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Advanced Nano-biotechnology for Chlorinated Volatile Compound Pollutants Control

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Abstract

Volatile organic compounds (VOCs) include different organic chemicals that can be easily vaporized and transported long distances via the environment. VOCs and health effects are dependent on the type, concentrations and duration of exposure. Chlorinated volatile compounds (CVOCs) are the most toxic VOCs because of their potential to cause cancer in humans. Many CVOCs are present in significant amounts in our ecosystems, including air, water and soil, and are resistant to degrade, despite the fact that their use has recently been more carefully managed and restricted. These chlorinated compounds are highly toxic and numerous have been banned from commercial utilization because they are persistent in the environment and accumulate in biological systems. Although these chemicals have been banned for decades, they are still being measured in the environment and the food chain. This paper provides a comprehensive review of the recent applications of biotechnology and nanotechnology in CVOCs remediation in various environmental systems. It is divided into many sections; each focuses on specific subtopics, covering diverse perspectives on the principal topic. Sections presented in the paper include; occurrence of CVOCs in the environment, sources, potential human health effects, recent biotechnology and nanotechnology used for CVOCs remediation, advantages and disadvantages of each strategy of treatment and future perspectives in this aspect are also provided. Finally, this paper presents advanced technologies available, to remind CVOCs emissions with their relative merits and demerits, better understand this integrated technology, and to effectively apply them in air, soil, and groundwater remediation. Consequently, we hope that this paper will guide and inspire the application of biotechnology and nanotechnology to the remediation of CVOCs.

Keywords: Chlorinated VOCs, Environnemental pollutants, Biotechnology, Nanotechnology, Remediation

1. Introduction

Environmental pollution is a significant issue for humanity owing to great changes in ecosystem behaviour and the loss of biodiversity, and because it can be the cause of diverse diseases and physiological disturbances in humans. Volatile organic compounds (VOCs) are a class of persistent pollutants found in various products that readily evaporate into the environment under normal circumstances. VOCs are more volatile, mobile and resistant to degradation and can be transported long distances into the environment (Huang et al., 2014). Several different definitions of VOCs have been developed at this time such as the Environmental Protection Agency (EPA) definition. According to these terms, VOCs are simply defined as organic compounds whose composition allows their evaporation under normal internal atmospheric conditions of temperature and pressure. In 1997, the Agency for Toxic Substances and Disease Registry (ATSDR) declared VOCs pollutants a danger to public health (Montero-Montoya et al., 2018). Chlorinated volatile organic compounds (CVOCs) are compounds that can occur naturally from a variety of sources whereby these compounds are omnipresent contaminants that have been identified in groundwater, surface water, soil and air (Huang et al., 2014). CVOCs have attracted worldwide attention to its grave dangers to the ecological system and human health. Approximately 1.5 million tonnes of chlorine compounds are released into the atmosphere annually (Valdés et al., 2021). The most common routes of exposure to CVOCs from polluted environments were drinking, respiration, food and eating, and swimming. Industrial processes, like the combustion of fossil fuel, petrochemicals, paint, coatings, pesticides, plastics, and the industry of dry cleaning have contributed to a large proportion of anthropogenic CVOCs emissions (Valdés et al., 2021). Therefore, halogenated VOCs represent a large group of compounds of interest owing to their common use, persistence in the environment, and potential toxicity. Most of these substances are capable of inducing a number of adverse effects on human health, both acute and chronic. In this context, surveillance of these kinds of compounds in air (ambient and indoor), water and soil as well as their management appears to be essential and valuable from a human health perspective. Diverse conventional techniques have been found to be effective in removing contaminants from water, air and soil over decades, including pumping and processing air stripping, adsorption, in situ air stripping, and solvent extraction. These conventional methods have limitations, like costly small-scale operations, production of unwanted by-products, and transfer of pollutants from phase to phase; hence, further efforts should be invested in waste disposal (Yadav and Pandey, 2018). Owing to these limitations of the conventional process, new technologies more efficient and economical for CVOCs removal have to be explored that are capable of avoiding the problem of conventional methods. Biotechnology and nanotechnology are recent trends opening new horizons for environmental remediation and sustainability. Consequently, this paper is a trial to gather previous achievements in the range of VOCs, which can have an influence on the environment and human health, covering issues such as the occurrence of CVOCs, properties, health effects, and recent remediation techniques, involving advanced biotechnologies and nanotechnologies.

2. Volatile Organic Compounds

Volatile organic compounds (VOCs) are organic chemicals that easily generate vapours at room temperature and are therefore emitted as gases from specific solids or liquids (Montero-Montoya et al., 2018). VOCs include very wide varieties of molecular types that can be classified in many ways, for instance by structure (e.g., straight chains, branched ring structures), by the kind of chemical bonds (alkanes, alkenes, alkynes, saturated, unsaturated), by specific functional groups (e.g., aldehydes, ketones, alcohols, etc.), or by specific elements involved (e.g., chlorinated hydrocarbons that composed of chlorine, hydrogen, and carbon) (Huang et al., 2014). VOCs are those present in the air with low, readily evaporated boiling points. There are various VOCs kinds, which are categorized according to the boiling points (Atif et al., 2018); VOCs, Semi-(SVOCs), and Very- (VVOCs). These categories are shown in Table 1.

Table 1. VOCs classification based on boiling points; VOCs, SVOCs, and VVOCs

Kinds	Boiling points (℃)	Examples
VVOC	< 0 to 100	Methyl chloride, propane
VOC	< 250	Methanol, ethanol, toluene
SVOC	240 to 400	Phenol, cosmetics, pesticides

3. Physical and Chemical Properties of CVOCs

The physico-chemical properties of CVOCs affect their environmental fate and behaviour. A correlation between these properties is useful to predict their behaviour, reactions, activity and prediction of the appropriate remediation technique. Most VOCs are colourless liquids with a particular sweet odour at room temperature, whereas some are gases (chloromethane, chloroethylene and chloroethane) and solids (hexachloroethane) (Huang et al., 2014). The high volatility related to their low boiling points not only helps to predict their thermodynamic properties, but also to investigate their fate. Their environmental stability is attributed to their half-life or periods of degradation. Here, for small molecules (C1-C2), they had high atmospheric stability, resulting in relatively long lifetimes (ranging from a few weeks to hundreds of years). Consequently, chlorinated compounds are highly persistent in the environment and have half-lives, in some cases, of several thousand years (e.g., tetrachloromethane or chloroform) (Huang et al., 2014). The presence of chlorine atoms influences the physical and chemical properties of organic compounds, including density, water solubility and volatility (Tsai, 2017). As the number of chlorine atoms augments, their ability to transfer from aqueous medium to the gas phase is also higher. They possess also low water solubility, hydrophobic compounds (Brahushi et al., 2017), low surface tension, low flammability, and electrical non-conductiveness.

4. Sources of CVOCs

Since the 20th century, CVOCs has been produced in large quantities worldwide for use as solvents, preservatives, dry cleaning products, degreasing compounds, synthetic resins, and pharmaceuticals (Zhang et al., 2018). The generation of chlorinated hydrocarbons from leaks, spills or improper disposal led to damage large volumes of soil and groundwater in many industrial and urban areas (Dolinová et al., 2017). CVOCs were emitted from disinfection processes of water through the chlorination reaction. Moreover, they enter the environment via the use of household products. These compounds are part of a group of ubiquitous pollutants found in contaminated soil, air, surface water and groundwater, and they have also been deposited in the membranes of different living organisms (Justicia-Leon et al., 2014). The main CVOCs sources in the environment are represented in Figure 1.

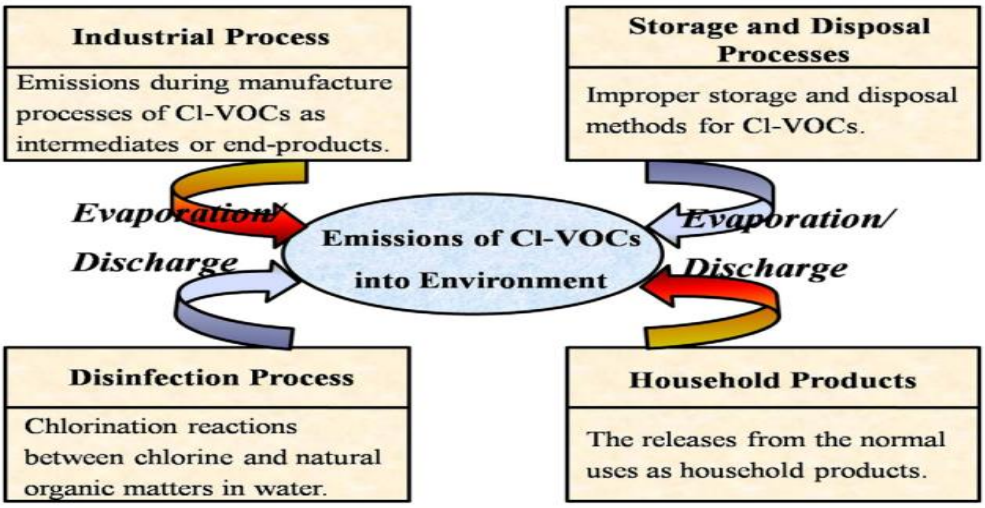

Figure 1. Main CVOCs sources in the environment (Huang et al., 2014)

The commonly utilized CVOCs include:

4.1 Chloroform

It is the most abundant solvent for processes in the pharmaceutical industry, production of dyes, pesticides, disinfection by-products during water disinfection are another important source (Fernanda et al., 2020). It is mainly emitted into the environment in the form of exhaust gases and sewage, with a total annual production capacity of 520,000 tonnes by the end of the 1990s in the U. S., the European Union and Japan (Huang et al., 2014).

4.2 Dichloromethane

It is a solvent in the pharmaceutical industry, where most of its release to the atmosphere is during the manufacture and consumption of its products, like varnish stripper and aerosol products. According to the EPA, up to 85% of U.S. production is released to the environment, 86% of which is gas (EPA, 2017). Indeed, the U.S. EPA's TCRI reported that almost 170,000 tonnes of 230,000 tonnes were released into the atmosphere in 1988 (IPCS, 1996).

4.3 Carbon Tetrachloride

It was broadly utilized as a solvent in the chemical industries, dry cleaner, degreaser, pesticides, and precursors of refrigerants in the past before the Montreal Protocol. The overall level of production was 960000 tons a year in 1987 (IPCS, 1998).

Although strong laws have been developed all over the world to protect these ecosystems, illegal operations and ineffective management plans pose a significant threat to air, soil and aquatic life, quality of water in the environment of marine, and in a logical order, they influence on the human health.

5. Chlorinated VOCs in Environmental Ecosystems

5.1 CVOCs in Ambient Air

CVOCs are airborne contaminants that can be measured in the atmosphere. These compounds act as precursors to the secondary organic aerosols of tropospheric ozone, which are part of $PM_{2.5}$ (Tsai, 2017). They are considered as trace gases that pose a danger to the environment for two main reasons. Firstly, CVOCs in diverse environmental media are toxic (e.g., chloromethane and chloroform) and have biological active impacts (Hunkeler et al., 2012). Secondly, ozone in the polar stratosphere is catalyzed by chlorinated radicals of the volatile halocarbons, like chloromethane, chlorofluorocarbons, tetrachloromethanes, and other chlorine substances (Montzka et al., 2011). Generally, chlorinated hydrocarbons, short-chain alkanes (C5, C6) and benzene had significant external sources, whereas long chain n-alkanes, terpenes, naphthalene, and styrene had important internal sources (Xu et al., 2016). Several carcinogenic air-chlorinated VOCs, including tetrachloroethylene, trichloroethylene, and vinyl chloride (VC), have been detected in ambient air at low concentrations identified as hazardous air contaminants in Korea and Japan (Tsai, 2017). Chloroform, 1,2-dichloropropane and VC at the industrial and urban areas in Thailand were found to be at acceptable levels, according to the local standards of ambient air quality (Average standard, 57, 82 and 20 $\mu g/m^3$, 24 h, respectively) (Sakunkoo et al., 2021). Additionally, methylene chloride, chloroform, tetrachloroethene, trichloroethene, chlorobenzene, and 2-chlorotoluene liberate from the treatment plants of wastewater to the air (Zhang et al., 2020). Trichloroethylene is one of the most common compounds found in indoor environments in China (Dai et al., 2017). The WHO reported that there was no safety threshold for trichloroethylene (WHO, 2010).

Actually, in Egypt there are few publications on indoor benzene, toluene, xylene, and formaldehyde (Abd El-Shakour, 2015; Saleh et al., 2022). However, systematic reviews of CVOCs concentrations across the whole country have been sparse. Abd El-Shakour et al. (2015) reported that annually, the outdoor and indoor mean concentrations of 1,2,3-trichlorobenzene were detected to be 3.49 $\mu g/m^3$ and 1.45, respectively. There is also a lack of indoor air standards in Egypt for VOCs. However, the recommended total VOCs should not be measured more than 1 mg/m^3. A number of countries and regions have suggested standards or guidelines for indoor concentrations of CVOCs. Actually, the standard values of indoor CVOCs, below which no adverse health effects will occur (i.e., the safe level), should be involved in the national standards in all countries. Table 2 summarizes the standards or guidelines of indoor CVOCs concentrations around the world. Comparison of 3 indoor CVOCs concentrations in various countries was represented in Table 3.

Table 2. Standards or guidelines of indoor CVOCs concentrations (μg/m^3) around the world

Country	**Organization**	**Trichloro-ethylene μg/m^3**	**Perchloroethylene μg/m^3**	**Dichlorobenzene μg/m^3**	**References**
China, Hong Kong	Government of HKSAR	230 (8 h)	250 (8 h)	-	IAQMG (2021)
USA, California	OEHHA	600 (Chronic)	20 (Acute) 35 (Chronic)	800 (Chronic)	OEHHA(2021)
Canada	Healthy Canada	-	40 (Chronic)	60 (Chronic)	HC (2021)
Japan	MHLW	-	-	240 (Chronic)	Azuma *et al.* (2020)
UK	Public Health England	Unit risk: 4.8×10^{-6} per μg/m^3	40 (24 h)	-	PHE (2021)
Germany	UBA	-	20	-	GEA (2021)
France	ANSES	800 (14 days–1 year)	250 (>1 year) 1380 (1–14 days)	-	ANSES(2021)
Worldwide	WHO	Unit risk: 4.3×10^{-7} per μg/m^3	250 (1 year)		WHO (2010)

Abbreviations: ANSES, The French Agency for Food, Environmental and Occupational Health & Safety; AQSIQ, Administration of Quality Supervision, Inspection and Quarantine, Government of HKSAR, Government of the Hong Kong Special Administrative Region; MHLW, Ministry of Health, Labor and Welfare, OEHHA, California Office of Environmental Health Hazard Assessment; UBA, Umweltbundesamt (German Environment Agency); WHO, World Health Organization; HC (Health Canada); PHE (Public Health England); GEA (German Environment Agency).

Table 3. Comparison of indoor CVOCs concentrations (μg/m^3) in different countries

Country	**Trichloroethylene μg/m^3**	**Perchloroethylene μg/m^3**	**Dichlorobenzene μg/m^3**	**References**
China	0.415	0.512	11.400	Liu et al. (2022)
USA	0.16	1.70	50	Logue et al. (2011)
Canada	0.21	1.94	5.52	Zhu et al. (2013)
Japan	0.10	0.40	31	Azuma et al. (2016)
Australia	Lower than the detection limit	0.37	Lower than the detection limit	Maisey et al. (2013)

Therefore, the regulatory actions to reduce stationary emissions and further, study the relationship between human health hazard and long-term exposure to their atmospheric concentrations should be performed.

5.2 CVOCs in Soil

Food demand is growing rapidly, significantly stimulating the use of chlorinated substances such as pesticides in advanced agricultural systems at an increasingly rapid rate. The increased use of chlorinated compounds has been followed as a historic model in the agricultural system worldwide for approximately 5-6 decades to eliminate pests. An average of two million tons of organochlorine pesticides has been used globally every year to control insects, weeds and pests (De et al., 2014). The main countries that consume pesticides are the United States, China, India, Argentina, Canada, Japan, Brazil, Italy, France and Thailand (Sharma et al., 2019a). *Egypt consumed approximately 0.2% of the global intake of organochlorine pesticides in 2016.* The common sub-categories are organochlorine pesticides, synthetic pesticides largely utilized worldwide, which belong to the class of chlorinated hydrocarbon derivatives. Whereas, several organochlorine compounds are forbidden and/or limited according to the Stockholm Convention (Wittayanan et al., 2017), and regulations of many countries, they remain globally at significant levels (NIP, 2014). Although many of these substances have been banned in developed countries, they are still utilized for agricultural purposes because they are inexpensive (Jayaraj et al., 2016). A number of reports have revealed that residues of chlorinated hydrocarbons are still detectable in a number of Egyptian environments, which are released elsewhere and then transported here by air or Nile water; however, those residues are declining (Dahshan et al., 2016). There is a tendency to produce eco-friendly products. Many organochlorines also remain in the ecosystem for a longer period of time, and they readily diffuse into the environment (air and water) via the overflow, permeation, wastewater and spillage during washing of the equipment (Syafrudin et al., 2021).

5.3 CVOCs in Water

5.3.1 Groundwater

Groundwater has become the basis for socio-economic development. It is the sole source of drinking for approximately 2.5 billion people worldwide (Grönwall and Danert, 2020). Contamination of groundwater and drinking water by CVOCs, caused by industrial wastewater, poses serious problems to human health (Huang *et al*., 2014). Figure 2 represents schematic diagram of the fate of CVOCs released into diverse environments. Tetrachloroethylene, dichloroethylene, trichloroethylene and VC are main important contaminants in the groundwater. Typically, groundwater pollutants come from two sources: (1) landfills, disposal lands of solid wastes, sewer leakages and storage tank leakages, and (2) agricultural and farmyard drainage. VOCs are transported for long distances in groundwater, due to their relatively low sorption affinity and degradation resistance. VOCs are the most common pollutant in groundwater compared to the surface water, due to their high volatility. Liu et al. (2020) cited that VOCs were determined in groundwater in Lanzhou, China, and that the most considerably detected VOCs were dichloromethane, chloroform and 1,2-dichloroethane.

5.3.2 Surface Water

The widespread, inappropriate, and unregulated use of CVOCs can lead to water pollution that can have negative effects on humans and animals, and has therefore been thoroughly investigated. Surface water and groundwater along the Pampanga River in the Philippines are contaminated by decomposition products of chlorine compounds (Navarrete et al., 2018). Their concentrations were also found to exceed regulatory limits, indicating that these compounds are still being utilized illegally and remain a fundamental environmental issue despite bans and limitations (Navarrete et al., 2018). The largest pollutants commonly detected in the surface waters of the White Nile in Sudan are organochlorines, like heptachlor (Nesser et al., 2016). Moreover, Behfar et al. (2013) determined high residual levels of organochlorines in Karum River at Khuy Zestan area in Iran ranged from 71.43 to 89.34 μg/L. In Nigeria, Modibbo et al. (2019) detected higher residual concentrations of organochlorines in water samples taken from four sampling sites in Lake Njuwa, Adamawa State. Additionally, Bai et al. (2018) studied their residues along the Shaying River in China. Indeed, contamination by organochlorines pesticide residues remains a major environmental issue despite the ban and restriction on their utilization under the Stockholm Convention and Fertilizer and Pesticide Authority. Kandile et al. (2018) investigated and recorded the existence of disinfection by-products of CVOCs, like $CHCl_3$, $CHCl_2Br$ and $CHClBr_2$ with concentrations below the permissible limits in drinking water of the Nile River and above the permissible limits in the produced Water of South Alamein Water Treatment Plants.

For this subject, the coupling of a routine chemical monitoring (including seasonal variations) and biological monitoring using biomarker tests of organochlorines and other CVOCs along the Rivers (surface water) and also ground water is necessary to provide inputs for the control and reduction of environmental pollutants and for reducing the human health hazards. Furthermore, knowledge of the pollutants in both surface water and groundwater is important in developing efficient strategies for water management to control the surface water and ground water contaminations.

Figure 2. Schematic diagram of the fate of CVOCs released into diverse environments (Huang et al., 2014)

6. Human Health Effects of CVOCs

A chlorinated compound classified as a contaminant with a high risk to human health. Many VOCs are currently regulated with maximum contaminant levels between 0.002 and 0.005 mg L^{-1} in water (EPA, 2000). There are a number of routes of human exposure, including dermal exposure and inhalation, as well as the oral route, as shown in Figure 3. The high volatility of VOCs makes inhalation easy to get into the human body. Exposure to these pollutants can cause a variety of health problems, like endocrine disruption, cardiovascular disease, cancer, diabetes, and malfunction of the immune and reproductive systems. Consequently, several VOCs have been prioritized by the U.S. EPA and European Commission (EC), due to their negative epidemiological impact on the human (Yadav and Pandey, 2018). Most VOCs, particularly those that are airborne, are reasonably expected to be carcinogens, especially, if they are more exposed (Table 4) (Yadav and Pandey, 2018).

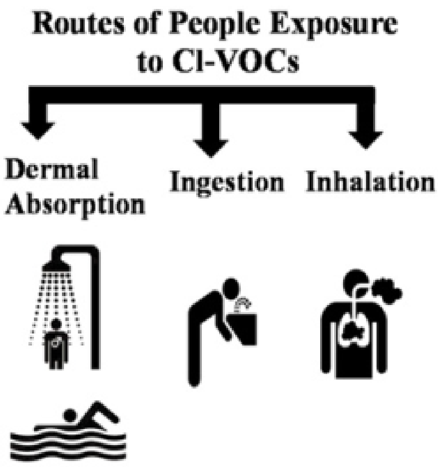

Figure 3. The main routes of human exposure to CVOCs (Huang et al., 2014)

Table 4. List of CVOCs and their effective health groups by the US-EPA (Yadav and Pandey, 2018)

CVOCs Compounds	**Carcinogenic impact**
VC	***High level of harmfulness***
1,2 dichloromethane	Group 1
Dichloromethane	***Medium level of harmfulness.***
1,2,3-Trichloropropane	Group 2A
Tetrachloroethylene	
Trichloroethylene	
Carbon tetrachloride	Group 2B
1,2-Dichloropropane	

7. Remediation of Chlorinated Volatile Compounds, CVOCs

Today, there is a growing need in many countries for the protection of the environment and the health of living systems against various pollutants in the ecosystem. A variety of methods are available for CVOCs removal. The removal techniques can be divided into two types (Tkachenko et al., 2020): Non-destructive techniques; physical removal of contaminants without changing the chemical structure and the nature of these compounds usually unchanged (e.g. stripping of air and methods of adsorption); Destructive techniques: designed methods to break the bonds of C–C and C–Cl in the contaminant molecule, thereby changing their physical and chemical characteristics, and therefore reducing or removing their risks to the public health and the environment.

Various conventional techniques are effective in removing pollutants from water, air and soil for many years, but these methods have some limitations, like costly small-scale operations, creating unwanted by-products (Yadav and Pandey, 2018). Therefore, due to these limitations, new, more efficient and economical technologies for the removal of CVOCs are being applied that can avoid the problems of conventional techniques. Biotechnology and nanotechnology are recent trends that are promising for CVOCs remediation and sustainability. In the following section the bioremediation techniques for polluted environment: concept, advantages, limitations, strategies and prospects will be discussed.

7.1 Bioremediation Technology of CVOCs

7.1.1 Definition of Bioremediation

Bioremediation is defined as a process in which biological organisms are utilized to eliminate or neutralize an environmental contaminant through a metabolic process. These involve microscopic organisms, like bacteria, fungi and algae (Enerijiofi, 2021).

7.1.2 Microorganisms Used in Bioremediation

Many microorganisms, like *Bacillus*, *Pseudomonas*, *Sphingomonas*, *Flavobacterium*, and *Mycobacterium* are capable of bio-remediating diverse kinds of environmental pollutants under aerobic conditions in which oxygen is a growth limiting factor in microbial treatments (Giri et al., 2021). They can use a variety of complex organic compounds as a source of carbon and energy and degrade them (Giri et al., 2021). Bacteria, like Pseudomonas, Aeromonas and sulfate-reducing one, are increasingly utilized in the bioremediation of polychlorinated biphenyls, chlorinated substances and solvents, trichloroethylene, and chloroform under anaerobic conditions via reduction reactions that use electrons to decompose and convert pollutants into less toxic substances (Tegene and Tenkegna, 2020).

7.1.3 Factors Affecting Microbial Bioremediation

The effectiveness of bioremediation depends on many factors, including biotic or biological factors and abiotic or environmental factors (Bala et al., 2022). Biotic or biological factors: the main biological factors include the activity of enzymes, interactions (competition, succession, and predation), mutation, transfer of the genes, biomass production, population size and its composition (Bala et al., 2022). Abiotic or environmental factors: they involve a performance based on oxygen and the concentration of nutrients, pH, temperature, and other ecological parameters (Mazumder et al., 2022).

In this regard, for successful bioremediation, it must be able to access the existing microorganisms as well as the physicochemical properties of the medium. The microbial population responsible for the remediation of pollutants, the accessibility of the contaminants and all prior factors are considered.

7.1.4 Types of Bioremediations

There are two types of bioremediation based on the general applications of organisms called In-situ and *Ex-situ*. *In-situ* treats pollutants at their point of origin, such as the contaminated soil. It prevents the spread of contamination when moving and transporting the source of pollution. This technique efficiently treats chlorine, paint, toxic metals and hydrocarbon-contaminated areas (Tekere et al., 2019). *Ex-situ* refers to the treatment that takes place after transferring the contaminated wastes to the area of treatment, for instance the soil; it was removed and transported to an area, where the bioremediation could be applied.

It should be mentioned here that the selection of appropriate types of In- situ or Ex- situ bioremediation depends on a number of factors, including cost, site characteristics, the pollutant type and its concentration.

7.1.5 Advantages and Disadvantages of Bioremediation

While bioremediation is recognized as a promising technology for restoring contaminated and degraded lands, traditional bioremediation processes have certain limitations (Table 5).

Here, it is difficult to hypothesize from the laboratory scale to the field study. Field monitoring is required to document CVOCs degradation. Making assumptions about outcomes from pilot-scale to large-scale operations is also problematic. Microbial growth is restricted during transport from contaminated sites. Furthermore, to degrade CVOCs, pure culture is not enough; therefore, by using mixed bacterial strains, an effective elimination due to the interaction between these mixed cultures can be achieved.

Table 5. Advantages and disadvantages of bioremediation process for chlorinated pollutants (Kumari et al., 2018)

Disadvantages	**Advantages**
(1) Not all toxic wastes are liable to rapid and complete microbial degradation	(1) Since bioremediation is a natural process, there is widespread public acceptance of toxic waste disposal
(2) Occasionally, more toxic intermediate metabolites than the parent compounds are produced during microbial degradation	(2) It is a comparatively economical, low-tech, energy-saving technology for treating hazardous wastes
(3) Microbial degradation of hazardous wastes requires very specific conditions, like microbial populations, appropriate ecological growth conditions, and adequate concentrations of nutrients and pollutants	(3) When hazardous wastes are microbially degraded, harmless residual products such as CO_2, water and cellular biomass are produced
(4) Extrapolating microbial degradation from laboratory scale to pilot scale is very difficult	(4) Microbiological degradation helps to completely destroy a wide variety of toxic and harmful pollutants
(5) Bioremediation is a very slow process, so it takes months to years to clean up the environments	(5) Microorganisms break down contaminants and can multiply in the presence of contaminants. As pollutants degrade, biodegradation populations decrease
(6) Because microbial degradation of toxic wastes is	(6) Several legal dangerous compounds can be

a slow process, it takes longer time than other physio-chemical techniques to fully biodegrade these wastes	transferred into harmless products. This eliminates potential future liability related to treating and disposing of pollutants
(7) Regulatory uncertainty stays regarding acceptable performance standards for bioremediation and there is no acceptable endpoint in bioremediation treatment	(7) Microbiological degradation is an eco-friendly technology, thus minimizing the environmental impacts
(8) Recent technologies, like genetic engineering are required to develop highly effective microorganisms that degrade toxic and hazardous wastes	(8) Bioremediation technology is efficiently ideal for detoxification of hazardous wastes present in different environments

7.1.6 Recent Biotechnological Advancements of CVOCs Remediation

In situ bioremediation techniques have received increasing attention and have been recently introduced to remove CVOCs from many ecosystems as an alternative to traditional methods (Xiao et al., 2020). As with any technology, there can be serious issues related to CVOCs, and the following situations can seriously influence on the remediation objectives: Less effective in separate phases or strongly adsorbed fractions; Limited substrate availability; and Incomplete degradation pathways due to energetic and kinetic limitations with accumulation of volatile and more hazardous by-products, like VC. Hence, several innovative strategies were provided in this section to overcome the aforementioned biodegradation limits. Actually, the microbial dechlorination is a stepwise reduction process. At each stage, one chlorine atom is lost and replaced by one hydrogen atom, i.e., the more toxic CVOCs are converted to more acceptable substances, like ethylene, via biological reduction reaction of dechlorination (Fig. 4).

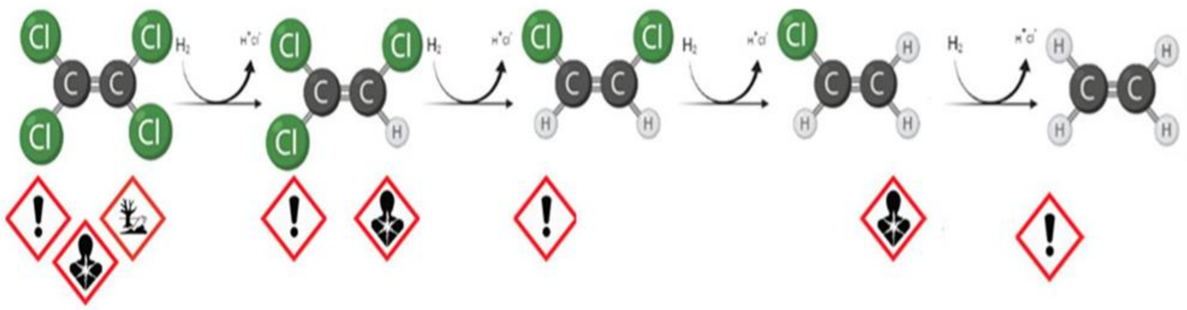

Figure 4. Dechlorination reduction reaction and hazard pictograms related to each chlorinated compound (Rossi et al., 2021)

It is well known that the degradation rate decreases with the degree of chlorination. This is due to a corresponding decrease in efficiency and a limited group of CVOCs-respiring microorganisms (Lu et al., 2017). Owing to carcinogenic and highly volatile compounds due to the potential formation and accumulation of toxic intermediates, such as VC, addition of electron donors alone is not sufficient to achieve the bioremediation goals (Rossi et al., 2021). Those issues can be addressed through coupling diverse technological strategies to augment the bioremediation efficiency.

This section describes different strategies to promote the reduction reaction of CVOCs dechlorination by the use of innovative technologies. Next, four recent approaches to greener and more sustainable technologies are proposed (Dell'Armi et al., 2022).

7.1.6.1 New Approaches Using Sustainable Electron Donor Sources

In groundwater and soil, microorganisms can efficiently reduce the levels of CVOCs via a biological process called bioreductive dechlorination. This is an anaerobic reaction that converts more chlorinated ethene or ethane to less chlorinated or harmless non-chlorinated end products (Borden et al., 2019). Lack of a suitable electron donor is usually the limiting factor in bioremediation of CVOCs, possibly leading to incomplete dechlorination and chlorinated intermediates (such as VC) that are more toxic than the parent pollutant can accumulate (Blázquez-Pallí et al., 2019). To overcome this drawback, an enhanced process for in situ anaerobic bioremediation of chlorinated compounds has been developed, involving the injection of appropriate substances that provide sustained electron donors to promote the reductive process of dechlorination. In this regard, a major innovative strategy provides the use of fermentable biopolymers (Amanat et al., 2021). Recently, there has been an increasing interest in polyhydroxyalkanoates, biologically synthesized polyesters are used to sustain the in situ dechlorination process due to their important properties, and also it ferments slowly under anaerobic conditions to volatile fatty acids and H_2, resulting in a stable and efficient release of the required electrons (Amanat et al., 2021).

In view of perspective advancement in applying the technology to better fit circular bio-economical approaches, more sustainable options should be considered via the use of polyhydroxyalkanoates produced from renewable natural resources. The major objective is to assess fermentable biopolymers, derived from urban and agricultural wastes, and this offers relevant opportunities to convert the wastes into biodegradable and inexpensive substances to be applied in bioremediation of CVOCs, it therefore fits perfectly into the concept of a circular bioeconomy.

7.1.6.2 Coupled Strategies

A. Combination of adsorption and biodegradation

The in situ application of combined adsorption and biodegradation using activated carbons has emerged as a promising remediation technique for CVOCs. This is a novel approach to create optimal conditions for better contact between microorganisms, pollutants, and nutrient distributions. Strategies for simultaneous adsorption and biodegradation should overcome the saturation of adsorbent materials, extend the operational time of reactive media, and overcome the kinetic limitations of dechlorination bioreduction (Siggins et al., 2021). Ciampi et al. (2019) found concentrations of tetrachlorethylene and trichlorethylene in groundwater in the range of 1.1 - 110 μg/L and 1.5 - 150 μg/L, respectively; exceeding the Italian standard limits (1.1 and 1.5 μg/L, respectively), they are completely remediated. These results open the door to various application configurations, like direct injection of reactive adsorption products into aquifers or installation of biobarriers. Alternatively, an external bioreactor filled with an adsorbent/electron donor mixture can be utilized to process contaminated samples (water or soil).

From our point of view, the environmental problem in direct use of adsorption is that geological factors control the movement of the pollutants and influence on the effectiveness of remediation techniques. The efficiency of activated carbon-based adsorbents applied in situ is strongly influenced by subsurface heterogeneity and consequent uncertainties in reagent supply and distribution.

High-resolution characterization and information integration of geological heterogeneity is a key factor in characterization refinement, design of remediation, optimal intervention, and performance monitoring (Ciampi et al., 2019). Possible linkages with geophysical methods can support in-situ characterization and provide continuous information to monitor remediation processes (Ciampi et al., 2019).

From our perspective, there are still unanswered questions about the effectiveness and durability of pollutant degradation, especially biological degradation, despite the rapidly increasing number of field applications.

B. Sustainable adsorption biochar and biodegradation

Biochar as a fertilizer has a positive effect on improving soil quality and creating better habitats for microorganisms (Jien, 2019). Biochars play an important role as electron acceptors for microbial extracellular respiration and growth (Cai et al., 2020). In addition, electrochemical properties are important in the relationship between biochar and bacteria (Viggi et al., 2017). Interestingly, biochar has been utilized as a potential support for the growth of certain bacterial strains and to promote the biodegradation of CVOCs (Faheem et al., 2020). The aim of this interest is to use cheap materials that are already approved as fertilizers in relation to the environment. A recent study on the combined process of adsorption and biodegradation using biochars was reported by Siggins et al. (2021), the removal rate of trichlorethylene was greater than 99.7%. Other studies have cited a superior combined strategy by using biochars with other polluting compounds (Xu et al., 2020).

Certainly, such combinations are promising sustainable bioremediation systems, but one future decision to consider is the specific interactions between biochars and daughter products (particularly VC), because its affinity may be lost due to increased polarity/hydrophilicity. At the same time, promoting the development of biochar guidelines or quality standards is an important issue, but essential for safe application. Sharing information and working with biochar producers is essential, combined with a control mechanism to certify biochars before it is used in the environment, i.e., for field applications, supporting bioremediation.

7.1.6.3 New Approach of Microbial Electrochemical Technology (MET)

As mentioned in the previous section, overcoming the bioremediation limits is usually the goal of innovative bioremediation technologies. Microbial electrochemical technology (MET) is a recent strategy to control the microbial metabolism using simple electrochemical sets (Zeppilli et al., 2021). METs exploit the ability of microorganisms to interact with conductive substances and exchange electrons via extracellular electron transfer mechanisms (Zeppilli et al., 2020). The latter can occur directly through the presence of specific membrane proteins or indirectly through redox mediators with electronic functionality (Fig. 5). Usually, the microorganisms organize themselves in biofilms on the electrode surface (Aulenta et al., 2021). Biofilms use conductive materials as electron acceptors for microbial metabolism. Therefore, the bioelectrochemical interface is called bioanode. On the other hand, for biocathode, the conductive materials act as electron donors for metabolism. METs are being investigated for several bioremediation applications, including the removal of CVOCs. METs can be divided into two main devices, represented by microbial fuel cells and microbial electrolyte cells. Fuel cells represent an energetic application of MET and are mainly based on the combined oxidation of organic substrates by a bioanode with an oxygen-reducing cathode to generate electricity. In fact, biocathode can be utilized to supply reductive energy for CVOCs dechlorination via direct or indirect pathway (Rossi et al., 2021).

Recently, sequential reduction-oxidation treatments of CVOCs have been developed in several studies (Rossi et al., 2021). To address the bioremediation of groundwater polluted by chlorinated compounds and by-products such as VC, intermediates were formed in an anaerobic cathodic chamber and degraded in an aerobic anodic one. Despite promising results in recent years, bioelectrochemical systems are still being studied on a laboratory scale.

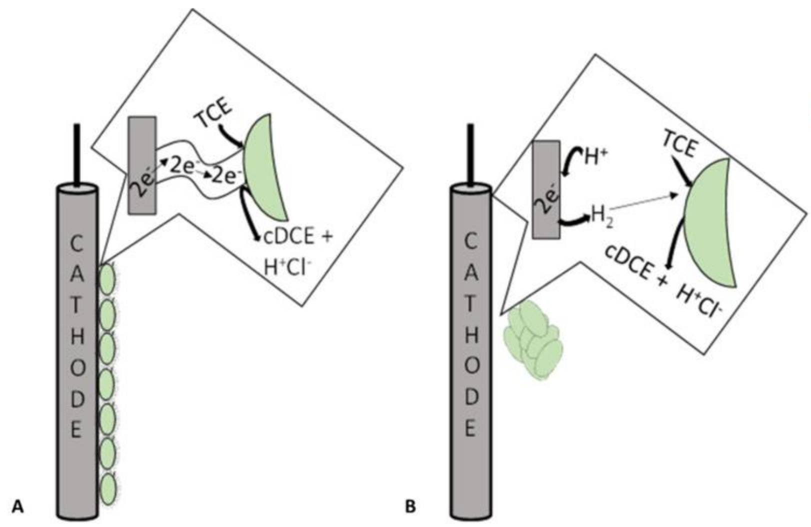

Figure 5. Schematic of microbial dechlorination of CVOCs by direct (A) or indirect (B) routes at the biocathode (Rossi et al., 2021)

7.1.6.4 Immobilization of Oxidoreductase Enzymes for Bioremediation

Many attempts have been performed over the years to enhance the biodegradation of CVOCs using immobilized oxidoreductases. This new and advanced biotechnology has increased the demand for the production of enzymes and has led to the development of new techniques to extend the duration time of biocatalysts. These are inevitable to facilitate large-scale and economical applications. However, free enzymes are less stable and have very limited reusability. In this sense, enzyme immobilization technology greatly improves the recycling efficiency or reusability and storage stability of enzymes in continuous processes, and the resulting immobilized biocatalysts have long-term stability against pH, temperature, and pressure compared to free enzymes (Gondil et al., 2020). Several natural and synthetic carriers have been used for enzyme immobilization, including nanomaterials, cellulose, silica, polymers, and activated carbon (Sharma et al., 2019b).

7.1.6.5 Genetic Engineering Approach

Genetic engineering is the latest designer technology that can modify microorganisms and adapt them to perform effective bioremediation (Muzafar, 2020). Today, new insights into genetic approaches are increasing the potential for obtaining recombinant enzymes. This pathway primarily involves the study of microbial enzymes, like esterases, oxidoreductases, monooxygenases, and phenol oxidases involved in diverse remediation processes. For instance, enzymes produced by engineered white rot fungi could decompose polychlorinated biphenyls (Sadanoski et al., 2018). Further, efficient bioremediation of γ-hexachlorocyclohexane by microorganisms that are genetically engineered has been cited (Gong et al., 2016).

In our view, additional research on bioremediation of CVOCs is needed, including further investigation of established techniques to optimize key environmental conditions and improve the mechanisms by which bioremediation occurs.

7.2 Advanced Nanotechnology for CVOCs Remediation

Protecting the environment and the health of living systems is now a national goal. As a result, there is a growing need worldwide to restore the Mother Nature through various pollutants in the ecosystem. In recent years, both biotechnology and nanotechnology have received great attention worldwide for remediation of chlorinated compounds from contaminated sites. The pollution from chlorinated aliphatic hydrocarbons is widespread and presents a scenario that is particularly difficult to remediate with a single strategy.

7.2.1 Concept of Nanotechnology, Definition of Nanoparticles and Environmental Applications

Nanotechnology refers to the design, characterization, fabrication, and application of structures, devices, and systems via nanometer-scale changes in shape and size. Nanoparticles can be defined as synthetic particles with a size less than 100 nm in at least one dimension (Jeyaraj et al., 2019). Particles less than 100 nm in diameter exhibit novel size-dependent properties compared to bulk materials. Nanomaterials with their unique properties enable entirely new applications. The unique properties of these nano-sized materials offer advantages for different applications, for example, biomedical, pharmaceutical, cosmetic and environmental fields (Srivastava and Mishra, 2022).

Nanotechnology has played a major role in the detection of various contaminants, control of the pollution, and diverse remediation treatment techniques. All these improvements will result in reduced energy consumption, pollutant detection, environmental remediation, water, soil and air purification, cleaner production and prevention, with significant benefits to human health and lifestyles (Srivastava and Mishra, 2022).

7.2.2 Nanotechnological Strategies of CVOCs Remediation

It involves the application of reactive nanoparticles, such as nanoscale metals, metal oxides, bimetallic particles, zeolites, carbon nanotubes (CNTs), and fibers for transforming and detoxifying the pollutants (Micić et al., 2017). Nanotechnology strategies to remediate CVOCs include three main methods used to treat and remove CVOCs; adsorption by nano-adsorbents, decomposition by nano-catalysts, and finally, filtration and separation by nano-filters.

7.2.2.1 Adsorption by Nanoadsorbents

Adsorption is an approach to remove environmental pollutants. Carbon-based nanomaterials are one of the best-studied groups of nanostructures used in adsorption applications, offering adsorption and remediation specificity (Awasthi et al., 2017). Fullerenes, CNTs and graphenes are most commonly utilized in environmental applications due to their physical and chemical properties such as high electrical conductivity and excellent adsorption performance (Kumar et al., 2020). Moreover, among carbon-based nanomaterials, CNT and graphene-based nanomaterials have been recognized as a new generation of adsorbents for CVOC removal. CNTs are derived from graphite sheet structure and can be folded into a cylindrical shape to create single-walled (SWCNTs), double-walled CNTs (DWCNTs), and multi-walled CNTs (MWCNTs) (Ahmad et al., 2019) (Fig. 6).

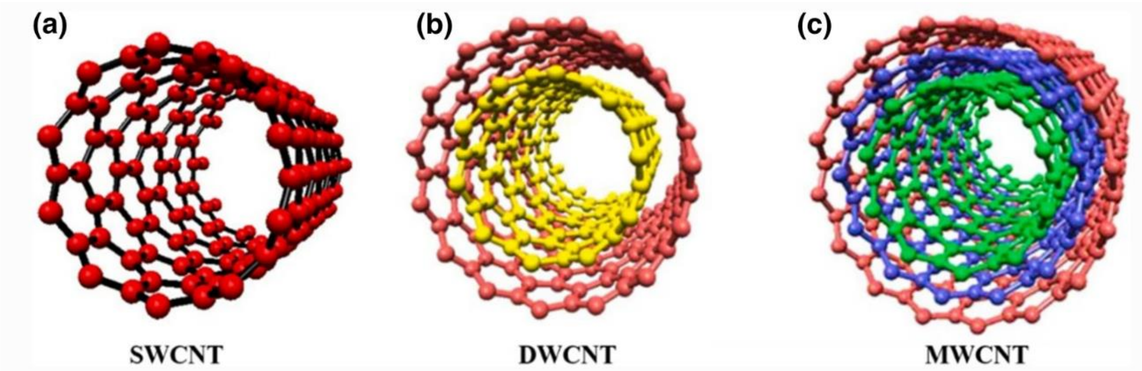

Figure 6. Schematic structures of single wall (a) SWCNT, double wall (b) DWCNT, multi-wall CNTs (c) MWCNT (Ahmad et al., 2019)

Laboratory studies have shown that carbonaceous nanomaterials and their composites are excellent adsorbents for halogenated organics, like trichlorethylene, trichloroethane, trichlorobenzene, dichlorobenzene and polychlorinated biphenyls (Adeleye et al., 2016).

Recently, CNTs have emerged as efficient adsorbents for water purification due to their remarkable wastewater treatment capacity and ability to remove organic, inorganic, and biological contaminants from water streams. Further, CNTs are also utilized for nanofiltration of contaminants from aqueous solutions (Jha et al., 2016; Ahmad et al., 2019). Jha et al. (2016) revealed results on an effective adsorption and the control of trichloroethene in a pure membrane hybrid CNT system. In addition, CNTs have also been efficiently used to remove CVOCs from the contaminated soil (Sarkar et al., 2018). Hamdi et al. (2015) also reported that the addition of CNTs functionalized with amino groups declined the uptake of dichlorodiphenyldichloroethylene in lettuce roots from 78% to 23%. Furthermore, Yoosefian et al. (2022) reported that Pd-CNTs have excellent adsorption characteristics for perchloroethene, suggesting this molecule as a potential adsorbent to detect and/or adsorb as VOCs in the atmosphere. On the other hand, graphene nanocomposites are considered other promising carbon nanomaterials for CVOCs removal. Zheng et al. (2018) revealed that graphene oxide-based nanomaterials are proven to be effective in removing carbon tetrachloride and methylene chloride from air streams.

It should be noted that toxicity is a major concern for used carbon-based nanomaterials, as they are small enough to be inhaled or absorbed by the body. Therefore, extreme safety and precautions must be taken when performing the experiments with carbon-based nanomaterials.

7.2.2.2 Degradation by Metallic Nanocatalysts

A. Nano Zero Valent Iron

Metal nanoparticles have been extensively investigated for groundwater, soil, and sediment remediations. Successful performance demonstrates its higher reactivity to a wide range of chlorinated compounds (Mdlovu et al., 2019). Decades ago, granular zerovalent iron (ZVI) was found to be an efficient medium for the decomposition of volatile compounds (Velimirovic et al., 2018). However, granular iron particles are susceptible to corrosion in aqueous media, the reduction rate of CVOCs is typically slow, and toxic intermediates, like VC are detected (He and Zhao, 2005). Recently, nano ZVI has become a promising strategy for the treatment of CVOCs from polluted soil and groundwater (Mdlovu et al., 2019; Galdames et al., 2020). Iron nanoparticles were found to augment the reduction reaction of trichloroethylene dechlorination (Brumovsky et al., 2022). The nanometer size enhances mobility via the porous media, and the low toxicity of nano-ZVI augments the remediation processes while preserving soil properties, allowing subsequent application of other processes, such as biological remediation, unaffected (Lefevre et al., 2016). In fact, nano-ZVI remediation is the most widely used technique for soil and groundwater remediation in both Europe and the United States (Galdames et al., 2020). In situ, nano-ZVIs can be distributed through various sub-surfaces or incorporated into porous reactive barriers (Faisal et al., 2018). Recently, significant efforts have been made to improve the stability and attraction of magnetic particles of nano-ZVI and to limit its aggregation in water and soil by applying coatings (Mdlovu et al., 2019).

B. Bimetallic Iron-Based Nanoparticles

Adding suitable metals (Ag, Cu, Ni, etc.) to nano-ZVI is an effective strategy to significantly enhance the removal rate of CVOCs (Ruan et al., 2019). Some researchers have investigated incorporating metals into iron oxides to facilitate electron transfer and speed up the conversion of Fe^{3+} to Fe^{2+}, and thus producing high free radicals and greater catalytic activity, avoiding the tendency of the nanoparticle aggregates to be formed (Zhang et al., 2019). Experimentally, Ruan et al. (2019) found that >95% of 2,4-dichlorophenol was dechlorinated to phenol by Nano-Fe/Ni, whereas Nano-ZVI showed no dechlorination.

Undoubtedly, Nano-ZVI and bimetal-based Nano-ZVI are important choices with high selectivity for contaminants, enabling continuous and beneficial applications in the environment. Otherwise, toxicity and safety issues limit the use of nano-ZVI for site remediation in many communities.

7.2.2.3 Promising Nanophotocatalysts for CVOCs Remediation

Photocatalytic reactions arise from the semiconductor bandgap when a material is irradiated with photons of appropriate energy, exciting electrons from the valence band to the conduction band and creating holes in the valence band. These electrons and holes move to the oxide surface and undergo reduction/oxidation reactions respectively. The principal processes involved in photocatalysis and the key reactions that take place during this process are represented in Figure 7. TiO_2 is by far the most widely studied photocatalyst due to its low cost, chemical stability, high reactivity, and eco-friendly properties (Gharaee et al., 2018). The main drawback of TiO_2 is its large bandgap energy. This reduces efficiency under visible light and causes electron/hole recombination. Considerable research has therefore been expended in developing semiconductor-based photocatalysts that are sensitive to visible light and exhibit both efficiency and stability. To enhance the photocatalytic performance of TiO_2 under visible light, several studies have been carried out, including metal doping, coupling with narrow band gap semiconductors, and fabrication of heterojunctions, an efficient strategy to augment the visible-light photocatalytic activity of TiO_2 (Gharaee et al., 2018; Zhang et al., 2018). Gharaee et al. (2018) created a photocatalytic system by preparing an Ag /Cu/ TiO_2 composite that exhibits high-visible light photocatalytic activity to degrade 2,4-dichlorophenol. Moreover, Esmaeili et al. (2018) reported that when $Fe_3O_4/TiO_2/Ag$ exposed to visible irradiation degrade 60% of 2,4-dichlorophenol. Other studies revealed that a degradation of diverse chlorinated compounds by an advanced system ($TiO_2/UV/O_3$) was performed in groundwater samples (Dutschke et al., 2022). Currently, $BiVO_4$ has been considered an important photocatalyst to remediate dichloroacetic acid under visible light (P ámai et al., 2017).

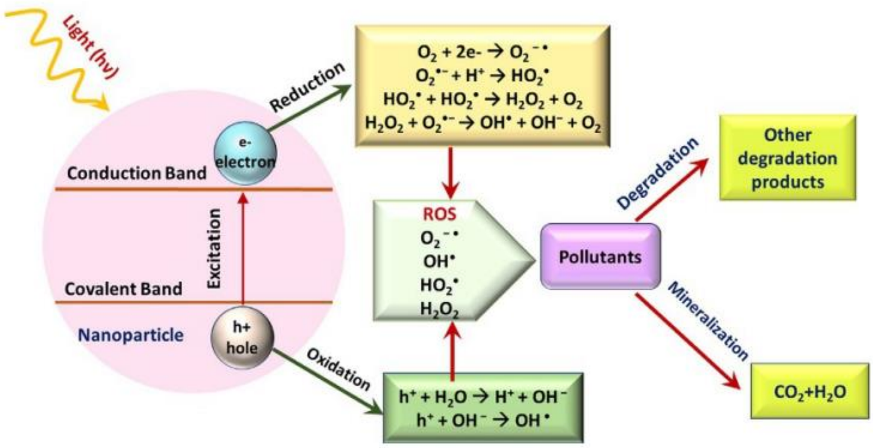

Figure 7. Main processes involved in photocatalysis and the key reactions that occur during the treatment (Abu Shmeis, 2022)

7.2.2.4 Membranes and Nanofiltration

Nanofiltration is a membrane-based process with pore sizes in the nano range of 1-10 nm. Nanomaterial-based membrane filtration is one of the most promising technologies in environmental remediation. It is preferred over other technologies because it consumes less energy, does not require regeneration, is highly selective and can be operated in continuous mode (Ying et al., 2017). Furthermore, the presence of nanomaterials in membranes may help to overcome the limitations of traditional polymer membranes, like poor chemical resistance and high fouling rates (Abu Shmeis, 2022). Removal of CVOCs (chloroform) from water by polyvinylidene fluoride nanofiber membranes has also been reported (Feng et al., 2012). Electrospun nanofiber membranes are another promising membrane utilized for the adsorption and removal of airborne CVOCs, like trichloromethane and chloroacetic acid (Singh et al., 2010). These membranes offer low-cost manufacturing of air filter membranes with high affinity for removing CVOCs, thereby avoiding serious environmental hazards, like the greenhouse impact and photochemical smog (Abdulhamid and Muzamil, 2022).

In this context, the use of nanotechnology can be an effective option for protecting the environment. From this perspective, there really need more powerful ways to remediate CVOCs contaminants by combining nanotechnology with other technologies to bring clean safety to the environment in the future.

In the following section, different technologies are coupling to reach more efficient recent technology to solve the limitations of using traditional or single technology in treating and remediating the CVOCs present in different environments.

7.2.3 Strategies of Coupling Technologies

7.2.3.1 Nanotechnology and phytoremediation

A combination of nanotechnology and phytoremediation offers a possible alternative method to treat CVOCs. A limited number of studies have used nanomaterials to facilitate phytoremediation of CVOCs contamination. Nanomaterials can support phytoremediation by directly degrading CVOCs pollutants, increasing CVOCs phytoavailability, and augmenting overall plant growth and health. The use of nanomaterials to facilitate phytoremediation could be an efficient CVOCs removal strategy.

It has to be obvious that agronomic practices must also be optimized for combined remediation by nanomaterials and phytotreatment. On the other side, the potential nanomaterial phytotoxicity must be evaluated prior to the initiation of in situ remediation process.

7.2.3.2 Nanobiotechnology

The term refers to a synergistic combination strategy of nanotechnology and biotechnology. The following section describes the most common combination scenarios as previously reported (Hidangmayum et al., 2022).

A. Synergetic coupling of catalytic degradation and microbial biodegradation

As mentioned above, a common bioremediation strategy for stimulating microbial activity is to inject appropriate electron donors, thereby optimizing metabolic processes. However, the real drawback is the need to release the electron donor into the groundwater for a long period of time. The introduction of nano-ZVI as an electron donor provides reducing power to in situ bacteria that have been successfully utilized for the reductive dehalogenation of diverse CVOCs (Wu et al., 2019).

B. Nanobiocatalyst system

Recently, nanoparticle-based immobilized biocatalytic systems have a promising extent for the efficiency of bioremediation of environmental pollutants (Rani et al., 2017). A recent report by Zdarta et al. (2021) clearly demonstrate that immobilized oxidoreductases can efficiently remove organic contaminants from wastewater, often achieving removal rates of over 90%. Furthermore, Vidal-Limon et al. (2018) evaluated the biodegradation of the chlorinated compound dichlorophene using the laccase enzyme of *Coriollopsis gallica* immobilized on nanostructures. Therefore, immobilizing enzymes on nanomaterials improves their stability, activity, separation and reusability.

Indeed, such combinations are the trend of the future and address several issues that need to be resolved in the near future to facilitate large-scale application of immobilized enzymes in the treatment of environmental pollutants in all media.

C. Biogenic nanocatalysts

A recent greener trend is the biogenic production of nanomaterials using plants, microorganisms and agricultural wastes (Nasrollahzadeh et al., 2021). Biogenic nanocatalysts have been studied in soil, freshwater, and marine ecosystems over the past decade (Smuleac et al., 2011). Additionally, Hosseinkhani et al. (2014) reported that Pd nanoparticles produced by marine bacteria completely degrade trichloroethylene within 1 h (dechlorination).

So far, there are no studies in the literature on the amount, diffusion and distribution mechanisms of nanoparticles in water, air and soil. Thus, for safety reasons, the fate and transport behavior of these nanomaterials in different environments should be investigated.

7.2.3.3 Photocatalysts Combined with Building Materials: Self-cleaning Systems

The combination of photocatalysts and building materials offers self-cleaning properties, antimicrobial surfaces, and the ability to decontaminate the air in the field. Several types of building materials have been studied for this purpose, including concrete, cement, mortar, and coatings. Over the past decades, many projects have utilized photocatalytic building materials for air purification from VOCs in diverse European cities (Jensen and Pedersen, 2021). In fact, contaminant removal efficiency can be attributed to the photocatalytic material itself, location, surface area, atmospheric conditions, direction and speed, height of the sample, or distance from the photocatalytically active surface.

Although this recent application was initially sounded for its innovation, it also has specific limitations due to its dependence on weather conditions and rainwater to clean the photocatalytic surface.

7.2.4 Cost Stimulation and Removal Performance

In many cases, the true cost of developing a particular technology was not available and had to be estimated using standard costs. Adeleye et al. (2016) reported the cost estimation for a large number of nanomaterials. It has been found that activated carbon adsorbents are generally considered to be the most effective treatment technology for chlorinated compounds based on the removal efficiency and cost. Further, in the case of commercial P25-TiO_2 photocatalysis, the cost effectiveness is $0.51 per gram of 2-chlorophenol treated, compared to $0.14 per gram for activated carbon, this estimation neglected the cost of activated carbon regeneration that seems to be more expensive. Magnetic- nanoparticles are capable of achieving removal capacity of 80 mg/g for 2-chlorophenol at approximately $0.05 per gram. However, this cost estimation did not take into consideration the ability of magnetic nanoparticles to be cheaply reused many times. Treatment of chlorine compounds by nano-ZVI has also been reported, but appears to be much cheaper than other conventional systems.

In fact, the actual cost of these new technologies is even higher, and information on the costs of these new technologies is still very scarce. This is partly due to the novel nature of the field and the limited commercialization of nanotechnology-based techniques.

8. Recommendations for Future Perspectives

Promising applications of using nanotechnology and biotechnology to remediate pollutants in all biological systems cannot be overlooked. At the same time, however, uncertainty and negative perceptions of nanotechnology interventions in the environment must be taken more seriously. Therefore, the following strategies can be defined as future guidelines to fill this research gap:

1. The scientific community needs to work together to fully understand how nanotechnology, biotechnology, and hybrid nanobiotechnology can significantly impact the remediation of environmental contaminants (e.g., remediation of contaminated water, soil and air from industrial processes).

2. The need for standardized performance assessment, i.e. standard methods for the characterization and monitoring of nanomaterials. However, with the abundance of research and the existence of several nanomaterials, it is difficult to compare them and determine which one is better suited for remediation goals.

3. A key point for future commercialization of recent technology applied to large-scale processes is a feasibility study to estimate the actual *in situ* cost of applying CVOCs remediation technology.

4. Legislation controlling the field use of Nanotechnology and Biotechnology: Researchers must elucidate the fate of nanomaterials and their ecotoxicity for remediation. In addition, evaluation of the adverse effects of microorganisms used in bioremediation on ecosystems.

9. Conclusions

Content of this state of the art is designed to help scientists interested in applying advanced biotechnology and nanotechnology to CVOCs remediate by providing a new and complementary set of information. The first topic of this work deals with CVOCs, including their sources, physical properties, harmful effects, and their occurrence in the environment. Then, it provides knowledge of recent advances in bioremediation technology to achieve sustainable remediation goals. Biotechnology is mainly aimed at overcoming the traditional limitations of bioremediation through new scenarios such as: Introduction of sustainable electron sources, combinations of biodegradation and adsorption, microbial electrochemical technology, immobilization of oxidoreductases, and genetic engineering. According to the state of the art, nanotechnology has emerged as a promising alternative to traditional pollution remediation techniques. Then it expands upon the recent advances in nanomaterial engineering approaches and discusses some recent hybrid techniques as examples of the use of alternative nanomaterials for improved stability, catalytic efficiency and CVOCs remediation. Finally, it provides a perspective on the future aspects of nanotechnology, biotechnology and nanobiotechnology for environmental remediation applications.

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