratory and field studies and in developing atmospheric modelling studies and climate impacts of HFEs. Therefore, this knowledge should be useful in understanding future laboratory and field studies and in developing atmospheric modelling studies. It is believed that this comprehensive report has answered some existing questions about the climate impact of

HFEs, thereby making an important contribution to policy formulation and economic development of green alternatives to CFCs, HCFCs and HFCs.

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# **3. The Role of Mushrooms Cleaning the Pollutants** in The Environment

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#### Abstract:

People have eaten mushrooms for centuries, because of their rich flavour and high protein content, but mushrooms are so much more than that. Fungi have a unique ability to degrade chemical pollutants such as oil and insecticides, as well as heavy metals and radiation. Fungi can able to filter water, sustaining countless life cycles that are beneficial to ecosystems. Mycoremediation is a remedial technology that uses fungi mycelium (the vegetative component of a fungus) in contaminated soil locations. A mushroom's enzymes are effective at breaking down a wide range of pollutants. This method is about employing fungi's natural capabilities of decomposition to restore and regenerate the land.

# **3.1 Introduction:**

Because of heavy metal pollution, the world's most significant ecological issue is that natural resources like air, water, and soil have become scarce (Kour *et al.*, 2018; Ramya *et al.*, 2018). The governing council of the United Nations environment program issued a treaty in 2001 to stop or reduce the use and production of persistent organic pollutants (POPs). Synthetic organic compound pollution of the environment has grown to be a serious issue on a global scale. Due to their toxic effects on the environment and human health, the United States Environmental Protection Agency (USEPA) has prioritized several classes of chemicals that have been targeted by pollutants. The waste and effluents from homes and agricultural fields are deteriorating in an environment with poor management (Akhtar *et al.*, 2020).

These substances include benzene, toluene, ethylbenzene xylene, trinitrotoluene, Penta chlorophenols, polychlorinated biphenyls, 1,1,1-trichloro-2 (4-chlorophenyl) ethane, and polycyclic aromatic hydrocarbons. Polycyclic aromatic hydrocarbons (PAH), which are produced by burning fossil fuels, mining coal, drilling for oil, and burning wood, are recalcitrant environmental pollutants (Lau *et al.*, 2003; Verdin *et al.*, 2004). DDT (dichlorodiphenyltrichloroethane) was one of the first synthetic pesticides that gained widespread use DDT (dichlorodiphenyltrichloroethane) was a wide gain to one of the first synthetic pesticides. DDT has been utilized for pest control in forestry and agriculture all over the world since the 1940s. One of the most widely used organochlorine pesticides was dichloro diphenyl trichloroethane (DDT).

#### The Role of Mushrooms Cleaning the Pollutants in The Environment

Industries have proliferated like mushrooms around the globe as a result of increased commercialization, polluting the air, water, and soil with toxic chemicals and using excessive amounts of dangerous pesticides and insecticides in agriculture. Oil spills, tank leaks, and wastewater disposal all result in toxic pollutants like hydrocarbons entering the environment. Understanding how pollutants behave in natural settings and developing strategies for reducing or eliminating them are necessary due to the enormous amount of pollutants, their persistence and mobility in natural environments, and their frequent toxicity (O.M. Adedokun *et al.*, 2005). To solve the issue, scientists are making a lot of effort.

The practice of bioremediation involves using biological processes to eliminate pollutants from the environment. Significant research in this area has been done with the help of bacteria that can degrade oil spills, like *Pseudomonas putida*. Many environmental researchers are interested in the capacity of fungi to degrade toxic pollutants and hydrocarbons. Fungi are heterotrophs, which means they absorb nutrients to sustain themselves. Exoenzymes, potent hydrolytic enzymes that the fungus secretes, break down food outside the body into simpler compounds that the fungus can absorb and use. The surface area and small volume of fungal hyphae increase the fungus' ability to absorb substances. Due to their capacity to break down organic materials to create extended mycelia networks and the low specificity of their catabolic enzymes, fungi can use pollutants as a growth substrate. They can thus be used in a variety of remediation contexts, some of which involve working with plants. Additionally, edible and/or therapeutic fungi have functions in nature (S.T. Chang *et al.*, 1982).

#### 3.2 White Rot Fungi (Mushroom):

Practical considerations include the availability of White rot fungi and the potential benefit of the bioremediation method because of its low cost and eco-friendly nature. Another bioremediation technology is quite different from the well-established white-rot fungi method. (For instance, the systems of bacteria. Due to the fact that most contaminated sites contain a variety of different pollutants, this feature makes using white-rot fungi in bioremediation the most advantageous (Mester *et al.*, 2000).

White rot fungi live on woody tissues that are primarily composed of three biopolymers: cellulose, hemicellulose, and lignin. Examining the ecological riches of white rot fungi is necessary to comprehend their capacity to degrade contaminants. Taxonomic classification of fungi that can thoroughly degrade the heterogeneous polyphenolic polymer lignin found in lignocellulosic substrates (Pointing *et al.*, 2001). The term "white rot" describes these fungi attacking wood, leaving the substrate looking bleached as a result of the removal of lignin. Although a few ascomycete genera in the family can also cause white rot decay, basidiomycetes make up the majority of white rot fungi (Eaton *et al.*, 1993).

Lignin is incredibly resilient and gives the plant its strength and structure. It undergoes mineralization in a strictly aerobic setting (Field *et al.*, 1993; Pointing *et al.*, 2001). The significance of lignin biodegradation is the destruct of the matrix, lignin creates which facilitates the bacteria' easier access to cellulose and hemicellulose, the real substrates (Field *et al.*, 1993; Canet *et al.*, 2001). The typical biological solution is to break down biopolymers using highly specific enzymes.

This method is typically very effective because the organism only produces a small amount of this substance. Lignin, which gives the plant strength and structure, is extremely resistant. It is mineralized in an obligate aerobic environment. The physiological significance of lignin biodegradation is the destruction of the matrix it forms, allowing the microorganism better access to the real substrates: hemicellulose and cellulose (Field *et al.*, 1993; Canet *et al.*, 2001). Protein (enzyme) quantity needed to cleave the polymer (Evans *et al.*, 2001). The typical biological solution is to break down biopolymers using highly specific enzymes.

However, because lignin is hydrophobic and highly insoluble, which complicates the catalysis by water-soluble enzymes, the way white rot fungi degrade wood differs (Harvey *et al.*, 2001). Randomly peroxidase-catalyzed polymerization of substituted p-hydroxy-cinnamyl alcohols produces lignin in plants (Field *et al.*, 1993).

This polymer is three-dimensional, with various ether and carbon-carbon bonds connecting its monomers, and its stereoregularity protects it from enzyme attack and the enzymatic degradation of lignin. lignin's chiral carbon which further complicates the situation because it exists in both L and D configurations. Plants cannot absorb or break down lignin because of its large molecular size.

#### **3.3 Role Play of White Rot Fungi Enzymes:**

Degrading fungi excrete ligninolytic enzymes into the extracellular environment, where they begin to oxidize substrates (Mester *et al.*, 2000). White rot fungi have developed very generic mechanisms to break down lignin extracellularly as a result (Bar *et al.*, 1994).

The three principal families of lignin-modifying enzymes thought to be involved in the degradation of lignin are laccases, lignin peroxidases, and manganese peroxidases (Reddy *et al.*, 2001). One electron is removed or added to the lignin molecule during the crucial step in the degradation of lignin by laccase the creation of intermediates by ligninolytic peroxidases (LiP and MnP Chemical's ground state (Reddy *et al.*, 2001).

Different enzymes are produced by various white rot fungi species according to their genetic makeup and growth circumstances. Key degrading enzymes include lignin peroxidase (LiP), manganese-dependent peroxidase (MnP), and laccase. The lignin degradation system of enzymes used by this group of fungi serves as the primary mechanism of biodegradation. These enzymes' ability to break down lignin and xenobiotics is well known (Lamar *et al.*, 1992; Vyas *et al.*, 1994). *Lentinula edodes* were DDT degradation in 7 days 29% were degraded and in 28 days 70% were degraded the *Lentinula edodes* (G. Prathima *et al.*, 2023).

Environmental science mainly uses GC methods to identify organic pollutants in recent sediments, track the abiotic and biotic transformations of petroleum-type pollutants, and distinguish the oil pollutant from the native organic material of recent sediments.

This helps us better understand the mechanisms by which organic pollutants move between soil, water, and air environments, as well as during experiments on soil bioremediation. In the modern era, it is difficult to imagine an environmental laboratory using GC without at least a gas chromatograph (Wang *et al.*, 1999).

#### 3.4 Bioremediation Properties of Mushrooms:

Fungi and their mycelial "root systems" help ecosystems by ingesting nutrients from the plant matter they decompose and redistributing them to other plants and trees. Fungi's natural function as super-charged decomposers and nutrient dispersers has served as the foundation of nearly all ecosystems. Oxalic acid, one of the enzymes produced by fungi, was thought to be the catalyst for the breakdown of minerals and rock that resulted in the calcium-rich soil that plants grow in (Stamets *et al.*, 2016). Fungi are ideal agents to turn to for solutions to the problem of human waste and pollution because they consume difficult-to-breakdown substances. Fungi have been around for billions of years and have adapted to every type of environment imaginable.

Many fungi, for example, have evolved the ability to survive in the absence of sunlight (something plants are not able to do as of yet). As we will see, the highly adaptable nature of fungi makes them ideal agents for environmental healing.

Through mycoremediation, mushrooms can help to make amends for an environmentally damaged planet by using their natural powers of absorption, decomposition, and adaptation. Mycoremediation is defined as the use of mushrooms (the fruiting body of fungi) to remove waste from the environment (Kulshreshtha *et al.*,2014)."Clean technology" is a popular concept in today's world, where we are becoming more aware of climate change and environmental clean-up. It is an attempt to maximize production while simultaneously reducing waste generation, waste treatment, and waste conversion into some useful form.

# 3.4.1 Remediation of polluted water with fungi:

Without water, humans cannot survive. Because it hinders development, a lack of access to clean drinking water can keep people in poverty. Currently, 785 million people in the world lack access to clean drinking water. Additionally, 2 billion people lack adequate sanitation, which is highly dependent on access to clean and safe water (Reid *et al.*,2021). A type of bioremediation known as microfiltration uses fungi to break down pollutants in water before they reach larger bodies of water, helping to keep water sources clean.

# 3.4.2 Removal of Pollutants from the Chicago River of E. coli:

It has been demonstrated that the Oyster mushroom *Pleurotus ostreatus* could clean water by removing impurities from both soil and water (Scout *et al.*, 2017). In an effort to reduce the pollution that has accumulated in the Chicago River water since the 1700s, one labbased study looked into mycoremediation. Oyster mushroom mycelia were used to remove 99.25% and 99.74% of *E. coli* from lab-made infected water as well as water directly from the Chicago River over a 96-hour period (Pini *et al.*, 2020).

# **3.4.3 Filtration of Farm Runoff Water:**

Fungal filters, a mycelial network that functions as a micro-filtration system and releases enzymes that break down toxic contaminants, are now being used to treat contaminated farm run-off.

#### **3.4.4** Toxic Wildfire Ash is Removed from California Water Supplies:

Wildfires are an environmental problem linked to contaminated water. Co Renewal, a company that specializes in mycoremediation, studied the toxic ash residue left behind by California wildfires in waterways and came up with solutions to clean up both the impacted soil and waterways. Asbestos, lead, arsenic, and plastics were found in dangerous concentrations in the toxic ash from wildfires. Installing hay bales filled with Oyster mushroom mycelium reduces these heavy metals, dangerous Polycyclic aromatic hydrocarbons (PAHs), and TNT.

#### **3.4.5 Remediating polluted soil with fungi:**

Industrialization causes heavy metals like lead, cadmium, nickel, chromium, arsenic, selenium, and others to contaminate the soil (Kumar *et al.*,2019). Through plants, animals, or other links in the food chain, toxins that are left to break down in the soil eventually make their way back to us. In the process of biosorption, biological materials serve as toxin absorbents. As was previously mentioned, the *Pleurotus* species, of which Oyster mushrooms are a member, produces a disproportionately large amount of mycelium compared to other species. Which gives it a remarkable capacity to absorb heavy metals and other petroleum wastes from the soil. This amplified.

#### **3.4.6 Remediation of Diesel-contaminated land:**

The one that had been sporulated with Oyster mushroom spores, had turned what had once been a contaminated wasteland into a thriving ecosystem and had biodegraded the most dangerous oil of all the plots. This experiment decreased the soil's PAH count, or the quantity of these frequently carcinogenic aromatic hydrocarbons, from 10,000 parts per million (ppm) to less than 200 ppm, in just eight weeks (Stamets *et al.*,2016).

#### **3.4.7 Degradation of Plastics and Other Humans:**

There would be an enormous amount of non-biodegradable plastic waste on the planet even if we stopped making plastic products right away. About 242 million tons of plastic waste was released onto the earth in 2016. Several Kingdom Fungal species, including *Pleurotus ostreatus* (Oyster Mushroom) (Kulshreshtha *et al.*,2014; Da Luz *et al.*,2013), *Trametes Versicolor* (Turkey Tail), (Jang *et al.*,2009) and *Lentinula edodes* (Shiitake) have been identified as having the ability to degrade plastics and PAHs (Tsujiyama *et al.*,2013).

#### **3.5 Conclusion:**

Mushroom is a tremendous boon to the idea of using this for the bioremediation process as a real-world solution. The cultivation of edible mushrooms on agricultural and industrial wastes may thus be a value-added process capable of converting these discharges, otherwise considered wastes, into foods and feeds. Besides producing nutritious mushrooms, it reduces the genotoxicity and toxicity of mushroom species. Bioremediation through mushroom cultivation will alleviate two of the world's major problems i.e., waste accumulation and the production of proteinaceous food simultaneously. Thus, there is a need for further research on the exploitation of the potential of mushrooms as bioremediation tools and their safety aspects for consumption as a product.

#### 3.6 Acknowledgment:

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# 4. Green Solvent-Based Gel Type Adsorbent Materials for Wastewater Treatment

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# Abstract:

A novel type of materials for the treatment of wastewater is gel-based adsorbents with green solvents. To create them, natural or synthetic polymers are dissolved in environmentally friendly solvents such water, ethanol, glycerol, or ionic liquids, and then they are crosslinked to create a three-dimensional network. Due to their high porosity, swelling ability, and mechanical strength, the resultant gels may effectively trap a variety of wastewater contaminants, including microplastics, heavy metals, dyes, and organic compounds. Adsorbents of the green solvent-based gel type have a number of benefits over those of the traditional kind, including affordability, simplicity of synthesis, biodegradability, and recyclability. Additionally, they can be modified with functional groups or nanoparticles to improve the efficiency and selectivity of their adsorption. Green solvent-based gel type adsorbents are promising materials for the development of sustainable and efficient wastewater treatment technologies.

# Keywords:

Wastewater treatment, Ionic liquids, DESs, Hydrogels, Organogels, Adsorption.

# 4.1 Introduction:

One of the biggest issues facing contemporary society is water contamination. Large quantities of pollutants, including heavy metals, oils, aromatic compounds, and dyes, are released as a result of industrial activity. The main effect is a decline in the supply of potable water, which is already scarce.[1]

A variety of industrial fields use dyes, including textiles, printing, plastics, food, cosmetics, paper, and others. This explains why more than 700 000 tons of dyes are produced annually. Despite rigorous environmental rules regarding their discharge and advancements in dyeing techniques, more than 15% of total production is regrettably released into the environment each year. The majority of colors are not biodegradable and thermally stable and some of their metabolites are also carcinogenic. They have the potential to influence photosynthetic activity from an environmental perspective.[1]

Adsorption is one of the most popular physical techniques. Various adsorbents, including polymers, metal-organic frameworks, carbon-based materials, natural fibers, and inorganic compounds like halloysite nanotubes, have been proposed. However, in recent years, gel phases, particularly supramolecular gels, have also been suggested as workable substitutes.

Low molecular weight gelators (LMWGs) interact weakly and cooperatively to generate these gels, which causes a fibrillary network to self-assemble and become capable of encasing solvent molecules.[1]

A hydrogel is a biphasic material that is composed of porous, permeable solids and at least 10% by weight or volume of interstitial fluid composed completely or mainly by water. Hydrogels are used in various industries due to their versatile and environmentally sensitive nature. They can come in two forms: solid and liquid. Hydrogels have many applications in the biomedical area such as wound care.[2]

Hydrogels have many benefits for green chemistry. They can dispense needed nutrients or chemicals. Hydrogels are also environmentally sensitive and versatile. They can be used in various industries such as biomedical, industrial, agricultural, electrical, healthcare, and hygienic products.[2]

Eutectogels are gels that are formed by gelling natural deep eutectic solvents (NADESs). They are more stable than hydrogels and greener than ion gels. Eutectogels have many applications such as in the fields of food, medicine and materials.[3]

#### 4.2 Self-Sustaining Supramolecular Ionic Liquid Gels for Dye Adsorption:

This is a new type of gel that can be used to remove dyes from water. The gel is made up of two types of molecules: an ionic liquid and a gelator. The ionic liquid is a salt that is liquid at room temperature and the gelator is a molecule that can form a gel when mixed with the ionic liquid.[1]

The resulting gel is self-sustaining and can be used to remove dyes from water without the need for external energy sources. The gel is self-sustaining and can be used multiple times without losing its effectiveness.[1]

Ionic liquid gels have many potential applications in a more sustainable future. They provide the ability to build functionality at every level, the solid component, the ionic liquid, and any incorporated active functional agents. Some of the potential applications include electrochemical devices, sensors, and catalysts.[1]

Some of the Rheological and Morphological studies can be carried out like Gelation Tests, Thermal Stability and Gel phases. Gelation tests were carried out both in conventional solvents and in ILs.

In general, salts used were soluble in alcohols and glycerol, but insoluble in highly polar solvents like water, phosphate buffer, ethylene and triethylene glycols. However, in most cases, they were completely soluble in DMSO and DMF.[1]



Green Solvent-Based Gel Type Adsorbent Materials for Wastewater Treatment



# Figure 4.1: Structures of Gelators, ILs and Dye Used; Schematic Representation of the Adsorption Process.[1]

Gelling ability was tested both in conventional solvents and in ILs. Solvents having different polarities and hydrogen bond donor abilities were chosen. However, we used both aliphatic and aromatic ILs and, in the case of imidazolium-based ones, the effect due to a different sizes, shapes, and coordination abilities of the anion ([BF4]–, [PF6]–, [SbF6]–, [NTf2]–) was Analyzed.(Fig-1) Then, we tested the removal efficiency of gel phases toward a cationic dye like Rhodamine B (RhB) in a static system or in a dialysis membrane or immobilized in a column as adsorbent. In the latter case, a removal efficiency of over 95% was obtained in less than 10 min. To better modulate application of our gel phases, we first performed a complete investigation of their properties (gel–sol transition temperature, kinetic of gel phase formation, morphology, self-repairing ability, rheological behavior). The soft materials showed very interesting properties, like self-strengthening ability and good load-bearing capacity.[1]

# **4.3** Stimuli Responsive, Self-Sustainable, and Self-Healable Functionalized Hydrogel with Dual Gelation, Load-Bearing, and Dye-Absorbing Properties:

It describes a hydrogel that has the ability to respond to stimuli such as temperature and pH. The hydrogel is self-sustainable and self-healable. It has dual gelation properties which means it can transform from a fibrillar opaque hydrogel to a transparent hydrogel upon heating.[2]
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Hydrogels comprises the most important and transformable functional class of materials due to their moderate mobility, flexibility, and physicochemical properties that could be finetuned selectively through changing the molecular structure of the gelator and/or through various external stimuli. They are formed through self-assembling low-molecular-weight gelators (LMWGs) in aqueous medium by maintaining a delicate balance between polar and nonpolar parts of the gelator. The polar part interacts favorably with water molecules and enhances its solubility, whereas the nonpolar part tends to come closer to each other and minimize their exposure toward water (hydrophobic interaction), thus facilitating self-assembly within these molecules.[4], [5]



#### **Methyl Orange**

#### Figure 4.2: Chemical Structures of C16EMorphBr, Crystal Violet (CV) Dye and Methyl Orange (MO) Dye [2]

Here we discussed the morpholinium-based ester functionalized surfactant 4-(2-(hexadecyloxy)-2-oxoethyl)-4-methylmorpholin-4-ium bromide (C16EMorphBr) with a melting point of 78.53 °C. The surfactant has the characteristic feature of ILs (arbitrarily, ILs are defined as electrolytes with mp  $\leq 100$  °C) and has established surface-active properties. C16EMorphBr forms hydrogels at 7.20% (w/v) critical gel concentration and pH 7.4. The structure of the surfactant is given in (**Figure 4.2**).[2]

The formed hydrogel exhibits phase transition from opaque to transparent through changing the temperature from 25 to 50 °C. The dual gelation properties are due to the changes within its supramolecular framework from bilayer lamellar to cylindrical due to the exclusion of water molecules. This phase behavior was characterized using various state-of-the-art physical, spectroscopic, microscopy, and scattering techniques. The porous xerogel that forms after exclusion of the water molecules from the opaque gel shows self-sustaining, self-healing, moldable, and load-bearing properties. Rheology and tensile strength and compression tests were performed to study the mechanical properties of the xerogel. The same xerogel is then used as an absorbent for the selective removal of anionic dyes from an aqueous solution.[2]

Some properties and characteristics are discussed in this chapter as follows:

- *Gelation:* The pre-weighed solid C16EMorphBr was added in a glass vial, and 10 mL of water was added in the vial. The mixture was then heated at 60 °C on a water bath to get the transparent homogeneous solution, which was then cooled to room temperature to get the fibrillar opaque hydrogel visually (**Fig. 4**).[2]
- *Turbidity:* As a function of temperature and DSC analysis were performed to confirm the reversible transition of an opaque hydrogel into a transparent hydrogel on changing the temperature from 25 to 50 °C. The phase behavior was monitored by measuring the transmittance as a function of temperature where a dramatic increase in transmittance was observed as the temperature reached between 45.50 and 50.0 °C with visual appearance of the hydrogel turning from opaque to transparent. Explore the morphology of the hydrogel to understand the structural arrangement of the gelator within them. To do that, we have examined the morphology of the opaque gel through scanning electron microscopy (SEM), field emission scanning electron microscopy (AFM).
- Self-Sustaining, Self-Healing, and Load-Bearing Properties of Xerogel: The selfsustaining nature of the xerogel indicates that the gel with immobilized solvent molecules is stable and intact and stands by itself without any support and without changing its shape such as a cylinder, ring, and rectangle. The xerogel was obtained from the removal of water from the fibrillar opaque gel. We observed that the xerogel exhibited excellent self-sustainability.
- *Thermogravimetric Analysis:* A thermogravimetric analyzer SDT Q600 was used to study the thermal stability of the gelator. The temperature range studied was between 25 and 500 °C in a N2 atmosphere at a heating rate of 10 °C/min. Tstart, the temperature at which the decomposition starts, was measured to be 198 °C for the gelator.
- UV-Visible Spectroscopy: The gel-to-gel transition through turbidity measurement was studied through measuring the transmittance of the hydrogel as a function of temperature from 25 to 70 °C on a Varian Cary 50 UV spectrophotometer. Dye absorption experiments were carried out at 25 °C at 463 nm (λmax of MO) and 588 nm (λmax of CV).
- *Differential Scanning Calorimetry (DSC):* The phase transition between the opaque and transparent gel and melting point of the gelator was measured by performing DSC measurements on a METTLER TOLEDO DSC 1 STARe instrument in triplicate under a
- N2 atmosphere in the temperature range of 30-90 °C at a heating rate of 2 °C min<sup>-1</sup>.

- *Scanning Electron Microscopy (SEM):* A gold-coated gel was dried at 25 °C and was analyzed for its morphology by a scanning electron microscopy instrument (Hitachi S-3400 N) operated at 15 kV.
- *Field Emission Scanning Electron Microscopy (FE-SEM):* A Hitachi S-4800 field emission scanning electron microscope (FE-SEM) operating at 5 kV was used to study the morphology of the opaque gel sample. The gel sample (20–30 mg) was dried under reduced pressure, coated (90 s, 2–3 nm thickness) with platinum, and then placed on a microscope cover glass.
- *Transmission Electron Microscopy (TEM):* A Philips CM-200 electron microscope working at an acceleration voltage of 200 kV was used to take the images of the opaque gel sample. The gel sample that is stained with 1% sodium phosphotungstate solution was deposited on the copper grid of 200 mesh size that was coated with the carbon Formvar.
- *Atomic Force Microscopy (AFM):* An atomic force microscope (Park XE 100) was used to investigate the morphology of the vacuum-dried (30 °C for 72 h) opaque gel sample by placing the dried gel sample on a microscopic glass.
- *FT-IR Spectroscopy:* The interaction involved in the phase transition from opaque to transparent was characterized through measuring the FT-IR spectrum of the partially dried gel samples (opaque and transparent) and solid C16EMorphBr sample on a Shimadzu FT-IR-8400S spectrophotometer. K)
- Small-Angle Neutron Scattering (SANS): SANS measurements for the gel samples were performed at sample temperatures of 25 and 50 °C on a Quokka (ANSTO, Australia). Data are presented as a function of the scattering vector, q, by using the incident neutron wavelength, λ, as where, a q range of 0.005–0.400 Ű–1 was selected with 2 and 14 m as the sample-to-detector distances and 5 Å (Δλ/λ =10%) as the incident wavelength. The experimental data were reduced from raw counts on the 2D detector to a radially averaged 1D scattering pattern with the assumption of radially isotropic scattering. The sensitivity of each detector pixel was calibrated by comparison of its response to a flat scattering was then radially averaged (accounting for instrument configuration) to provide the intensity as a function of q. The absolute intensity scale was provided by normalizing each sample by its thickness (1 or 2 mm) and then comparing to either the scattering from an empty beam measurement. The data modeling program SAS view was used to fit the SANS data.
- *Tensile Strength Measurement:* Tensile tests of the xerogel were performed on a Testometric M100-1CT instrument with a loading rate of 75 mm min-1. The specimen had a thickness of 2.5 mm and width of 20 mm. The gauge distance between the clamps was 7 mm. Cyclic loading-unloading tests were performed by loading the xerogel under tension to strains of 200 and 500% and then unloading to zero force.

# 4.4 Multifunctional self-healing Eutectogels induced by supramolecular assembly for smart conductive materials, interface lubrication and dye adsorption:

It describes a self-healing eutectogel that has multifunctionality such as high ionic conductivity and self-healing property which makes it potentially useful in a smart ionic conductor. The eutectogel also has corrosion resistance and showed good lubricating

performances on steel interfaces. In addition, the eutectogel showed excellent dye adsorption, effectively removing dyes from aqueous solutions[3] Deep eutectic solvents (DESs) are a special kind of ionic liquid formed by mixing a quaternary ammonium salt with a hydrogen-bond donor in a certain stoichiometric ratio, and the melting point is lower than that of the individual components. Like traditional ionic liquids, DESs have low volatility, good conductivity, low flammability, wide range of liquids, and electrochemical windows. They also have other advantages, including low cost, easy availability, and non-toxicity. These solvents are widely used in electrochemistry, material synthesis, separation and purification, and catalysis.[6]

X-DBS was synthesized by a condensation reaction between D-sorbitol and halogenated benzaldehyde. The gelation behavior was examined using the "stable to inversion of a test tube" method The gel-sol transition temperature was determined using a conventional ball-drop method. The xerogel was prepared by freeze-drying, followed by solvent exchange.[7]



Fig. 3 Chemical Structures of gelators X-DBS and DESs used.

*Gelation ability of X-DBS:* Five DES samples were prepared by mixing choline chloride (ChCl) and conventional hydrogen-bond donors (glycerol, ethylene glycol, monopropylene glycol, 1,3-propanediol, and urea) in a 1:2 M ratio. Then, the gelation performances of X-DBS were tested in the samples. The gelation behaviour, critical gel concentration (CGC) and gel-sol transition temperature (Tg) were determined to evaluate the gelation ability of the gelators in different DES samples. The storage modulus (G') and recovery rate were determined to examine the mechanical properties and self-healing ability.(fig-9) At the same concentration, the G' of the eutectogels formed by F-DBS in different DESs followed the order ChCl-urea > ChCl-Gly > ChCl-EG > ChCl-MPG > ChCl-PDO, and all the G' values exceed 104 Pa, indicating good mechanical strength of the F-DBS-based Eutectogels.

#### Injectable and Self-Healing eutectogel:

Self-healing properties of the eutectogels, continuous step-strain scanning measurement was performed by alternately applying 0.1% and 25% strain at a fixed frequency of 1 Hz). The eutectogel quickly and completely recovered their mechanical properties after the first damage. The rate and degree of recovery remained almost constant after three cycles, indicating that the F-DBS-based eutectogel is reversible and durable. The self-healing property of the eutectogel could also be observed with naked eyes. Three samples of eutectogels were connected to form one integrated block within 0.5 h, Indicating the selfhealing behavior. Notably, the F-DBS/ChCl-Gly eutectogel with a concentration of 2% could support a weight of 200 g, showing its load-bearing capacity Also, the viscosity of the F-DBS/ChCl- Gly eutectogel decreased gradually as the shear rate increased from 0 to 1000 s1, and its value gradually recovered to the initial state as the shear rate decreased, indicating the typical shear-thinning behavior and creep-recovery performance of the gel. These favorable properties endowed the eutectogel with injectability, thus, the F-DBS/ChCl- Gly eutectogel could be injected through a common syringe. The excellent properties of the eutectogels, including good mechanical strength, remarkable self-healing ability, and high electrical conductivity, make the eutectogels a promising multifunctional material with several applications. [3] Based on these results, we propose a feasible selfassembly mechanism for F-DBS in DES, as illustrated in (fig-11). DES can turn into supramolecular eutectogels by the addition of F-DBS (2% w/v), which self-assembles into nanofibers, forming supramolecular eutectogels. Upon mechanical damage, the hydrogen bonding interactions (between the C-F group and urea) located in the side chains of the fiber are weakened and broken in the damaged area, thereby reducing the strength of the gel. After removing the mechanical destructive force, the fibrous aggregates spontaneously diffuse and encounter again, reforming hydrogen bonds, and the eutectogel is repaired.[3]

#### Application of eutectiogel as an efficient material for dye adsorption:

Supramolecular gels have been proven to effectively remove various pollutants, such as dyes and oil spills from water[8], [9]. Moreover, as environmentally friendly and low-cost green solvents, DESs also show potential application performance in terms of dye adsorption. [10] Therefore, the FDBS-based eutectiogels are well suited to this "water purification" application as the filtration network of the gel matrix has a high surface area (as a consequence of its nanoscale structure, as verified by SEM and AFM) - which maximizes the potential interactions with pollutants.

# **4.5 Environmentally friendly eutectogels comprising L-Amino Acids and Deep Eutectic Solvents: Efficient Materials for Wastewater Treatment:**

Eutectogels are a new class of materials that can be used for wastewater treatment. They are made up of deep eutectic solvents (DESs) and L-amino acids. DESs are a type of ionic liquid that is made up of two or more components that form a eutectic mixture. L-amino acids are the building blocks of proteins and are biodegradable. The combination of these two materials creates a gel-like substance that can be used to remove pollutants from wastewater. The article explains that eutectogels have several advantages over other materials used for wastewater treatment. They are environmentally friendly, biodegradable, and can be easily synthesized. They are also efficient at removing pollutants from wastewater.[11]

The development of non-conventional solvents, driven by sustainable chemistry, has impacted also the field of gels, giving rise to gels in ionic liquids known as ionic liquid gels (ILGs) and, very recently, in deep eutectic solvents (DES), yielding eutectogels.[11], [12]

#### General procedure for the preparation of DES:

The suitable amounts of phenylacetic acid and choline chloride were weighed in a round bottom flask. The resulting mixture was heated at 60 °C for 30 minutes and stirred until obtaining a limpid liquid, which was then dried under reduced pressure at 60 °C for 1 h and kept in a desiccator over calcium chloride.[11]

#### General procedure for the preparation of eutectogels:

Gels were prepared by weighing into a screw-capped sample vial (diameter 1 cm) the suitable amounts of amino acid and DES. The sample vial was heated in an oil bath at 80 °C for 30 minutes, during which a clear solution was obtained. The vial was then rapidly cooled at 4 °C and then left to stand at room temperature. The tube inversion test method was used to assess gel formation.[11]

#### Tgel determination:

Tgel were determined by the falling drop method. A vial containing the preformed gel was placed upside-down in a water bath. The bath temperature was raised gradually (1 °C/ min) until the gel collapsed and flow was observed. Tgel values were reproducible within 1 °C.[11]

#### **Opacity Measurements:**

Opacity measurements were recorded with a spectrophotometer. The opacity of the gel phases was determined with UV-Vis measurements as a function of time, at a wavelength of 568 nm at 25 °C. Samples for a typical measurement were prepared by injecting into a quartz cuvette (light path 0.2 cm) the limpid hot solution of salt, recording spectra until gel formation. The gel phase obtained at the end of the measurement was stable after the tube inversion test.[11]

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#### Dye Adsorption tests:

Dye adsorption tests were firstly carried out in vials by placing onto the 250 mg of preformed eutectogel (3 wt %), 500  $\mu$ L of a 1.8×10-4 M aqueous solution of dye. After a given time, an aliquot of solution was withdrawn, suitably diluted, then the relevant UV-vis spectrum was recorded. Concentrations were obtained based on calibration curves obtained by measuring the absorbance of aqueous solutions of the dye at increasing concentrations. The removal efficiency of gels was also investigated in a gel column using a previously reported procedure. To this aim, 1g of eutectogel were placed on the bottom of a column, (Æ=4 cm), whose septum was previously covered with a layer of sand. Blank experiments assured that no dye was adsorbed by the sand alone. Then, 3 mL of aqueous solution of the dye was added from the top of the column. An out flow of discolored water from the bottom of the column was observed and it was introduced again in a next column containing another aliquot of gel. This procedure was repeated a third time when clear water out flowing from the column was observed. The experiment was performed under atmospheric pressure and at 25 °C.

# 4.6 Conclusion:

A new type of materials for wastewater treatment, which are gels made from natural or synthetic polymers and green solvents. These gels have many advantages over conventional adsorbents, such as low cost, easy synthesis, biodegradability, and recyclability. They can also be modified to enhance their adsorption performance and selectivity for different contaminants. The abstract suggests that these gels are promising materials for the development of sustainable and efficient wastewater treatment technologies.

# 4.7 Reference:

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# 5. Water Pollution: Unraveling the Genesis, Consequences, and Resolutions

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# 5.1 Introduction:

The sustenance of all life forms relied on the presence of water. Water plays a pivot role not only in household activities, but also remain fundamental for agriculture, industry, fisheries, tourism, and many more activities. However, expanding population, coupled with rapid urbanization and industrialization expansion has pushed the globe towards in a situation of water scarcity and limited water resources.

Additionally, the degrading water quality has been caused by the contamination of water resources with an increasing trend of pollution, which poses possible health risks and negative effects of water contamination. Water pollution has significant effects on numerous Sustainable Development Goals, highlighting how linked environmental, social, and economic issues are. By defending human health, maintaining ecosystems, advancing sustainable development, and creating international alliances, efforts to fight water pollution help fulfill a number of Sustainable Development Goals.

The chapter aims to delve comprehensively into diverse forms, sources, and impacts of water contaminants. Furthermore, detailed discussions encompass the key technologies followed in conjunction with the efforts of regulatory bodies engaged to resolving pressing concerns related with water contamination. The technological advancements are fundamental in enhancing water quality and safeguarding the sustainability of water resources.

# **5.2 The Basics of Water Pollution:**

In accordance with Section 2(e) of the Water Act, "Pollution is defined as any contamination of water, alteration of the physical, chemical, and biological characteristics of water, or disposal of sewage waste in the water that is likely to cause nuisance, renders the water harmful to public health or safety, domestic, industrial, or other legitimate uses, or is harmful to the life and health of the animals and aquatic plants".

Additionally, it denotes the presence of pollutants in quantities that could cause measurable degradation of the water quality or utility in rivers, lakes, bays, seas, streams, underground water, or oceans. For instance, due to an excessive presence of hazardous chemicals or bacteria, water deviates from its intended suitability, rendering it unfit for its designated purpose.

Most often, the use of water in different processes is subjected to contribute water contamination. Although certain types of water pollution can be brought on by natural phenomena, still majority are connected with anthropogenic activities, as depicted in Figure 5.1



Figure 5.1: Anthropogenic Activities and Water Pollution

When one or more of the factors listed below exceeds a predetermined concentration in water, it is considered to be polluted.

- *Physical parameters:* The physical criteria include appearance, odor, turbidity, flavor, temperature, and electrical conductivity (EC). Color and turbidity are visible symptoms of water pollution, while taste or smell of the water might serve as indicators, potentially representing its unsuitability for consumption.
- *Chemical parameters:* The concentrations of metal ions, carbonates, sulfur compounds, chlorides, fluorides, and nitrates are included in the chemical parameters.
- *Biological parameters:* Aspects like viruses, bacteria, microorganisms, yeast, algae, and fungi are included in the biological parameters. All aquatic forms are significantly impacted by the presence of toxins. Water contamination may lead to decline in population of both lower and higher flora and fauna. Therefore, the biological traits give a less clear view of extent of water contamination.

# **5.3 Sources of Water Pollution:**

Both natural and man-made factors contribute to water contamination adding pollutants into water bodies like rivers, lakes, oceans, and groundwater, imposing potential impacts on aquatic ecosystems and human health. Depending on the contaminants released into water bodies, the sources of water pollution can be divided in four different categories:





Figure 5.2: Sources of Water Pollution

- *Point Sources (PS):* These sources originate from a single, well-known source, such as a sewer or industrial outfall pipe. Manufacturing operations are frequently connected with point sources. Discharges from large animal feeding operations and water treatment plant pumps are also considered point sources (Dozier, 2005).
- *Non-Point Sources (NPS):* These sources originate from a variety of different or diffuse sources rather than from a single, recognizable point. Non-point sources of pollution can be originated from both urban settings like neighborhood yards and agricultural-producing regions like crop fields. These diffuse sources release contaminants into water bodies through runoff, adding pesticides and fertilizers from grounds and agricultural fields (Dozier, 2005).
- *Natural Sources:* A rise in the level of naturally occurring substances is also referred to as pollution. Such an increase is brought on by natural sources. Siltation, which is made up of dirt, sand, and tiny minerals, is one such natural source. A large number of aquatic bodies experience it as a common natural occurrence. Unchecked destruction makes the ground brittle, and floodwaters fill rivers, streams, and lakes with mountainous silt (Owa, 2013).
- Anthropogenic Sources: Anthropogenic or man-made sources of water pollution refer to human activities that cause water pollution. Anthropogenic sources include, residential (sewage and wastewater), industrial, and agricultural wastes that enter rivers, lakes, streams, and oceans. This category also includes specific substances that run-off water leaches from the soil and introduces to diverse water bodies (Owa, 2013).

Depending upon the nature and producers of pollutants, there are four types of water pollution sources:

- *Sewerage/Community wastewater:* Water contamination arises from the discharge of drains and sewers into freshwater ecosystems. Instances encompass substances like soaps, detergents, food wastes, and human and animal excrement. Urban areas are flooded with significant challenges imposed by the mismanagement of community wastewater.
- *Industrial wastes:* It includes waste or effluents produced by several industries in their process section and disposed into the environment after partially or fully treatment. The contamination water through industrial waste, may contain radioactive materials, poisonous compounds, acids, alkalis, metallic salts, phenols, cyanides, ammonia, and many other contaminants. They also contribute to the thermal pollution of the water, which have a greater potential to change the characteristics of water.
- *Agricultural sources:* Agrochemicals such as fertilizers (which contain nitrates and phosphates) and pesticides (which include insecticides, fungicides, and herbicides) also have a greater potential to contaminate the water at different surface water resources through run-off.
- *Thermal pollution or heat:* Thermal and nuclear power facilities, which utilize water as a coolant and generate hot water, are significant sources, contributing thermal pollution. The release of hot water into water bodies may cause the local aquatic life to perish.

# **5.4 Impacts of Water Pollution on Environment:**

The pollutants in the water impose a profound and far-reaching adverse impact on the environment, altering the entire ecosystems on disrupting the ecological balance, specifically in aquatic life. There would be hardly any aspect of the natural world remains untouched by the consequences of contaminated water bodies. Spillage of oil in coastal areas, stagnant water near to the industrial and urbanized area are the common instances of water pollution. Some forms of pollution are simple to spot and recognize. However, other kinds might not even be visually appeared until they start to create serious issues. Water in a lake, creek, or river may appear pure even if it is contaminated. The consequences of many forms of water contamination are intricate and frequently poorly understood. The similar pollutants may have various effects on different organisms, which depends on various factors including shelf life of pollutants, temperature, precipitation, water flow, etc. The impacts of water pollution on the environment are multifaceted and intricate, touching every aspect of aquatic ecosystems and beyond (Goel, 2006, Owa, 2013, Chaudhry and Malik, 2017).

Some of the key impacts of water pollution on the environment are described below:

• *Eutrophication:* The term "eutrophication" refers to an increase in chemical nutrients in the environment, typically in the form of nitrogen- or phosphorus-containing compounds. It could lead to an increase in primary productivity in addition to other negative effects such a lack of oxygen and severe losses in water quality, fish populations, and other animal populations.

- *Loss of Biodiversity:* A loss of biodiversity may come from the degradation of aquatic habitats brought on by water pollution. In addition to upsetting food chains and limiting species variety, polluted water can injure or kill aquatic plants, animals, and microbes.
- Ocean Acidification: Various anthropogenic activities caused release carbon dioxide into the atmosphere. The water becomes tainted as a result of dissolution of carbon dioxide in the oceans and seas, which lowers its pH and fastens acidification. The formation of calcium carbonate shells in shellfish and other aquatic life can be decreased due to ocean acidification, along with other physiological problems for marine life.
- *Habitat Destruction:* Water pollution causes sedimentation, siltation, and erosion, which physically modify or destroy aquatic environments. Fish spawning grounds, bird nesting grounds, and other crucial habitats are also harmed as a result of water pollution.

# 5.5 Effects of Water Pollution:

The water pollution impacted nature in two ways, as it poses harmful effect on living beings as well as the environment (Fig. 3). Insufficient access to clean water causes over 0.2 million deaths annually, according to the 2018 Composite Water Management Index (CWMI) study from NITI Aayog. In a separate report by NITI Aayog, it is projected that by 2030, over 600 million individuals, constituting approximately 40% of India's anticipated population, could potentially experience water scarcity.



Figure 5.3: Impacts of Water Pollution on human beings and environment

Water contamination exerts detrimental impacts on human well-being. Both surface water and groundwater are contaminated with pathogenic microbes causing compromised water quality, which pose risk to the human health. Additionally, the contaminated water affects nutritional balance of plants and animals and also influence the human health directly or indirectly (Haseena et al., 2017). The excess of nutrients like nitrogen and phosphorus along with other substances promote development of aquatic vegetation causing algal bloom and

quick weed proliferation. Ultimately, the natural equilibrium of water bodies is disrupted with changes in water's smell, taste, and occasionally color.

Furthermore, contaminated water can spread many diseases and cause a variety of health problems. contamination with various toxic substances like cadmium, arsenic, mercury, nitrates, fluorides, etc. causes a variety of issues in living things (Fazal-ur-Rehman, 2019). Itai-Itai disease, also known as ouch-ouch disease, is an achy condition of the bones and joints brought on by cadmium contamination. It also causes lung and liver cancer. Black foot disorders with symptoms including diarrhea and peripheral neuritis, as well as skin and lung cancer, can be brought on by arsenic poisoning. Mercury poisoning causes the element to be converted by bacteria into methyl mercury, which then undergoes biomagnification in the food chain and causes the deformity known as Minamata illness, which also causes meningitis, hemolysis, diarrhea, and even death. Blue baby syndrome or methemoglobinemia, both of which are caused by nitrate pollution and which are fatal for infants, reduces oxygen delivery. Fluoride can lead to fluorosis, which can cause dental issues as well as respiratory, neuromuscular, and gastrointestinal system malfunction (Halder and Islam, 2015, Lin et al., 2022).

#### **5.6 Water Pollution Control:**

Water pollution control is of paramount importance due to the short- and long-term consequences of water contamination on both the environment and human well-being. Water pollution control involves the implementation of measures and strategies to prevent, mitigate, and manage the contamination of water resources caused by various pollutants. The measures ultimately help to safeguards the environment, human health, and aquatic ecosystems. Moreover, employing a combination of regulatory actions, technological innovations, and community engagement may resulted to effective control of water pollution. The control and prevention are quicker and less expensive than cleanup, however, it is difficult to regulate pollution due to vast variety of pollutants their complexity. Cooperation between scientists, lawmakers, citizens, and industry produces the best methods for reducing pollution (Goel, 2006). A number of control strategies have been proposed to combat water contamination. The following steps are needed to be ensured for effective management of water pollution.

#### **Step 1: Implementing Control measures:**

As the initial phase of the process, activities polluting the water should be strictly controlled. The neighborhood ought to curtail practices like dumping sewage, untreated effluent and solid waste in water bodies and avoid using plastic bags. Society can take a variety of actions to put control on water pollution at their premises.

#### **Step 2: Wastewater treatment:**

Water treatment is the next stage in reducing the contamination level in water resources. By cutting down on water wastage, water contamination can be reduced. The contaminated water can be treated physically, chemically and biologically to remove impurities. The treatment process involves the following three stages:

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- Primary Treatment
- Secondary Treatment
- Tertiary Treatment



Figure. 4: Different stage of water treatment

**Primary Treatment:** This stage involves filtration, sedimentation and coagulation are used in the treatment process. The processes involving primary and secondary treatment typically followed to clean wastewater enough to discharge safely into the environment. The treatment must go at advanced level to make water safe for water intents and purposes like drinking water. The basic water treatment involves the following steps:

- A. *Sedimentation:* In the wastewater treatment facility, the sedimentation process is completed in enormous tanks that were created specifically for the task. The contaminated water is allowed to settle, allowing silt, clay, and other debris to fall to the bottom and the water to slowly drain. Fine particles must be eliminated in the following step since they do not settle.
- B. *Coagulation:* Coagulation is the process by which colloidal suspension and fine particles are mixed to form larger particles. Coagulants (also known as flocculants), such as potash alum, are used to complete the process. The large particles are either transferred in the following stage or sink to the bottom.
- C. *Filtration:* By running the water over a bed of sand, coal that has been finely divided, or other fibrous materials, suspended particles, flocculants, bacteria, and other organisms are filtered. Sludge refers to the total contaminants that were gathered in these procedures. It serves as a priceless fertilizer. It emits sludge gas on composting, which can be used in cooking or heating purpose.

**Secondary or Biological Treatment:** After primary treatment, the water is still unfit for drinking and must undergo additional purification. This is accomplished through a biological or secondary process. One typical technique is to spread contaminated water over

a sizable bed of stones and gravel to foster the growth of various bacteria that require nutrients and oxygen. A swiftly moving food chain develops over time. As an illustration, bacteria eat organic material from contaminated water, while protozoa feed on bacteria. Algae and fungi are examples of living forms that contribute to the cleanup effort. This is referred to as secondary water treatment. It entails the subsequent procedures.

- a. *Softening:* Hard water is treated in this way to get rid of unwanted calcium and magnesium cations. Water is either transported via cation exchangers or treated with lime and soda ash to precipitate  $Ca^{2+}$  ions as carbonates to softens the water.
- b. *Aeration:* By pumping air through soft water, oxygen is added to the water throughout in aeration process. This promotes the bacterial breakdown of organic material into safe byproducts like carbon dioxide and water. Oxygen reduces carbon dioxide, sulfur dioxide, etc., however treated water is still unfit for drinking. Therefore, it is necessary to eradicate the harmful germs with advanced treatment methods.

**Tertiary treatment:** Water is truly disinfected during the tertiary treatment. The most popular disinfectant for destroying germs is chlorine. However, chlorine also interacts with minute amounts of organic matter in water to create poisonous and potentially cancercausing chlorinated hydrocarbons. Therefore, it is preferable to limit the amount of organic material in water before introducing chlorine gas. Chlorine treatment is recommended over other disinfection techniques such ultraviolet radiation, ozone gas treatment, or reverse osmosis, considering the cost of treatment with other techniques.

In a treatment facility, the waste is sent through a number of chambers, screens, and chemical processes to lessen its toxicity and bulk. Most of the suspended particles and inorganic elements in sewage are removed during basic treatment. The secondary stage accelerates biological processes to remove organic material. When water needs to be reused, tertiary treatment is performed.

Here, 99% of the particulates are eliminated, and the water is subjected to a number of chemical procedures to ensure its purity.

#### **Step 3: Purification:**

To significantly eliminate pollutants and dangerous components from water, significant water purification activities should also be done. Here are some of the most effective water purification methods:

- *Boiling:* Boiling water for a long time is the simplest way to purify it. High temperatures force the bacteria and virus to vanish, purging the water of any contaminants.
- *Water Purifier:* The type of water filtration most frequently found in modern homes is an electric water purifier. The purest drinking water is produced by a water purifier using a multi-stage process that includes UV and UF filtration, carbon block, and contemporary water filtration technologies.
- *Distillation:* In order to ensure that the water is free of impurities, distillation involves collecting the condensed water after evaporation. This takes longer and removes minerals, thus it is less efficient than a RO filter.

#### **Step 4: Spreading awareness:**

After completing the above steps, raising awareness among the general public and disseminating information are essential for boosting participation in the endeavor to prevent water pollution. The concerted efforts of all communities to decrease water pollution can result in long-term improvements or maintenance of water quality.

#### **5.7 Measures Taken by the Government to prevent water pollution:**

The Indian government has started a number of programs to preserve and safeguard the nation's rivers and other bodies of water.

- **a.** National River Conservation Programme (NRCP): The National River Conservation Plan (NRCP), created by the Ministry of Environment and Forests (MoEF), aims to preserve rivers from pollution and improve water quality.
- b. **National Lake Conservation Programme:** The Ministry of Environment and Forests is implementing the National Lake Conservation Plan (NLCP) to manage, and conserve contaminated and degraded lakes in urban and semi-urban areas.
- c. **National Green Tribunal:** In compliance with the National Green Tribunal's instructions, the concerned States and Union Territories (UTs) are attempting to implement Action Plans for the restoration of water quality in the identified polluted stretches of rivers.
- d. Atal Mission for Rejuvenation and Urban Transformation: It is the goal of the Atal Mission for Rejuvenation and Urban Transformation (AMRUT) to provide every residence with access to a water tap with a dependable water supply and a sewer connection.
- e. **Jal Jeevan Mission:** The Jal Jeevan Mission (JJM), which was launched in August 2019, is being carried out by the Indian government in collaboration with the states with the goal of supplying drinking tap water to every rural home in India by 2024, including those in habitations where the water quality is poor (Singh et al., 2023).

For water pollution control, a comprehensive and well-coordinated strategy involving governmental organizations, businesses, communities, and individuals is required. Through the application of these strategies, community organizations can protect ecosystems, conserve water resources, and ensure that future generations will have access to clean and safe waters.

# 5.8 Summary:

Water quality is one of the most pressing issues that developed and developing countries are facing today, since it poses a threat to human health, reduces food production, interferes with natural processes, and slows down economic development. Water contamination is now having a severe impact on the whole community and is a global problem. The accidental release of household and agricultural residue, growing populations, overuse of fertilizers and pesticides, and industrialization are the main causes of water pollution. The wellness of people is negatively impacted by the transmission of viral, bacterial, and parasite illnesses through water that has been contaminated. Adopting adequate trash disposal procedures and treating waste prior dumping in water resources and consuming are vital. Awareness and learning initiatives at community level are also among the established step to maintain the uality of water.

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# 6. Chemical, Physical and Water Resources Management of The Geographical Locations Over

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# Abstract:

The modern economy is the resources based economy, and the development of a country or a region is based on the resources and especially on the natural resources. Retrival of the resources through scientific technology developments is main way to acquisition of the resources like water, air, heat, natural vegetation soil, Animals, metal, fossils etc. Depends on the resources availability, the resources were classified in to physical resources, forest, Agricultural, and Animal and fisheries resources. There are many parameters will be controls the enhancement and reduction of the each resources. Geographically the visakhapatnam district located beside the coast of Bay of Bengal and one of the north eastern coastal districts of Andhra Pradesh State and it lies between 17°15' and 18°32' Northern latitudes and 81°54 ' and 83°30' Eastern longitudes, The total geographical area of the district is about 11, 34, 282 hectares. The physical resources mainly controlled by the climate, soil and water. Physical resources will play major role in development in human life span and growth. Comprehension about the identification of physical resources and their management for future should be main concern in this paper. This study will be useful to sustainable development of resources in the district.

# Keywords:

Resources, Visakhapatnam, Andhra Pradesh, Physical, Animal, forest.

# 6.1 Introduction:

The modern economy is a resource-based economy and the development of a country or a region is based on Natural resources. Nature has given us abundant resources in the form of

water, air, heat, natural vegetation, soil, wild animals, metals, fossil fuels, etc. Man by his technical skill and knowledge is using all these resources in some way or the other right from the dawn of civilization. In the process of utilization of resources man often misuses its availability, thus affecting the natural ecosystem. In the context of present day shortage of available resources, a scientific inventory of these valuable natural resources and proper way of their utilization assume considerable importance. Responsible management of natural resources is essential to achieve sustainable development and livelihoods for present and future generations. Resource refers to the positive interaction between man and nature. Man improves his knowledge and develops new resources to meet his increasing demands. More recently the concept of natural resources has been broadened to include the total natural environment, that is, the entire surface layer of the Earth; because all parts of the Earth's surface are production of necessities and amenities that people demand. Thus from this point of view all living and non-living elements of the Atmosphere, the Oceans, and Earth too have valuable resources. All these resources are to be utilized scientifically and managed with care to provide necessities and comforts to the present and future generations.

The planet Earth holds a finite stock of resources and should vary through time and across space. **Zimmerman (Peach and Constantin** (1972) states: 'the word "resource" does not a substance, but a function that a thing or a substance may perform, or to an operation or 'as dynamic as civilization itself.' Each major human civilization was sustained by a particular set of resources and technologies for their exploitation (**Simmons 1996**). The archaeological record talks of the Stone Age, the Bronze Age and the Iron Age. In reference to the Industrial Revolution of the nineteenth century, **Simmons (1996**) states that: 'industrialization based on fossil fuel energy represents a turning point in the history of human-nature relations.' the twentieth century will be seen as the era of oil and gas. Natural resources are living and non-living components of nature which are being used by humans for meeting their requirements.

The natural resources are obtained only from Earth, what we called Earth resources. Natural resources may be classified in to (I) Biotic and Abiotic, (II) Exhaustible and Inexhaustible, (III) Potential and Developed Resources, (IV) Energy, Mineral and Agricultural Resources. Biotic resources nothing living and renewable resources which include Forests and their products, agricultural crops, animal fodder, and fishes Abiotic resources consist of non-living things and mostly non-renewable. Minerals and fossil fuels, Minerals are a biotic resources. These resources are exhausted by use while their rate of formation is exceedingly slow. Once these minerals, petrolium are taken out the

We cannot be replaced what we called Exhaustible. Resources which can be renewed by reproduction or by physical, mechanical, or chemical processes are known as inexhaustible resources like solar energy, water and human beings are examples of inexhaustible resources. The power that could be generated if all the water power resources in the country are used is known as its potential resources and hydroelectricity generated is known as a developed resource. The potential resources when they are developed by man. Human effort transforms the environment to satisfy the needs of man. The resources used as power to run various machines are known as energy resources. Electricity is becoming more important in the world's economy. Nuclear energy obtained from uranium and thorium is a modern source of energy.

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#### A. Recent Trends in Resources Development:

Man interacts with the elements of nature and thus transforms the natural endowments for his benefit. As wants and knowledge expand with time, man involves himself more and more in creating newer and superior resources. He has also invented machines which were, perhaps, rather simple in the beginning, and mass production of goods within a very short time. Almost every member of a modern society is getting the benefit of such resources.

# **B. Resource Management:**

The conservation of natural resources is a concept that deals with the rational use of resources. This is not only necessary to assure long-term resource use but also to protect the ecosystem. Now days, every country is very particular regarding its natural resources and tries to genuinely adopt conservation policies. Resource conservation is the scheduling of resources use so as to provide the greatest yield for the greatest number over the longest time period (**Haggett, 1972**). John F. Kennedy, in a special message to the Congress in 1962, interpreted conservation as "the wise use of our natural environment, the prevention of waste and despoilment while preserving, improving and renewing the quality and usefulness of all our resources'. Conservation of resources is essential for the survival of man. Conservation of resources has economic, aesthetic and scientific value for mankind.

# C. Sustainable Development:

The question of sustainable development has emerged due to overexploitation of resources and due to mismanagement of technology. The aspects which require monitoring of sustainability include climatic change, biodiversity, disposal of hazardous and toxic wastes, disposal of pollution generating industries and food and ecological security.

**Swaminathan** (1991) has identified nine principles for desired success in promoting ecologically-sound agriculture. They are (i) land, (ii) water, (iii) energy, (iv) nutrient supply, (v) genetic diversity, (vi) pest management, (vii) post-harvest system, (viii) systems approach, and (ix) location-specific research and development. With his technological and scientific skills, man has made rapid developments in agriculture, irrigation, mining, industries, transportation, forestry, land management and other areas. Unfortunately, in doing so, there has been much disruption of the functioning of natural environment. Now, people have begum to realize the side effects of the developmental activities and have started their efforts in minimizing these effects by adopting methods and technology for issues associated with development.

Sustainable development is the need of the present time not only for the survival of mankind but also for its future protection. On the technical level. Visakhapatnam district comprises of rich forests and more than 40 percent of the total geographical area is under forests. But in the recent years there is decline in the extent of forest cover and also degradation in the floral species due to anthropogenic activities. Agriculture is another important resource of the district and it is the main occupation of the people. Visakhapatnam is known for marine fisheries and large quantities of fish are being exported to foreign countries. Visakhapatnam is fast growing industrial city and experiences rapid urbanization. Except city region, the

rest of the 90 percent of study area is economically backward. Now, the government of India is trying hard to evolve a workable and acceptable strategy for developing the backward areas and allocating more funds for rural development programmes. For that, problems of each region should be studied to identify the areas of need and to make sound recommendations and land use including its landforms, climate, soils, forests, animals and agriculture. Hence, an attempt is made to assess resource base of the study area and possibilities of multiple uses of available resources for the development of the study region.

Many disciplines such as Environmental, Biological, Bio-geographical and Earth sciences have focused on the distribution pattern of natural resources and their conservation. Krishna Murthy (1980), discussed about the types of forests, forest products, relationship between forests, ecology and environment. Pushpa Kumar (1982) has analyzed wild life sanctuaries in Andhra Pradesh. Natarajan (1982) studied the resources and development of inland fisheries of Eastern Ghats. Some of the studies dealt with resources conservation and environmental management, which include Saxena (2007), Singh (2009), Dikshit (1991), and Sharma (1995). Prithwish Kumar Roy (2000) has analyzed the concept of resources and resource distribution both in India and the world. Bahuguna (1986) and venkata Reddy (1988) analyzed the degradation of forest areas and also assessed the impact of deforestation on environment and ecosystem. Sadhu singh (1980) Agarwala (1990) Sen Sarma (1993) and Singh and Sikka (1994) discussed about forest development and forest farming for improvement of forest resources in the country. Basil Hans has suggested a holistic approach in resource management for sustainable development. Ramakrishnan (2003) examines various possibilities of the studies analyzed the economic activities like development of forest based industries, employment generation, production of forest produces and possibilities for recreation development in forest areas. Deforestation and environmental degradation was discussed in detail by Savindra Singh (2004) Madhava Rao. Hermon (2003) has analyzed biological resources of India. Saxena (2007) has discussed about conservation of resources and sustainable development. Intensification of resource use and diversification of occupation pose serious challenges to balance economic for sustainable management of natural resources. International organizations like IGBP (International Geosphere & Biosphere Programme) have emphasized on resource management and sustainable development.

#### 6.2 Data and Methodology:

Visakhapatnam district is one of the north eastern coastal districts of Andhra Pradesh State and it lies between 17°15' and 18°32' Northern latitudes and 81°54 ' and 83°30' Eastern longitudes (Figure 1.1). It is bounded on the north partly by Orissa State and partly by Vizianagaram district, on the south by East Godavari district, on the West by Koraput district of Orissa and on the east by Bay of Bengal. The total geographical area of the district is about 11, 34,282 hectares and the total population of the district is about 38, 32,336 as per 2001 census. Administratively the district is divided into 3 Revenue divisions and 42 mandals including the urban and rural mandals of Visakhapatnam.

The study is primarily based on secondary data sources published by the time series data pertaining to natural resources, land utilization, area and production of principal crops, livestock and fisheries were obtained from the **Directorate of Economics** and Statistics.

Climatic data have been collected from the records of **India Meteorological Department**, Pune and also rain gauge stations located in the study region. The information about the distribution of forests, soils, crop yields, coffee plantation, sericulture and ground water potential in the study area have been collected from the **Departments such as Forest Department**, **Ground water Department**, **Coffee Board**, **Departments of Sericulture** and **Revenue Department** and **Planning and Statistics** department. Data pertaining to various aspects of resources have been collected from the records of **District Administration office**, and **Mandal offices**. The commonly used parameter for these studies is the coefficient of variability of rainfall given by the expression.

Coefficient of precipitation		Standard deviation	
Variability	=	Mean rainfall	x 100

These coefficients have been computed for all rain gauge stations in the study area and the rainfall variability Secondary data have been collected from **ground water department**, Visakhapatnam and water quality has been assessed. Based on this information, analysis of data was carried out and results are presented. The main aim of the study is o assess the resource potential of the study area particularly biotic resources. To analyze the general land use pattern of the study area. To study the physical resources including climate, soils and water resources. To find out ways to raise the existing resources to suggest measures for conservation and potential use of the available resources for sustainable development. In the present study, an attempt has been made to analyze climatic elements, rainfall and temperature and their seasonal distributions. A rainy day is defined by the **Indian meteorological department** as a period of 24 hours during which a total rainfall equal to or more than 2.5 mm is received.

# 6.3 Results and Discussion:

# A. Climate:

Climate is an active factor in the physical environment of all living things and human welfare range associated with climate change. Changing climate affects the frequency and intensity of weather events like floods, droughts, cyclones, heat waves and other disasters and in turn results in property damage, crop failures, famine or deaths. Therefore, climate plays a significant role in day to day life of man and economic activities of the people.

The study of precipitation distribution over the district is based on rainfall data collected from local rain gauge station shown in (Figure 1.2). The average annual rainfall in the district is 1082 mm and it increases from the coastal region towards the west and northwestern parts of the district which are hilly. The district gets rain both during the southwest monsoon and retreating monsoon seasons. The rainfall during the south-west monsoon months (June to September) amounts to 58 percent of annual rainfall and that during the post monsoon months of October and November amounts to 28 percent of the annual normal. September and October are the rainiest months each of which accounts for about 19 percent of annual rainfall. Significant rain of about 10 percent also occurs during the pre monsoon months of April and May. The mean annual rainfall distribution over the district

is shown in (Figure 1.3). The coastal plain receives rainfall between 950 mm and 1000 mm whereas the hilly region in the north and the west receives higher amounts of rainfall varying from 1150 mm to 1250 mm. The hill station, Araku gets the highest amount of 1265 mm of rainfall. The other high land stations, Dumbriguda receives 1224 mm of annual rainfall followed by Hukumpeta with 1200 mm of rainfall (Table 2.1). The isohyets run parallel to the coast in the plains towards interior and rainfall increases from the coast (950 mm) towards north (1250 mm). The rainfall distribution over the district during the four conventional seasons is shown in (Figure 1.4). The district receives the major portion of its rainfall from the south-west monsoon and higher amount of precipitation was recorded over entire region during south-west monsoon, compared to other seasons. Mean seasonal rainfall during the south-west monsoon varies from 550 mm along the coastal belt and 800 mm in the north due to orographic effect. The pattern of distribution of rainfall during this season is almost similar to annual pattern of rainfall. During the retreating monsoon season, the district exhibits different type of trends in distribution of rainfall. Coastal region receives higher amount of rainfall due to cyclonic activity. The rainfall decreases from 325 mm along the coast and 200 mm towards interior region. The two seasons seem to act in a complementary manner to each other in their spatial behavior, while the coastal stations receive less rainfall and hill stations receives higher rainfall in the south-west monsoon season; the former receives higher rainfall and less rainfall during the retreating monsoon. The rainfall maintained gradient towards the coast in the monsoon period and is towards interior during the retreating monsoon period. The district receives very meager amount of rainfall during winter and is the dry season. The rainfall varies from 25 mm in the east to 10 mm towards west. During the summer season, the region receives rainfall on account of convective activity. The rainfall pattern during this season resembles that of the south-west monsoon with lower rainfall amount i.e., 100 mm along the coast and increases towards interior and hilly regions where it varies between 150 mm and 200 mm.

#### **B.** Variability of Rainfall:

An important aspect of rainfall that determines its agriculture usefulness in any region is its variability which is a measure of its dependability or consistency. While preparing plans for agricultural development, this crucial aspect may be given special attention. is shown in (Figure 1.5). It is evident from the figure that the coastal areas have lower variability of 25% whereas interior areas have higher degree of variability of 30%. The highest coefficient of 35 is recorded in the north-west, hilly region of the district. It is a common observation that areas of high rainfall amounts have low rainfall variability and low rainfall areas have high variability. In the present study, however, it is interesting to observe that the highland stations which register high amounts of rainfall have higher variability compared to the coastal stations which receive lower rainfall. The lower coefficients of variability and greater rainfall dependability were observed in the coastal areas and higher coefficients and less rainfall stability in the interior areas.

# **C. Number of Rainy Days:**

On comparing the average number of rainy days per year in the district, coastal stations are found to experience less number of rainy days with 50 to 60 days per year where as hill stations have 70 to 80 rainy days (Figure 1.6). The trend resembles the yearly rainfall

distribution pattern which shows an increase from the coastal stations to the interior hilly stations. In order words, on an average, one day for every 7 days in the coastal zone and one day for every 5 days in the hilly zone may be expected to receive significant rainfall. This rainfall interpretation should useful to the Development of physical resources as soil.

# **D.** Temperature:

The Visakhapatnam district has various topographic diversities and long coastline determine the distribution with highest peak in May, which is the hottest month and the second peak in the month of September or October after the withdrawal of the monsoon. The temperature varies from place to place in the district during different seasons. In interior plains the temperature in summer are about 2°c to 3°c higher than in the coastal plains. But in the monsoon season this variation in temperature does not appear to be significant on account of the higher percentage of atmospheric humidity all over the district.

Similarly in winter the minimum temperature in the interior plains are lower than those on the coast by about two degrees which is due to the general dryness of the air in the interior and another reason is water body takes long time to cool down compared to land surface and hence higher winter temperature along cost. During May and the early part of June before the onset of the monsoon, the day temperature may occasionally exceed 43°c. There were cases when maximum temperature exceeds 45°c and people were subjected to discomfort due to heat wave conditions.

The average annual temperature is mapped and presented in Figure 1.7 It can be observed that the temperature decreases from  $26^{\circ}$ c along the coast to  $24^{\circ}$ c in the interior plains. The elevated regions in the north-west exhibit temperatures of less than  $24^{\circ}$ c and Araku valley in the north shows  $22^{\circ}$ c only. In the hilly tracts the temperature in general may be lower than in the coastal region by about a couple of degrees or so, depending on elevation. Figure 1.8 represents the temperature distribution during winter season.

The isotherms of the mean minimum temperature of the coldest month (December) show that the temperature decreases from  $18^{\circ}$  c along the coast to  $10^{\circ}$ c in the hilly region. Araku valley in the north records the lowest minimum temperature of  $8^{\circ}$ c in entire district. Mean maximum temperature of the hottest month Figure 1.9 shows that the highest temperature,  $36^{\circ}$ c prevails along the coast and it decreases slowly towards interior, foot hill zone and further low maximum temperature of  $32^{\circ}$ c in the hilly tracts in the north and north-west of the district. The general rule in the distribution of temperature i.e., temperature decreases with increasing distance from the sea coast is clearly exhibited.

# E. Humidity:

In study area the humidity decreases from the coast towards interior. The coastal stations like Visakhapatnam, Bhemunipatnam and Konada show higher percentages of relative humidity which vary from 75 percent to 85 percent whereas interior stations like Anakapalli and Chodavaram exhibit lower percentage of humidity varying from 55 percent to 75 percent. All the stations show high percentage of humidity during monsoon season.

# F. Wind:

Winds are generally light to moderate in speed with some strengthening during the summer and early south-west monsoon seasons. Wind direction and wind speed during different seasons at Visakhapatnam is shown by wind roses (Figure 1.10). The two main wind directions at Visakhapatnam are south-westerly during the south-west monsoon (summer) and easterly during the north-east monsoon (winter). The gales will occur during the cyclone season and wind speed varying from 20 to 60kms per hour (khr). The maximum percentage of calm condition occurs during winter period. Storms and depressions originating in the Bay of Bengal during the post monsoon season due to high temperature (>26°c) and strong winds during pre-monsoon season and heavy rains across the coastal zone of the district.

#### **G. Bio-Climatic Classification:**

The climatic data, monthly and annual rainfall and temperature have been analyzed as per the criteria laid down by **Koppen**. As the region is small and hardly exhibit climatic variation, the entire Visakhapatnam district may be broadly classified as Tropical Savannah (AW) climate. The general characteristics of this climatic type are the mean temperature of the coldest month is above 18°c and the rainfall in the driest month is less than 10-r/25 and the climate is hot and seasonally dry.

**Thornthwaite** scheme was also applied to identify bioclimatic types. The potential evapotranspiration is main parameter to understand the direct relation to growth and development of vegetation. Based on the computations from the water surplus, water deficiency, actual evapotranspiration from potential evapotranspiration, precipitation of any given station, the index of humidity and an index of aridity can be computed., moisture index can be derived. Using this water balance concept of Thornthwaite, moisture indices have been computed for all the stations under study to identify the climatic types of the Visakhapatnam district. As per the climatic classification of Thornthwaite under moisture regime, the district can be delineated into three climatic types, (Figure 1.11) moist sub humid ( $C_2$ ) along the hilly region, dry subhumid ( $C_1$ ) along the foot hill zone or interior plains and semiarid type of climate (D) along the coastal plains.

# 6.4 Soil Resources:

# A. Distribution of Soils in the Study Area:

Three types of soils can be distinguished in this district depending upon the parent rock formation. The main types of soils in Visakhapatnam district include red soils, alluvial soils and coastal sands. Black cotton soils are only at two places in negligible percentage (**Table 1.3 A**). They are brick red in clolour, coarse textured and of shallow depths less than one meter. These soils are acidic with pH ranging from 6.0 to 6.5. They are poor in humus, nitrogen and phosphate contents. Concretionary aggregates of both calcareous and ferruginous composition are commonly seen. These soils are generally found in and around Visakhapatnam, Chodavaram and Ananthagiri regions.

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The soils are grayish black to olive brown in colour. Usually these soils are of transformed nature, have uniform texture, high to medium plasticity and low to medium permeability. The pH is 7.0 to 8.0 and soil depth is over one meter, well supplied with plant nutrients, and rich humus. In the interior plains and foot hill zone the soils are red ferruginous loams and sandy loams in the hills and valleys, which support luxuriant growth especially of teak and its associates. At elevations above 1,000 meters the soils are bauxite ferrous, laterites supporting only grasses. Sandy soils of khondalites and quartzites which are brick red in colour and coarse textured. The third types of soils are coastal sand dunes of quartzites and these are highly permeable and porous with low organic nutrients.

In the hilly regions, red loamy soils are under a warm humid climate and weathering of parent rocks to brown to reddish, sandy to loamy type with frequent laterite rapping. The soils are medium to fine grained and essentially non-clay and hence susceptible to erosion particularly because of the undulating nature of the ground. The soils are deficient in lime, nitrogen and phosphoric acid and tend to be acidic. The soils in the broad valley are deep and the fertility status is moderately good when compared to the soils on the hill slopes. The lateritic soils though poor in fertility status respond readily to manuring and good cultivation. The fertility index or nutritional index is considered for determining the fertility of soils. The major indicators to determine the soil fertility is Organic Carbon (OC), phosphorous ( $P_2O_5$ ), and potassium ( $K_2O$ ). The concentration of organic carbon is low in the entire study area during 2009. (Table 1.3 B) Phosphorous concentration is low in the hilly region and it varies between medium and high ranges in the interior and coastal plains. Potassium concentration is high in hilly region and varies and also along the interior and coastal plains. When compared the fertility indices of soils of 2009 period with the values of 1998, the soils of study area have been loosing their nutrient values due to soil erosion. (Table 1.3 B) as the indices values are very low 2009.

# **B. Soil Degradation in Study Area:**

There are number of physical and cultural factors responsible for the depletion and erosion of soils, such as slopes, rainfall, temperature, wind, snowfall, and man's actions like deforestation, overgrazing and unscientific cultivation etc. Shifting cultivation is one of the environmental problems in the study area which is responsible for soil erosion in the forest areas of the district. Soil erosion due to run-off water is the main problem owing to the high intensities of rainfall and due to the vast elevation differences ranging up to 5,500 ft. from the sea level, the sea coast is also subjected to erosion due to sea waves. The erosion losses are much more in steep slopes which are generally situated in agency area and are aggravated where 'Podu' cultivation is in vogue which is the general practice in agency area. Because of the peculiar topography all types of soil erosion, viz., (i) Sheet erosion, (ii) Rill erosion, (iii) gully erosion, (iv) wind erosion and (v) wave erosion are noticed in this district. Run-off and internal drainage is excessive on the northern portion of the district and impeded of restricted in the middle and adjoining areas of Bay of Bengal. As regards soil conservation measures to be taken up in this district, it is necessary to take up graded bunding in about 4.20 lakh acres (areas with 1 to 10 percent slope), bench terracing in 0.24 lakh acres, gully control works in about 0.28 lakh acres and stone terracing in 0.25 lakh acres (area with 10 to 20 percent slope and where stones are available in plenty). Afforestation is to be done in 0.50 lakh acres and pasture development is about 0.14 lakh acres.

# C. Soil Conservation:

Under soil conservation programme in the study area, the district it is divided into six major catchments viz., (i) Champavathi, (ii) Gosthani, (iii) Narvagadda, (iv) Sarada, (v) Varaha and (vi) Thandava. These catchments can further be divided into sub-catchments to facilitate tackling the areas easily and effectively. Among these, the priority catchments are Thandava and Gosthani as there are already existing projects on these rivers.

# 6.5 Water Resources:

Most part of the study area is drained by Varaha and the rest by Tandava Rivers which are non-perennial. Much of the water is being wasted and flows down to the Bay of Bengal since there are very few projects of artificial drainage to tap this resource for use in dry periods. The normal annual rainfall in this area is 1202 mm. of this, during southwest monsoon (June to September) about 713 mm, northeast monsoon (October to December) about 295 mm, and during winter and summer periods (January to May) about 194 mm of rainfall are received. There are no major irrigation projects in the study area. The medium irrigation projects include Thandava, Konam, Raiwada, Kalyanapulova and Padderu reservoirs and the total net area being irrigated under these schemes accounts for 36,833 hectares (Table 1.4). The minor irrigation schemes include Ravanapalli, Ghamburamgedda, Seshugedda, Rangabolugedda and NTR reservoirs which include 2,211 hectares of irrigated area. Other sources of minor irrigation include dug wells, shallow tube wells and deep tube wells. The total area irrigated under principal crops is 183,192 hectares during 2007-2008. There are many minor irrigation tanks which are not able to irrigate the entire registered avacut areas because of heavy rate of siltation. The existing Machkund and Jalaput reservoirs also are getting silted up though at a reduced rate because of certain important soil conservation works executed in the watersheds. In order to protect these reservoirs and minor irrigation tanks soil conservation measures are to be taken up urgently.

In this district medium sized rivers and hill streams flow and hence perennial sources of irrigation are lacking. The major irrigation sources in this district are the rivers flowing in the district, the hill streams and irrigation tanks. The chief rivers in the district are Sarada, Varaha, Thandava, Gosthani, Champavati, and Meghadrigedda. River machkund also known as 'paleru' and 'sileru' flows on the northern border of paderu and chintapalle taluks and does not afford irrigation facilities. Amongst the rivers that flow, Sarada, Thandava and Varaha rivers provide maximum irrigation facilities in this district. There are two fresh water lakes viz., Komaravolu Ava and Kondakarla Ava which are although of not great depth have not dried up and proved themselves to be very useful for irrigation purposes.

The tapping of underground water through wells and tube wells is also very important. The use of underground water however lowers the water level in wells. Therefore the use of underground water has to be judicious and coordinated with the water supply available from other sources. The water table fluctuates on an average 3 meters between rain season and summer season. By and large shallow wells are common in Kondalites (5 m deep), moderate (5 m-8 m) in Charnockites, and deep (8m-15 m) in Quartzites. The supply of water in the hills is plentiful, moderate in the plains and poor along the narrow coastal belt. The pH of water turns more alkaline as one proceeds away from the hills.

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#### A. Water Resources in Hills and Foot Hill Zones:

There are many perennial streams in the hills and also in the plains. Due to high rain fall in Eastern Ghats the water supply is satisfactory in these areas and there is no scarcity for drinking water. The important perennial rivers are Sileru, Varaha, Thandva. In the Sileru Catchment area there is hydroelectric project at Machkund. For this project, reservoir is constructed at Jalaput which comes under Pedabayulu region. The flow of drainage is from north-west to south-east in accordance with the general slope of the land. Many of the hill streams in Chinthapalli drain into Sileru River, which in turn joins Sabari, a tributary to river Godavari. The Varaha River drains the areas of Chinthapalli, Narsipatnam and joins the sea at Revu-Polavaram. The Thandava River drains the Gudem agency, Chinthapalli and Golugonda plains and joins the sea at Pentakota. The catchment areas for most of the rivers are the groups of hills. There are few major tanks and many minor irrigation tanks in the area. Depth of water table varies considerably and leaves no relation to the proximity of sea or a perennial water source.

There is good number of small tanks in the forests. They retain water for some part of the year and dry up mostly in summer. Bore wells are laid in villages. These cater to the water needs of the villages. Undulating character of the terrain of this district lends itself favourable to irrigation from tanks and wells. A number of tanks and reservoirs are the sources of irrigation in the district. In the last 15 years, 3 medium irrigation projects have been constructed viz. Raiwada, Konam and Kalyanalova. Consequently, ground water table has increased in the command area of these reservoirs.

# **B.** Ground Water Quality:

An attempt has been made to analyze the ground water quality in the study area. Table 1.5(B) shows, the physico-chemical characteristics of ground water samples which were obtained during summer season of 2009. All the chemical constituents are expressed in mg/L (milligrams/liter) except pH. The pH of ground water in this study area is varying between 8.1 and 8.6 and they are within desirable limits. TDS values are varying from 133 mg/L in hilly area to 413 mg/L in the coastal plains. Rambabu and somasekhar Rao, 1996 have expressed that the dissolution of soil particles containing minerals under slightly alkaline conditions favors in increasing the TDS concentration in ground water. TDS value above 1500 mg/L cause gastrointestinal irritation according to Bhavani Sankar and Muthu Krishna, 1994. In the present study TDS values were within permissible limits. Hardness is an important criterion for determining the usability of water for domestic, drinking and industrial purposes. Total hardness of ground water in the study area varies from 153 mg/L in hilly areas to 413 mg/L in coastal plain areas. The acceptable limit of total hardness for drinking water is specified as 300 mg/L. The hardness of the water is due to the presence of calcium and magnesium. However, iron, strontium, barium, manganese and aluminum also contribute to hardness (Saritha et.al, 2009). It was observed that the water samples from interior plains and coastal plains exceeded desirable limits (Table 1.5 (A). Chloride concentrations are varying from 14 mg/L in hilly region to 140 mg/L in interior plains. The limit of chloride concentration for drinking water is 250 mg/L. Chloride concentration of the ground water is within the permissible limits in the study area. Fluoride concentrations vary from 0.1 to 0.3 mg/L and they are within permissible limit of 1.0 mg/L and ground water is free from fluoride pollution. Calcium concentrations of the ground water ranged between 5 mg/L in hilly region and 74 mg/L in coastal plains. The limit of calcium for drinking water is specified as 75 mg/L (Table 1.5(A). It was observed that the calcium concentrations are within permissible limits in all the regions of the district. Magnesium concentrations are varying from 16 mg/L in hilly region to 70 mg/L in interior plains and upland regions. The limit of mg concentration for drinking water is specified as 30 mg/L. Magnesium content in the water does not have any health hazard. But it contributes to hardness in water. It was observed that mg concentration crossed the permissible limits both in interior plains and coastal plains.

# C. Changes in the Levels of Ground Water:

Data with regarded to ground water levels in the study area and changes over a time period of 20 years are presented in (Table 1.5). The average depth of water levels from the ground level has been relatively higher in the hilly region when compared to other regions of the district both in pre-monsoon and post-monsoon seasons. It is also observed that the depths of water levels are showing an increase between 1989 and 2009. In hilly region the depth of ground water level increased from 10.85 m to 11.13 m in pre-monsoon season and the same trend is observed in post-monsoon season with an increase from 6.69 m to 9.32 m. between 1989 and 2009. Same trend was observed both in interior plains and coastal plains. The average depth of wells is increased from 5.37 m to 5.6 m in pre-monsoon season and from 2.87 m to 3.67 m in post-monsoon season in interior plains whereas the increase is from 4.6 m to 5.7 m in pre-monsoon and from 2.7 m to 3.8 m in coastal plains during 1989 -2009. It can be observed that in respect of post-monsoon season all the regions show a steady increase in the depth of water levels over a period of 20 years. There is an increase in depth of water levels during pre-monsoon season also but significant increase is observed during post-monsoon season between 1989 and 2009. This may be due to poor recharge of ground water which may be attributed as rapid changes in vegetation cover.

# **D. Management of Water Resources:**

The water distribution system should be such that loss of water should be minimum and it should remain free from pollution. A few general steps for distribution of water are: As far as possible water distribution be done through pipes so that loss will be minimum and water will remain free from pollutants. The channels and distributors of canals should be cemented, and in fields also either pipes be used or cemented channels be constructed. For irrigation, sprinkle and drip system be used. If possible, water tanks should be covered to avoid evaporation and also for cleanliness.

The overexploitation of underground water often results in the lowering of water table, intrusion of saline water, subsidence of land, etc. the prime need is the proper and limited use of water and also geological and hydrological survey of the region for assessment of water availability. The system of the recycling of water is used so that waste water can be used for irrigation purposes. The loss of vegetation is also a cause of drought and reduction of rainfall and indirectly a cause of lowering of the water table. In order to maintain humidity in the atmosphere which helps in rainfall and to minimize evaporation rate forest cover should be maintained.

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#### **E. Protection of Water from Pollution:**

Apart from availability of water, quality of water is also important, in other words water should be free from pollution. The nature and types of water pollution and its effects have been discussed. Nowadays, several techniques such as Physico-Chemical purification methods, hydrolysis, electrolysis, ion-exchange, absorption, chlorination, ozonisation, etc., are in use. Similarly, biological purification method is also in use. The conservation of water can be done only through proper water management system. Apart from above mentioned measures though expensive, water can be obtained from desalination of sea water and even by artificial rainmaking. Apart from conservation of water, mutual cooperation in use of water resources is necessary.

# 6.5 Acknowledgements:

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$1 a \mathcal{O} \mathcal{O} \mathbf{O} \mathbf{O} \mathbf{O} \mathbf{O} \mathbf{O} \mathbf{O} \mathbf{O} \mathbf$	Table 1.	.1: Tempo	oral variation	of Land	utilization in	Visakhapatnam	district
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Sr.	T J	Visakhapatnam (% to total geog. area)				
No	Land use categories	1987- 1988	2007- 2008	change in percentage		
1	Forest	41.8	39.53	-2.27		
2	Barren and uncultivable land	16.9	11.68	-5.22		
3	Land put non agriculture uses	7.0	9.22	+2.22		
4	Cultivable waste land	1.2	1.0	-0.2		
5	Permanent pastures & Grazing land	0.4	0.29	-0.11		
6	Tree crops	1.8	3.05	+1.25		
7	Other fallow land	1.3	2.8	+1.5		
8	Current fallow land	7.8	4.39	-3.59		
9	Net sown area	21.8	27.96	+6.16		

# Table 1.2: Visakhapatnam District - Seasonal and Annual Rainfall (Mm)

	Mean Seasonal Rainfall						
Sr. No	Station	Southwest monsoon (A)	Retreating monsoon (B)	Winter season	Summer season	Mean annual rainfall	
				( <b>C</b> )	( <b>D</b> )		
1	Chinthapalli	783.2	200.9	16.0	182.8	1,182.9	
2	G.K. Veedhi	818.0	195.0	12.0	163.0	1,188.0	
3	Paderu	762.0	219.0	13.0	185.0	1,1993	
4	G. Madu gula	762.0	211.0	15.0	176.0	1,164.0	
5	MunchingTut	785.0	197.0	8.0	170.0	1,160.0	
6	Pedabaval u	780.0	229.0	8.0	177.0	1.194.0	
7	Hukumpeta	772.0	241.0	9.0	178-0	1,200.0	

	Mean Seasonal Rainfall								
Sr. No	Station	Southwest monsoon (A)	Retreating monsoon (B)	Winter season	Summer season	Mean annual rainfall			
				( <b>C</b> )	( <b>D</b> )				
8	Araku	8004	235.0	9.1	220.3	1,264.8			
9	Ananta.,Iri	745.0	241.0	15.0	170.0	1,171.0			
10	Dumbriguda	786.0	235.0	8.0	195.0	1,224.0			
11	Madugula	703.0	281.0	21.0	159.0	1,094.4			
12	Narsipatnam	676.2	281.9	27.1	180.4	1,165.6			
13	Rolugunta	705.0	307.0	26.0	160.0	1,198.0			
14	Kotauratla	605.0	283.0	27.0	110.0	1,165.6			
15	Makavarapalem	633.0	287.0	28.00	141.0	1,089.0			
16	Nathavaram	730.0	274.4	18.0	144.0	1,166.0			
17	K. Kotapadu	635.0	283.0	25.0	121.0	1,064.4			
18	Chodavaram	630.9	284.8	24.7	124.0	1,064.4			
19	Butchiahpeta	648.0	296.0	23.0	130.0	1,097.0			
20	Padmanabham	595.0	302.0	28.0	93.0	1,018.0			
21	Kasimkota	560.0	300.0	27.0	100.0	987.0			
22	Subbavaram	585.0	303.0	26.0	94.0	996.1			
23	Paravada	545.0	311.0	28.0	77.0	961.0			
24	Pendurthi	570.0	304.0	27.0	82.0	948.0			
25	Anandapuram	552.0	309.0	28.0	85.0	974.0			
26	Elamanchili	533.1	296.3	28.7	110.4	958.5			
27	Atachuthapuram	529.0	320.0	28.0	76.0	953.0			
28	Anakapalli	579.6	294.9	26.3	95.3	996.1			
29	Bheemunipatnam	514.4	330.3	30.0	84.0	951.5			
30	Visakhapatnam	521.0	323.9	27.8	75.3	954.3			

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a N	Name of the Mandals	Predominant S	Predominant Soils (%)				
Sr. No:		Sandy Loam	Red Loamy	Black Cotton			
1	Chinthapalli	0	92	0			
2	Paderu	0	55	40			
3	G.Madugula	0	100	0			
4	Munching put	0	100	0			
5	Pedabayulu	0	84	0			
6	Araku	0	78	0			
7	Ananthagiri	0	95	0			
8	Koyyuru	60	29	0			
9	Madugula	69	0	0			
10	Narsipatnam	40	36	0			
11	Kotauratla	0	100	0			
12	K.Kotapadu	40	0	40			
13	Sabbavaram	0	72	0			
14	Ravikamatham	40	45	0			
15	Pendurthi	0	84	0			
16	Nakkapalli	0	84	0			
17	Elamanchili	40	36	0			
18	Kasimkota	0	52	0			
19	Bhemunipatnam	36	61	0			

Table 1.3(A): Distribution Soils in Visakhapatnam District

 Table 1.3(B): Fertility Index of Soils

Sr. No	Stations	Organic Carbon (OC)		Phosphorous (P <sub>2</sub> o <sup>5)</sup>		Potassium (K <sub>2</sub> 0)	
		1998	2009	1998	2009	1998	2009
1	Hilly region						-
	Ananthagiri	1.42	1.15	1.90	1.63	2.67	2.57
	Paderu	1.15	1.14	2.42	1.57	3.00	2.38
	Chinthapalli	1.01	1.00	1.65	1.09	2.96	2.83
2	Interior Plains						
	Narsipatnam	1.40	1.03	1.87	1.57	2.46	2.82
	Chodavaram	1.07	1.16	2.65	2.25	3.0	2.29

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Sr. No	Stations	Organic Carbon (OC)		Phosph (P <sub>2</sub> o <sup>5)</sup>	Phosphorous (P <sub>2</sub> o <sup>5)</sup>		Potassium (K <sub>2</sub> 0)	
		1998	2009	1998	2009	1998	2009	
3	Coastal Plains							
	Elamanchili	1.16	1.09	2.76	2.24	2.96	2.38	
	Anakapalli	1.47	1.11	2.57	2.48	2.87	2.16	
	Visakhapatnam	1.42	1.11	2.67	2.45	2.96	2.32	

(**Source:** Soil Testing Laboratory & Dept of Agriculture Research Centre, Anakapalli, Visakhapatnam District)

Limits:	Low Fertility <1.16
	Medium Fertility 1.16 to 2.33
	High Fertility >2.33

# Table 1.4: MAJOR AND MEDIUM IRRIGATION SOURCES-2007-2008

# (Area in Hectares)

Sr. No	Irrigation Source	Name of the Project	Actual Net Area Irrigated
1	Major Irrigation		
		a) Thandava Reservoir	15896
		b) Konam Reservoir	4931
2	Medium Irrigation	c) Raiwada Resrvoir	6074
		d) Kalyanapulova Reservoir	2113
		e) Padderu reservoir	7819
		a) Ravanapalli Reservoir	1053
3		b) Gambheeram gedda Reservoir	104
	Minor Irrigation	c) Seshugedda	101
		d) N T R Reservoir	809
		e) Rangabolugedda Reservoir	144

(Source: Irrigation Department, Visakhapatnam.)
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Demonstern	ISI		WHO		
Parameter	Permissible	Excessive	Permissible	Excessive	
pH value	6.5-8.5	6.5-9.2	7.0-8.5	6.5-9.2	
TDS	500	2000	500	1500	
Hardness	300	600			
Chloride	250	1000	200	600	
Fluoride	1.0	1.5	1.5		
Calcium	75	200	75	200	
Magnesium	30	100	50	150	

Table 1.5(A): STANDARDS FOR DRINKING WATER

# Table 1.5 (B): Physico- Chemical Characteristics of Ground Water Samples in Visakhapatnam District

Samples	Hilly Region	Interior Plains	Coastal Plains
pH Value	8.4	8.1	8.6
TDS	133	380	413
Hardness	153	440	340
Chloride	14	140	65
Fluoride	0.1	0.1	0.3
Calcium	45	60	74
Magnesium	16	70	55

#### Table 1.6: AVERAGE DEPTHS OF WATER LEVELS (meters)

	Hilly Region		Interior Plains and Uplands		Costal Plains	
Years	Pre- monsoon (May)	Post- monsoon (Nov)	Pre- monsoon (May)	Post- monsoon (Nov)	Pre- monsoon (May)	Post- monsoon (Nov)
1989	10.85	6.69	5.37	2.87	4.6	2.7
2009	11.13	9.32	5.6	3.67	5.7	3.8

Source: Ground Water Board, Visakhapatnam District.



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Figure 1.2: Visakhapatnam district-locations of rain gauge stations



Figure 1.3: Mean Annual Rainfall (mm)









Figure 1.5: Annual Variability of Rainfall (%)



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Figure 1.6: Mean Annual Rainy days



Figure 1.7: Mean Annual Temperature (°C)

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Figure 1.8: Mean Minimum Temperature of the Coldest Month (°C)



Figure 1.9: Mean Maximum Temperature of the Hottest Month (°C)



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Figure 1.10: Visakhapatnam – Wind Roses



Figure 1.11: Climate Types (As per moisture index of Thornthwaite)

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#### 6.7 Tables & Figures Captions:

Table 1.1: Temporal variation of Land utilization and changes in percentage of land with respect to total geographical area in Visakhapatnam district during 1987-98 and 2007-2008.

Table 1.2: Indicates the mean seasonal and Annual Rainfall (mm) rainfall during the A). South west monsoon, B). Retreating monsoon, C). Winter Monsoon, D). Summer Monsoon of the Visakhapatnam District through cyclone warning centre, Visakhapatnam.

Table 1.3(A): The table indicates the percentage Distribution soils (sandy loam, red loamy, black cotton) at 19 mandels at Visakhapatnam district.

Table 1.3 (B): Fertility Index of Soils: This table indicates the concentration of fertility index of soils like Organic carbon (OC), Phosphorous  $(P_2o^5)$ , Potassium (K<sub>2</sub>o) at three stations 1). Hilly region, 2). Interior Plains, 3). Coastal Plains during 1998-2009 periods.

Table 1.4: This table indicates the major projects were conducted for three irrigation resources 1). Major 2). Medium 3). Manor for the area of land in hectares during 2007-2008.

Table 1.5 (A): This table indicates the Standards chemical (Permissible/excessive) concentration for Drinking Water from ISI and WHO (World Health Organization, Geniva)

Table 1.5 (B): This table indicates the Physico-m Chemical Characteristics of the ground water sample at 1). Hilly region 2). Interior Plains, 3). Coastal Plains in Visakhapatnam District.

Table 1.6: This table indicates the Average Depths of Water Levels (Meters), at premonsoon and post monsoon seasons during 1989-2009 periods, over 1). Hilly region, 2). Interior Plains and Uplands, 3). Coastal Plains.

#### Figures Captions:

Figure 1.1 The pie diagram indicates Land utilization in Visakhapatnam district Green color indicates the Forest land, Yellow color indicates the Net area sown, grey colure indicates the barren and unculturable land, merin color indicates the land put Non- Agriculture uses etc. In this diagram East Godavari district located at South-West direction and Vizianagaram located at North-East direction, Odessa located West to North –East direction.

Figure 1.2 This figure indicates the locations of rain gauge stations including 42 mandals in Visakhapatnam District, Right side down scale indicates in map one unit Equal to one kilometer in ground. The upper right symbol indicates the Map directions of the Figure.

Figure 1.3. This figure indicates Mean Annual Rainfall (mm) including 42 mandals in Visakhapatnam District, Right side down scale indicates in map one unit Equal to one

kilometer in ground. The upper right symbol indicates the Map directions of the Figure. The blue color lines indicate annual Isopitches (equal rainfall lines) in (mm).

Figure 1.4 Indicates the seasonal (monthly) rainfall (mm/month) variability during. Summer winter treating monsoon seasons over Visakhapatnam district. The blue lines indicates the (isohyets) over district.

Figure 1.5 indicates the annual (yearly)-(mm/year) variability of rainfall over Visakhapatnam district. From 2008-2009, one unit shows in ground one kilometer.

Figure 1.6 the Mean annual rainy days from 2008-2009 one unit over the ground indicates one kilometer. Upper right symbol indicates the direction of the Map.

Figure 1.7 Figure indicates mean annual temperature (<sup>0</sup>C) over the Visakhapatnam district the red lines indicates isothermal lines. One unit shows in ground one kilometer. one unit over the ground indicates one kilometer. Upper right symbol indicates the direction of the Map.

Figure 1.8 Indicates the mean minimum temperature of the coldest month(December) (<sup>0</sup>C) the red lines shows isothermal lines over the district. one unit over the ground indicates one kilometer. Upper right symbol indicates the direction of the Map.

Figure 1.9 Mean Maximum temperature of the hottest month (May) the red lines indicates the isothermal lines over the district. one unit over the ground indicates one kilometer. Upper right symbol indicates the direction of the Map.

Figure 1.10 Wind rose are ) Summer 2) Winter 3) South-west 4) north-east monsoon.

Figure 1.11 This figure indicates the climate types (As per moisture index of Thornthwaite) C1 -Dry sub humid, C2- Moist sub Humid, D-Semi-arid

## 7. Organic Pollutants: Impacts and Degradation Methods

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#### Abstract:

The presence of organic pollutants, such as organochlorine pesticides, halo hydrocarbons, polybrominated diphenyl ethers, polycyclic aromatic hydrocarbons (PAHs), dyes, and petrochemical products, has become a growing environmental concern due to their detrimental health effects. Despite the global ban on certain classes of organic pollutants, they continue to be produced through both intentional and unintentional industrial activities. Given their chronic impact, it is imperative to monitor and remediate these pollutants. This chapter provides an overview of the current status of methods for degrading organic pollutants in water and soil. Specifically, biological, physical, chemical, and advanced oxidation processes for treating organic pollutants are discussed. Additionally, emphasis is placed on understanding the physiochemical properties of these pollutants in the presented matrix to identify optimal solutions for their removal. Furthermore, the impacts of organic pollutants on human health and the environment are also discussed, highlighting the importance of raising awareness and minimizing their uses.

#### Keywords:

Organic pollutants, sources, impacts, health, and degradation.

#### 7.1 Introduction: Organic Pollutants:

Due to the increased industrialization, a variety of natural activities, and uncontrolled human willingness, chemical pollutants have infiltrated the soil, water, and atmosphere worldwide [1].

Organic pollutants are synthetic chemicals that originate from industrial activities and a lack of proper management. These pollutants are typically classified based on their boiling points [2], which reflects their chemical properties and ecological fate, as well as the diagnostic methods used for their detection. Organic pollutants encompass a range of organic compounds, including methane, propane, butane, benzene, and xylene, among others. The primary sources of these pollutants are agricultural activities, petrochemical industries, and organic solvents. While gases such as methane, ethane, propane, and butane are not classified as organic pollutants, their halogenated derivatives fall under this category. Organic pollutants include a diverse array of industrial chemicals, petrochemicals, pesticides, phenols, carbonyl compounds, ethers, aliphatic and aromatic esters, anilines, pyridines, and many others [3].

These pollutants are present in trace concentrations in various matrices, including soil, water, sediments, and air. Due to their persistent stability in the environment, bioaccumulation potential, long-range transportability, and environmental toxicity, they are internationally recognized as persistent organic pollutants [4].

#### 7.2 Effect on Health and Environment:

Organic pollutants have a tendency to accumulate in the environment through the food chain, owing to their high fat solubility. Consequently, they are typically found at elevated concentrations in fat-containing foods such as milk, eggs, fish, and meat, resulting in their subsequent accumulation in the human body. Organic pollutants can be categorized as polycyclic aromatic hydrocarbons (PAHs), perfluoroalkyl and polyfluoroalkyl substances (PFASs), pesticides (halogenated organic compounds), brominated flame retardants (BFRs), and so forth [5]. These pollutants are known to have deleterious health effects, including abnormal growth, brain malfunction, hormonal imbalance, metabolic disorders, and others [6, 7]. Chronic exposure to organic pollutants may also result in immunological effects [8], type 1 immune responses [9], allergy epidemics [10], asthma [11], cancer, reproductive defects, diabetes, and so on.

#### 7.3 Sources of Organic Pollutants:

Fire is considered to be the definitive foundation of organic pollutants, which can result from intentional, accidental, and premeditated burning of flora [12]. These pollutants are known to enter the atmosphere due to human-originated activities, such as various industrial sources, power stations, transportation, evaporation from soil and water surfaces, heating posts, domestic heaters, landfill transference, and usage of agronomic posies. In addition, the causes of organic pollutants can be attributed to uncontrolled chemical amenities, forestry fires, PCBs waste decay, and other factors, which originate from various sectors such as constructions, evaporation, cement trades, coal ignition, oil combustion, and reprocessing actions, municipal incineration, organochlorine pesticide plants, aluminum secondary plants, furnace and foundry coke construction, plants dangerous waste/plastic waste in landfills, organochlorine pesticide storage, and sewage sludge [13]. Natural events, including volcanic activities and forest fires, are also known to release dioxins and dibenzofurans, which contribute to organic pollutants. The wastewater and runoffs from plants or using organic pollutants, as well as atmospheric depositions, are the primary sources of accumulation of organic substances in environmental matrices, including soil, water, and sediments. Marine ecology serves as the principal reservoir for these pollutants, where they can accumulate through various means, such as river orientation and environmental settling. Generally, they are deposited over cradles of different sediments of water bodies, where they can be released after a period and reintroduced to the atmospheric region [10].

#### 7.4 Degradation Methods for Organic Pollutants:

Conventional methods of remediation, including incineration, chemical metal reduction, solvent extraction, ground filling, and stabilization or solidification, are employed to eradicate organic pollutants from soil and sand residues. However, the management of such

intricate infrastructure and the employment of skilled personnel with expertise in operating analytical instruments pose a significant challenge due to their exorbitant cost. Moreover, these methods are not entirely effective in eliminating toxic organic pollutants [14]. Consequently, alternative approaches are utilized to achieve complete elimination of organic pollutants as follow:

#### 7.4.1 Biological (Biodegradation) method:

One method i.e. biodegradation can get rid of the toxic organic compounds more effectively from water and soil through applying microorganisms [15]. The biodegradation system works without affecting the other parameters and does pure the environment. The naturally existing microorganism degrades the typical chemical substances into smaller non-harmful through a process called bioconversion [16, 17].

The technique offers excellent outcomes in terms of eco-friendliness, prominence, effectiveness, and economical acceptability over previous traditional techniques.

Several microorganisms, including bacteria, fungi, and algae, have been reported to play a significant role in the transformation and remediation of toxic organic pollutants. Among these microorganisms, Bacillus has been found to be particularly effective [18].

Various techniques, such as biostimulation, biosparging, bioaugmentation, and bioventing, have been employed to eliminate organic contaminants. Bioventing involves aerating the soil and water to facilitate the subsequent biodegradation of organic substances [19, 20].

Biostimulation involves the conversion of pollutant substances and the addition of other nutrients to the medium to maintain a balanced pH ratio and C:N:P ratio, which supports soil microorganism activities [21]. Bioaugmentation involves the insertion of microbial groups, such as bacteria or fungi, and other biocatalysts, such as genes or enzymes, to facilitate the degradation of organic/inorganic toxic compounds [22].

In bioremediation, both aerobic and anaerobic conditions are applied for pollutant degradation. Aerobic conditions require molecular  $O_2$ , such as mono- and dioxygenase, to act as an electron acceptor and co-substrate. In contrast, anaerobic conditions only require the presence of electrons for microorganisms to transform and degrade molecule assemblies into  $CO_2$ ,  $H_2O$ , and inorganic compounds (salts). Chlorinated compounds that are difficult to degrade are generally subjected to anaerobic conditions for their degradation [23].

A varied community comprising molds, yeast, and filamentous fungi is predominantly employed in the degradation of organic pollutants. Fungi possess the ability to enhance soil permeability and ion exchange strength, thereby facilitating the further decontamination of soil from pollutants. Several fungal species, such as Fusarium oxysporum, Trametes versicolor, and Phanerochaete chrysosporium, have been documented for their ability to degrade persistent toxic pollutants, including DDT, through the utilization of oxidation/reduction mechanisms. The exploration of diverse mycelia types has been demonstrated to be effective in the oxidation of aromatic compounds and their derivatives, such as pyrene and halogenated pyrenes.

#### 7.4.2 Chemical method:

The Fenton process, a traditional applied chemical approach, involves the application of a mixture of a soluble iron (II) salt and  $H_2O_2$ , known as Fenton's reagent, to degrade and eliminate pollutants. This process works by degrading  $H_2O_2$  to produce highly reactive hydroxyl radicals, which effectively degrade organic pollutants in water and wastewater sediments [24].

However, with advancements in chemical processes, new technological approaches such as microwave (MW) and high-intensity ultrasound (US) are commonly used for the chemical degradation of organic pollutants. These approaches result in the degradation or conversion of organic pollutants into small amounts of inorganic ions, non-harmful chemicals, and mineralized compounds such as CO<sub>2</sub> and H<sub>2</sub>O. Under US or MW heating, rapid degradation of pollutant water containing aromatic halides, halogenated phenols, and polychlorinated biphenyls can be achieved at a neutral pH. In acidic conditions, acidification with sulphuric acid to a pH of 1.7-2.0 facilitates complete degradation. Conversely, degradation and elimination of organic pollutants and other humic substances from soil matrices can be achieved using 0.1 or 0.5 N aqueous alkaline solutions of NaOH or KOH [25].

#### 7.4.3 Oxidation approach:

Advanced oxidation approaches are considered to be the foremost, favorable, effective, and eco-friendly methods for the removal of organic pollutants from various types of water. These approaches primarily rely on the utilization of hydroxyl radicals (•OH) for their oxidative capabilities [26].

It is recommended that these methods be employed for the degradation and conversion of organic pollutants through water or wastewater treatment [27]. Different advanced oxidation approaches rely on various chemical, photochemical, or electrochemical reactions, offering a promising, innovative, and environmentally friendly technique for the separation of organic pollutants from water.

These methods are known to involve reactions such as chemical, electrochemical, and photolytic processes, leading to the formation of intermediate hydroxyl radicals. The most commonly used approach is the Fenton method, specifically designed for the degradation and elimination of organic pollutants. However, the efficiency and utilization of this method can be significantly enhanced through the use of ultraviolet light or sunlight [28].

#### 7.5 Conclusions:

The chapter provides a concise overview of organic pollutants, their sources, and the adverse health effects they pose, with particular emphasis on the necessity for their degradation. Additionally, the text explores a growing inclination towards employing biological and chemical methods for the degradation of organic pollutants. These approaches yield the breakdown or transformation of organic pollutants into minimal quantities of inorganic ions, benign chemicals, and mineralized compounds, such as carbon dioxide ( $CO_2$ ) and water ( $H_2O$ ).

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