REVIEW ARTICLE



Biological-based methods for the removal of volatile organic compounds (VOCs) and heavy metals

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Abstract

The current scenario of increased population and industrial advancement leads to the spoliation of freshwater and tapper of the quality of water. These results decrease in freshwater bodies near all of the areas. Besides, organic and inorganic compounds discharged from different sources into the available natural water bodies are the cause of pollution. The occurrence of heavy metals in water and volatile organic compounds (VOCs) in the air is responsible for a vast range of negative impacts on the atmosphere and human health. Nonetheless, high uses of heavy metals for human purposes may alter the biochemical and geochemical equilibrium. The major air contaminants which are released into the surroundings known as VOCs are produced through different kinds of sources, such as petrochemical and pharmaceutical industries. VOCs are known to cause various health hazards. VOCs are a pivotal group of chemicals that evaporate readily at room temperature. To get over this problem, biofiltration technology has been evolved for the treatment of heavy metals using biological entities such as plants, algae, fungi, and bacteria. Biofiltration technology is a beneficial and sustainable method for the elimination of toxic pollutants from the aquatic environment. Various types of biological technologies ranging from biotrickling filters to biofilters have been developed and they are cost-effective, simple to fabricate, and easy to perform. A significant advantage of this process is the pollutant that is transformed into biodegradable trashes which can decompose within an average time period, thus yielding no secondary pollutants. The aim of this article is to scrutinize the role of biofiltration in the removal of heavy metals in wastewater and VOCs and also to analyze the recent bioremediation technologies and methods.

Keywords Volatile organic compounds \cdot Biological methods \cdot Bioremediation \cdot Toxic pollutants \cdot Biofiltration \cdot Phytoremediation

Abbreviations

| WHO | World Health Organization |
|-----|---------------------------|
| Hg | Mercury |
| Pb | Lead |

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| As | Arsenic |
|--------|----------------------------------|
| | |
| Zn | Zinc |
| Cu | Copper |
| Ni | Nickel |
| Со | Cobalt |
| Cd | Cadmium |
| Cr | Chromium |
| Fe | Iron |
| Sn | Stannum |
| Se | Selenium |
| H_2S | Hydrogen sulfide |
| VOCs | Volatile organic compounds |
| BTF | Biotrickling filters |
| mm | Millimeter |
| MBBR | Moving bed biofilm reactor |
| PBBR | Packed bed bioreactor |
| PCBs | Polychlorinated biphenyls |
| PAHs | Polycyclic aromatic hydrocarbons |
| | |

Introduction

Most of the earth's surface is covered with water while less than 0.002% is consumable for humans. According to the reports of the World Health Organization (WHO), one-sixth part of the total world population does not have access to freshwater. The reason behind this problem is water pollution. Water pollution comes from human activities such as industry, agriculture, or household waste that have a large negative impact on the water bodies (rivers and ocean), environment, and human health also (Owa 2014; Alrumman et al. 2016). Since industrialization, many freshwater bodies' rivers have been receiving a higher amount of pollutants (industrial and many other wastes) in which metals are also important topics of environmental concern. These heavy metals are deposited in the environment owing to anthropogenic activities. For many years, heavy metals have been growing concern over the harmful effects of humans and aquatic ecosystems (Tiwari et al. 2016). Heavy metals refer to trace metals that are toxic in nature at low concentrations with quite high density. Generally, the atomic mass range of heavy metals is found from 63 to 200 (Srivastava and Majumder 2008; Barupal et al. 2020a, 2020b). Metals that are toxic to a living being and refer as heavy metals are listed as follows: mercury (Hg), lead (Pb), arsenic (As), zinc (Zn), copper (Cu), nickel (Ni), cobalt (Co), cadmium (Cd), chromium (Cr), stannum (Sn), etc. (Wang and Chen 2009; Liang et al. 2019; Qu et al. 2020). The foremost sources of heavy metals are electroplating industries waste and mining and many more that are discharged into water bodies and soil (Ahmady-Asbchin et al. 2008; Zhou et al. 2020). In contrast to organic waste, heavy metal removal is very difficult due to its persistent and incorruptible nature (Gupta et al. 2001; Shukla and Pai 2005; Acheampong et al. 2010). Heavy metal's indiscriminate disposal into water resources causes accumulation of toxic metal in living organism's tissues, leading to diseases and disorders. The exposure of heavy metals to humans can occur through different routes, for instance, inhalation, vaporization, and food and drink ingestion. Apart from this, these heavy metals have several environmental impacts such as the destruction of aquatic life and habitat and algal blooms (Ngah and Hanafiah 2008; Akpor et al. 2014). Besides heavy metals, volatile organic compounds (VOCs) are well-known air pollutants and a topic of concern too.

VOCs are compounds with a wide variety of chemicals that have less water solubility and volatility at ambient room temperature because of the high vapor pressure (Cicolella 2008). VOCs include industrial solvents like toluene, benzene, esters, methane, perfluorocarbons, chlorohydrocarbons (Tiwari et al. 2019), methyl tert-butyl ether (Liang et al. 2020), trichloroethylene (Yang et al. 2019), chloroform, paraffin, and ketones (Lomonaco et al. 2020). VOCs also include hydraulic fluids, petroleum fuels, paints, ink, and dry cleaning agents, aromatics that are released in the air from the chemical and refinery industries. Some of these compounds are carcinogenic and some are mutagenic and toxic for living beings and hazardous to the environment. When VOCs oxidized in the presence of lights, they produce aromatic, chlorinated, and other compounds that are more toxic than their parent compounds (Zhao et al. 2014; Barupal et al. 2020c). VOCs like oxides of nitrogen generate ozone that forms smog which is harmful to living beings and the environment as well (Malakar et al. 2017).

VOCs pollute not only air but also water and soil. That is why it is a growing environmental concern. It is necessary to confiscate or alleviate VOCs and heavy metal from the environment. For this purpose, industries need some innovative technologies for the removal of heavy metal and VOCs from the wastewaters before discharging them into water bodies or environment. A number of physicochemical methods are used for heavy metal such as chemical precipitation, solvent extraction, adsorption, membrane separation, and ion exchange (Eccles 1995; Kurniawan et al. 2006) and for VOCs, ozonation, condensation, absorption, membrane separations, adsorption, catalytic oxidation, and incineration are employed (Kumar et al. 2011). Nonetheless, all these methods have some drawbacks like incomplete removal, required expensive equipment, monitoring system, reagent, and high energy requirements, and also generate undesirable by-products that require disposal as well. Furthermore, these methods might not be much effective and cost-effective. The biological process is an exquisite method for the management of heavy metal and VOCs and can also help to overcome some of the drawbacks of physiochemical treatment methods and provide economical, eco-friendly, and safe removal of pollutants (Mehta and Gaur 2005; Kumar et al. 2011). In this article, we discuss biological methods for pollutant removal (heavy metals, VOCs) like biofiltration, biofilters, microorganisms, biotrickling filters, bioscrubber, and biosorption.

Biological methods

Biological methods involve microorganisms for the elimination of wastewater. This method can be used for the exclusion of VOCs and heavy metals using microorganisms. Table 1 shows various microbes for the removal of different heavy metals. There are different kinds of biological methods that are widely used for pollutant removal such as biofilters, activated sludge, trickling filters, bioscrubber, and bioremediation; stabilization ponds are widely used for treating wastewater (Gunatilake 2015; Fig. 1). Here, Table 2 shows the various biological methods for the elimination of various contaminants, kinds of processes, and related plants/microbes. Biological methods gradually got popularity due to the following reasons: fewer chemicals and equipment and operating system required and its eco-friendly nature (Srivastava and Majumder 2008).

Table 1 Microbes mediated removal of heavy metal

| Aicroorganisms | Methods | Heavy metals and VOCs | References | |
|---|--------------------|------------------------|--|--|
| Eichhornia crassipes | Biofiltration | Pb, Cr, Zn, Mn, Cu | Tiwari et al. (2007) | |
| Izolla | Biofiltration | Sr(II) | Cohen-Shoel et al. (2002) | |
| Pseudomonas taiwanensis, Acinetobacter guillouiae, Klebsiella pneumoniae | Biofiltration | Cr(VI), Cu(II), Zn(II) | Majumder (2015) | |
| <i>Gracilaria</i> sp. | Biofilter | Al, Cr, Zn | Kang and Sui (2010). | |
| Rhizopus nigricans | Biosorption | Pb | Hassan and El-Kassas (2012) | |
| leurotus ostreatus | Biosorption | Pb | Barros Júnior et al. (2003) | |
| spergillus cristatus | Biosorption | Cd | Martinez-Juarez et al. (2012) | |
| spergillus niger | Biosorption | Cd | Bunluesin et al. (2007) | |
| lydrilla verticillata | Biosorption | Cd | Acosta Rodríguez et al. (2013) | |
| spergillus flavus I–V, Aspergillus fumigatus I–II | Biosorption | Hg | Murugesan et al. (2006) | |
| enicillium chrysogenum | Biosorption | As | Mamisahebei et al. (2007) | |
| Vaste tea fungal | Biosorption | As(III), As(V) | Shoaib et al. (2012) | |
| Vaste tea fungal | Biosorption | As | Velkova et al. (2012) | |
| spergillus niger | Biosorption | Ni | Tay et al. (2012) | |
| Pleurotus ostreatus | Biosorption | Cu | Shipra et al. (2012) | |
| spergillus lentulus | Biosorption | Cu | Sutherland and Venkobachar (2010) | |
| omes fasciatus | Biosorption | Cu | Parungao et al. (2007) | |
| enicillium canescens | Biosorption | Cr(VI) | Chhikara et al. (2010) | |
| ungal (living) mycelium of Phanerochaete chrysosporium | Biosorption | Cr(VI), Cu | Sethi et al. (2010) | |
| lucor | Biosorption | Cr(VI) | El-Kassas and El-Taher (2009) | |
| richoderma viride | Biosorption | Cr(VI) | Sala Cossich et al. (2002) | |
| spergillus niger | Biosorption Cr(VI) | | Javaid and Bajwa (2007) | |
| leurotus ostreatus | Biosorption | Cr(III), Cr(VI) | Park et al. (2005) | |
| spergillus niger | Biosorption | Cr(VI) | Kujan et al. (2006) | |
| accharomyces cerevisiae | Biosorption | Cu | Anaemene (2012) | |
| <i>andida</i> spp. | Biosorption | Cu | Mapolelo and Torto (2004) | |
| hiobacillus thiooxidans | Biosorption | Cu | Nagashetti et al. (2013) | |
| accharomyces cerevisiae | Biosorption | Cr(VI) | Abd-Elsalam (2011) | |
| accharomyces cerevisiae | Biosorption | Cr(VI), Cu | Davis et al. (2003) | |
| 'andida utilis | Biosorption | Cr(VI) | Arakaki et al. (2011) | |
| chizosaccharomyces pombe | Biosorption | Cr(VI) | Prakash and Kumar (2013) | |
| pent yeast | Biosorption | Cr(III) | Pandey et al. (2009) | |
| east biomass | Biosorption | Cr(VI) | Hamuda and Tóth (2012) | |
| accharomyces cerevisiae | Biosorption | Cu, Cd, Pb, Ni | Van Wyk (2011) | |
| accharomyces cerevisiae | Biosorption | Cr, Sn | Machado et al. (2009). | |
| accharomyces cerevisiae | Biosorption | Cu, Ni, Zn | Das et al. (2007) | |
| fycelial biomass of Pleurotus florida | - | | Yan and Viraraghavan (2000) | |
| accharomyces cerevisiae | • • • • | | Hamuda and Tóth (2012) | |
| train of Saccharomyces cerevisiae | Biosorption | Cr, Cu, Ni, Zn | Machado et al. (2008) | |
| lucor rouxii | Biosorption | Pb,Cd, Ni, Zn | El-Sayed (2013); Meena et al. (2017f, b) | |
| accharomyces cerevisiae | Biosorption | Cd | El-Sayed (2013) | |
| hodospirillum sp. | Biofiltration | Cd, Hg, Pb, Ni | Chatterjee (2002) | |
| Gallionella ferruginea | Biofiltration | As, Mn | Fe Katsoyiannis and Zouboulis (2004) | |
| <i>eptothrix</i> sp. | Biofiltration | As , Mn | Fe Katsoyiannis and Zouboulis (2004) | |

Table 1 (continued)

| Microorganisms | Methods | Heavy metals and VOCs | References Valls et al. (2000); Meena et al. (2017a, d) | |
|--|-------------------|---------------------------------|--|--|
| Pseudomonas sp. | Bioadsorption | Cr, As | | |
| Desulfovibrio sp. | Biofiltration | Cu, Zn, Ni, Fe, As | Jong and Parry (2003) | |
| Thiomonas sp. | Biofiltration | As, Fe | Casiot et al. (2003) | |
| Escherichia coli | Bioaccumulation | Hg, Ni | Deng et al. (2003) | |
| Thauera selenatis | Biofiltration | Zn, Cd, Co, Cu, Ni, Pb, Cr, Hg | Mergeay et al. (2003) | |
| Penicillium chrysogenum | Biological method | Zn, Cu, Ni, As | Loukidou et al. (2003) | |
| Aspergillus niger | Bioaccumulation | Ni, Cu, Pb, Cr | Dursun et al. (2003); Meena et al. (2017c, f) | |
| Coriolus hirsutus | Activated sludge | Cd | Miyata et al. (2000) | |
| Trametes versicolor | Biotransformation | Cr, Co | Blánquez et al. (2004) | |
| Mucor rouxii | Bioadsorption | Pb, Cd, Zn, Ni | Yan and Viraraghavan (2000) | |
| Brown algae | Biosorption | Cd, Cu, Zn, Pb, Cr, Hg | Davis et al. (2003); Meena et al. (2017e) | |
| Green algae | Bioaccumulation | Cu, Hg, Fe, Zn, Pb, Cd | Haritonidis and Malea (1999) | |
| Scenedesmus genus | Biological method | Cu, Ni, Cd, Cr, Cu | Pena-Castro et al. (2004) | |
| Sulfate-reducing bacteria (SRB) | Biofitration | Zn | Suriya et al. (2013). | |
| Enterobacter cloacae | Biofitration | Pb, Cu, Cr(VI), Hg, Cd | Rani et al. (2010) | |
| Bacillus sp., Pseudomonas sp., Micrococcus sp. | Biofitration | Cu, Cd, Pb | Hussein et al. (2004). | |
| Pseudomonas sp. | Biofitration | Cr(VI), Cu, Cd, Ni | Liu et al. (2004) | |
| Thiobacillus thiooxidans | Biofitration | Zn, Cu | Nagashetti et al. (2013) | |
| Sargassum filipendula | Biofitration | Cu, Ni | Rinku et al. (2012) | |
| Sargassum sp. | Biofitration | Cr(III) | Yavuz et al. (2006) | |
| Green algae (Spirogyra spp.) | Biofitration | Cr(VI) | Subhashini et al. (2011) | |
| Microalgae | Biofitration | Cu, Zn | Saravanan et al. (2011) | |
| Brown algae (Fucus vesiculosus) | Biofitration | Cu, Pb, Ni, Cd | Brinza et al. (2007) | |
| Pseudomonas sp. | Biofiltration | Benzene | Sene et al. (2002) | |
| Alcaligenes xylosoxidans | Biofiltration | Benzene | Yeom and Daugulis (2001); Meena et al. (2017g) | |
| Cladosporium sphaerospermum | Biofiltration | Benzene | Qi et al. (2002) | |
| Cladosporium resinae, C. sphaerospermum, Exophiala lecanii-corni, Mucor rouxii, Phanerochaete chrysosporium | Biofiltration | Butylacetate | Qi et al. (2002); Meena et al. (2017i) | |
| Pseudomonas sp. | Biofiltration | Chlorobenzene | Seignez et al. (2001) | |
| Candida utilis | Biofiltration | Ethanol | Christen et al. (2002) | |
| Rhodococcus fascians | Biofiltration | Ethylacetate | Hwang et al. (2002) | |
| Cladosporium resinae, C. sphaerospermum, Exophiala lecanii-corni, Phanerochaete chrysosporium | Biofiltration | Ethylbenzene | Qi et al. (2002); Meena and Zehra (2019) | |
| Cladosporium resinae, C. sphaerospermum, Exophiala lecanii-corni | Biofiltration | Methylethylketone | Qi et al. (2002) | |
| Rhodococcus sp. | Biofiltration | Methylethylketone | Amanullah et al. (2000) | |
| Cladosporium resinae, C. sphaerospermum, Exophiala lecanii-corni, Phanerochaete chrysosporium | Biofiltration | Methylethylketone | Qi et al. (2002) | |
| Pseudomonas aeruginosa | Biofiltration | Methyl-tertbutyl-ether, pentane | Dupasquier et al. (2002) | |
| Aspergillus sp. | Biofiltration | α-Pinene | | |

Table 1 (continued)

| Microorganisms | Methods | Heavy metals and VOCs | References | |
|---|--------------------------------|---|---|--|
| | | | Diehl and Saileela (2000); Meena and Swapnil (2019) | |
| C. sphaerospermum | Biofiltration | Styrene | Qi et al. (2002) | |
| Tsukamurella, Pseudomonas, Sphingomonas, Xanthomonas | Biofiltration | Styrene | Arnold et al. (1997) | |
| Pseudomonas putida | Biofiltration | Toluene | Park et al. (2002); Meena and Samal (2019) | |
| Pseudomonas pseudoalcaligenes | Biofiltration | Toluene | Oh and Park (2000) | |
| Exophiala lecanii-corni | Biofiltration | Toluene | Woertz et al. (2001) | |
| Scedosporium apiospermum | Biofiltration | Toluene | García-Peña et al. (2001) | |
| Paecilomyces variotii Exophiala oligosperma | Biofiltration | Toluene | Estévez et al. (2005); Meena et al. (2016a, 2016b, 2016c) | |
| Fusarium solani | Biofiltration | Hexane | Vergara-Fernández et al. (2006) | |
| Bacterial/fungal consortium Fusarium solani | Biofiltration | Toluene n-pentane | Dorado et al. (2008) | |
| Fungal consortium | Biofiltration | n-Hexane | Iranmanesh et al. (2015) | |
| Corynebacterium jeikeium, Corynebacterium nitrilophilus, Micrococcus luteus, Pseudomonas mendocina, Sphingobacterium thalpophilum, Turicella otitidis Pseudomonas putida | Biofiltration Biofiltration | Toluene Benzene, Toluene and Phenol | Strauss et al. (2000) Abuhamed et al. (2004) | |
| Paecilomyces variotii | Biofiltration | Toluene | Aizpuru et al. (2005); Meena et al. (2015) | |
| Pseudomonas putida | Biofiltration | Toluene | Park and Jung (2006); Maestre et al. (2007) | |
| Exophiala spp. Mytilus edulis | Biofiltration | Benzene, Toluene, Ethylbenzene, and Xylene (BTEX) | Mohammad et al. (2007); Torretta et al. (2015); Raboni et al. (2017) | |
| Pseudomonas aeruginosa, Aspergillus oryzae, Penicillium sp., Pseudomonas putida, Aspergillus oryzae, Pseudomonas putida, Penicillium sp., Chryseobacterium indologenes, Halosporangium sp. | Biofiltration | Styrene | Paca et al. (2009); Meena et al. (2013) | |
| Cladophialophora sp. | Biofiltration | Toluene | Prenafeta-Boldú et al. (2008) | |
| Bacillus cereus | Biotrickling | Toluene | Li et al. (2008); Kumari et al. (2018a, 2018b); Raboni et al. (2017) | |
| Stenotrophomonas maltophilia | Biofiltration | Toluene | Ryu et al. (2008) | |

Biofiltration technologies

Harm to environmental systems and human health by different types of pollutants release has led to the development of various methodologies for the treatment of pollutants and their source. In this regard, biofiltration has been known as a viable option for the removal of pollutants (Vikrant et al. 2018). It has the basic design like a fixed-bed bioreactor in which a microorganism is immobilized to a bed of inorganic or organic porous–supporting medium (Berenjian et al. 2012). The pollutants passed through the medium (Gómez-Borraz et al. 2017), degraded by microorganisms (Carpenter and Helbling 2017; Jeong et al. 2017). Microorganisms behave as a biocatalyst and developed biofilm. Supporting medium provides large surface areas and additional nutrients (Srivastva et al. 2017; Rene et al. 2018), homogenous distribution of the pollutants (Cassini et al. 2017), and water retention required to keep the biofilm alive (Mačaitis et al. 2014). These conditions

| Method(s) | Process | Pollutant(s) | Plant(s)\microbe(s) | Reference(s) |
|---------------------|--|---|--|---|
| Phytotransformation | Plant uptake and degradation of organic Compounds | Xenobiotic substances | Cannas | Subramanian et al. (2006) |
| Phytoextraction | Remove metals pollutants and organics from soil by accumulate in plant parts | Cd, Pb, Zn, As, petroleum, hydrocarbons and radionuclides | Viola baoshanensis, Sedum alfredii, Rumex crispus | Macek et al. (2000); Zhuang et al. (2007) |
| Phytostabilization | Use of plants to reduce the bioavailability of pollutants in the environment | Cu, Cd, Cr, Ni, Pb, Zn | Anthyllis vulneraria, Festuca arvernensis | Vázquez et al. (2006) |
| Rhizofiltration | Roots absorb Groundwater with pollutants, mainly metals such as Zn, Pb, Cd from water and aqueous waste streams | Zn, Pb, Cd, As | Brassica juncea | Verma et al. (2006); Meena et al. (2018) |
| Phytodegradation | Plants and associated microorganisms degrade organic pollutants | DDT, explosives, waste and nitrates | Elodea Canadensis, Pueraria | Garrison et al. (2000); Newman and Reynolds (2004) |
| Bioaugmentation | Addition of exogenous microorganisms with the ability of degrading the contaminants that are recalcitrant to the indigenous microbiota | | Bacillus cereus, Fusarium oxysporum, Actinobacteria, Agaricus bisporus | Jacques et al. (2008); Polti et al. (2014); García-Delgado et al. (2015); Meena et al. (2020) |
| Bioleaching | Specific microorganisms like <i>Thiobacillus ferrooxidans</i> and <i>T. thiooxidans</i> promote metal solubilization | Cr, Cu, Pb, Zn | Acidithiobacillus spp., Aspergillus niger | Akinci and Guven (2011); Ren et al. (2009); Zehra et al. (2020) |
| Biofilters | Application of bacteria in filters for the decontamination of polluted water and wastes | Cu, Cd | Micro-algal/bacterial biomass | Loutseti et al. (2009) |
| Bioventing | Combination of venting of soil to remove the volatile compounds with bioremediation that uses oxygen to degrade the organic contaminants | Phenanthren toluene | Multispecies system | Frutos et al. (2010); Hong and Xingang (2011); Zehra et al. (2015) |
| Composting | Nutrients are added to soil that is mixed to increase aeration and activation of indigenous microorganisms | Phenolic compounds heavy metals | Thermoascus aurantiacus, Eudrilus eugeniae | Ghaly et al. (2011); Soobhany et al. (2015) |
| Biosparging | Involving the injection of air below the water table to increase groundwater oxygen concentrations and enhance the rate of biological degradation of contaminants by naturally occurring bacteria | Trichloroethene and <i>cis</i> - dichloroethene | Pseudomonas cepacia G4, Pseudomonas cepacia G4PR1, Pseudomonas mendocina KR1, Pseudomonas putida F1, Methylosinus trichosporium OB3b | Tovanabootr et al. (2001); Meena et al. (2019a, 2019b) |
| Bioreactors | Slurry reactors (aqueous reactors) | Pyrene PAHs | Pseudomonas spp., Pseudomonas aeruginosa | Nasseri et al. (2010); Mohan et al. (2008) |

 Table 2
 Different biological methods for the removal of pollutants

altogether give suitable internal environments to pollutantdegrading microorganisms (Ibanga et al. 2018). In this process, separation is present between the microorganisms and the wastewater, while the wastewater flows through a support material on that microorganisms are immobilized (Cohen 2001; Chen and Hoff 2012). In biofiltration, the removal efficiency of VOC is also related to its bioavailability (Yang et al. 2019; Pettit et al. 2019). The removal efficiency of VOCs is directly correlated with Henry's constant. According to this, the lower solubility ratio of pollutants in water shows less biodegradability in the biofiltration process (Miller et al. 2019). The order of degradation is as follows: alcohols > esters > ketones > aromatic hydrocarbons > aliphatic hydrocarbons (Jaber et al. 2017; Vikrant et al. 2018).

Biofilters

The biofilters are easy to manufacture and operate and are economical as well. Using biofilter, the pollutants are transformed into a biodegradable form which can be decomposed

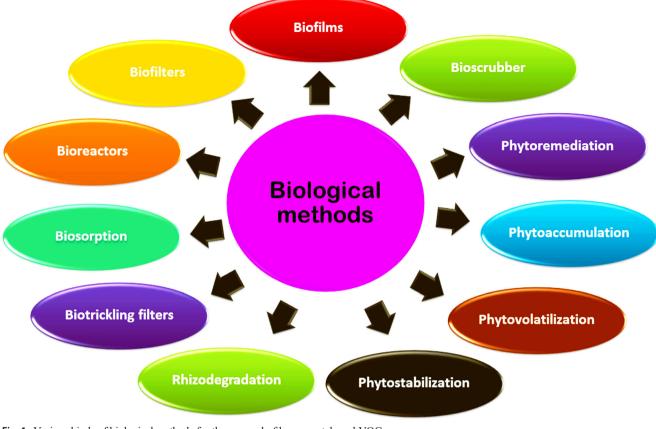


Fig. 1 Various kinds of biological methods for the removal of heavy metals and VOCs

within a moderate timeframe without any secondary pollutant production (Gopinath et al. 2018). A basic design of biofilter is constructed with a supporting medium which provides the required nutrients to the growing microorganisms (Fig. 2). Microorganisms have important roles in the process of pollutant breakdown present in the environment (Srivastava and Majumder 2008). A biofilter consists of biologically active material which is the 1 m in height (Kumar et al. 2013). Materials that are usually used in filters comprise compost, soil, bamboo, or peat activated carbon-based packing material (Lim et al. 2015; Kumar et al. 2019). The maintenance of a biologically active layer, known as the biofilm support medium, has to be kept wet (Zou et al. 2012). Biofilm is gradually developed by microorganisms (algae, protozoa, aerobic, anaerobic, and facultative bacteria, fungi, etc.) and surrounds the biofilter materials. It gives favorable conditions for the microbe's growth. Compost obtained from the leaves, bark, or other trees' parts is usually used as a basic filter material. Other materials which can be used as a support medium may include porous clay or polystyrene spheres. These mediums are sometimes used to increase active surface area and reliability, reduce backpressure, and increase the useful life of filter material (Leson and Winer 1991; Barupal et al. 2019). Biofilter's pollutant removal efficiency mostly depends on the attribute and nature of its filter media. Porosity and degree of compaction should be minimum to reduce the need for filter material replacement, ability to provide an optimum environment (medium pH, temperature, and moisture) and attachment surface for microbial populations, capacity to maintain high degradation rates, etc. (Leson and Winer 1991; Srivastava and Majumder 2008, 2015). These properties maintain healthy biomass of microorganisms on the surface of the filter media for the better completion of the biofilters.

For the attachment and colonization on the surface of the filter media, these microorganisms use transportation, preliminary adhesion, firm attachment, and colonization. Microorganisms use transportation, preliminary adhesion, firm attachment, and establishment to attach and colonize on the surface of the filter media (Chaudhary et al. 2003; Kumar et al. 2013). Biological methods that take place in a biofilter are as follows: attachment and growth of microorganisms, decay, and detachment (Srivastava and Majumder 2008; Berenjian et al. 2012). Microorganisms present in the biofilter are mostly aerobic; hence, they required O_2 which is supplied by incoming natural air. Oxygen must be dissolved into the water phase so that it can be easily available to the microorganism growing in the biofilter (Chandran et al. 2020). It has been found that most of the bacteria which form club-shaped

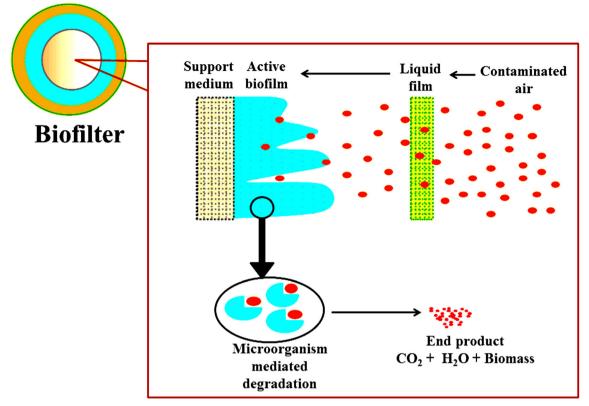


Fig. 2 Phenomena involved in the biofiltration process

(coryneform) endospore and occasionally pseudomonads are present in biofilters. *Streptomyces* spp. some time show their presence in a filter that is actinomycetes. Generally, some fungi such as yeast are not in biofilters. Some filamentous fungi which belong to the Deuteromycetes (*Aspergillus*, *Penicillium*, *Cladosporium*, *Alternaria*, *Fusarium*, *Trichoderma*, and *Botrytis*) and Mucorales (*Mortierella* and *Rhizopus*) commonly show their presence and contribution to the biofiltration process (Kumar et al. 2013).

Biofilter technologies for heavy metal removal

Heavy metals are removed through the biological remediation process occurring in a biofilter. Lethal heavy metals are passed through a moist biologically active film present in the filter medium (Majumder 2015; Gallardo-Rodríguez et al. 2019). Some biological waste material such as water treatment sludge, coconut, rice husk, swine hairs, and tea leaves were also used in biofiltration systems and they showed potential heavy metal removal capacity via ion exchange, surface adsorption, and complexation process (Lim et al. 2015; De Paris et al. 2019). These lethal heavy metals are either oxidized or reduced by microorganisms present in the active layer of the biofilter and produce less soluble and less toxic species. These less-soluble forms of metals formed by the process of precipitation/co-precipitation adsorption, absorption, and bioremediation (Kumari and Tripathi 2015) on the extracellular protein of the microorganisms and the surface of the adsorbent (Valls and De Lorenzo 2002; Li et al. 2016). Some heavy metals are aerobically transformed into less-toxic species, water, and biomass. An alternative vital route for heavy metals removal from water is the methylation of metals (White et al. 1997; Srivastava and Majumder 2008).

Biofilter technologies for VOC removal

It is an economical and excellently efficient treatment method for VOC removal. It is an effective technique over the conventional methods commonly recovered for air pollution management (Jantschak et al. 2004; Alinezhad et al. 2019). For the treatment of polluted air with VOCs, contaminated off-gas is discharged and sustained from the bottom. Contaminated air passes through the biologically active layer of the filter. Due to the turbulent nature of VOCs, the mass transport takes place through convection and diffusion. The substrate passes to the biofilm by passive diffusion or actively via enzymes (Miller and Allen 2004; Miller et al. 2019). Once pollutants are present in the air, they are diffused into the liquid-phase or absorbed directly on the biofilm. The target pollutants go through aerobic degradation in the biofilm. The cell membrane of the microorganism is conveyed VOCs into the cell, where the reaction occurs and VOCs metabolized. The final

products of the comprehensive biodegradation of pollutants are water and carbon dioxide along with microbial biomass (Adler 2001; Showqi et al. 2016). The oxidations of chlorinated organic and reduced sulfur compounds also generate inorganic acids (Leson and Winer 1991). Different types of VOCs present in the air can react with one another, alter one another's chemical properties, and also affect one another's bioavailability and the rate of biodegradation. Especially in the biofiltration process, these interactions might impact the efficiency of the purification process (Balasubramanian et al. 2012; Miller et al. 2019; Ghasemi et al. 2020). The oxygen availability is also an important factor as well as the retrodiffusion of metabolic by-products such as carbon dioxide, water, and biomass (Vergara-Fernández et al. 2018a, b).

Biotrickling filters methods

Biotrickling filters (BTFs) are structurally quite identical to biofilters. However, they have continuous re-circulation (cocurrently or counter-currently) of the liquid medium through the filter instead of pre-humidification in biofilters and also there is synthetic packing material used (Omil 2014). The procedure of gas absorption, gas diffusion into the biofilm, and liquid-phase, regeneration and successive biodegradation take place concomitantly in one procedure equipment. The waste gas being treated is carried through a packed bed in a biotrickling filter either co-currently or counter-currently to the liquid flow. An uninterrupted stream of the recirculating aqueous solution carrying the requisite nutrients for microbial growth is diffused evenly into the packed filter bed (Wambugu et al. 2017). The filtering material should have to resist crushing and constriction of biotrickling filter packing, and also it has to enable the gas and liquid flows through the bed to promote the growth of the microbes. Generally, the packing media are made up of granular activated carbon, ceramics, rocks, plastics, and resins (Mudliar et al. 2010).

During the development of biofilm, microorganisms are inoculated on the surface of the synthetic bed or organic packing material where microbes occur in the liquid phase and also grow primarily on the synthetic bed. An aqueous film surrounded the biofilm where contaminants are primarily absorbed by aqueous film then degraded by the biofilm as biotrickling filter comprises a liquid flow phase; it allows us to dispose of the by-products of decomposition, control pH, and nutrient concentrations. Nevertheless, biotrickling filters are great for the treatment of easily water-soluble pollutants, yet it is inappropriate for less-soluble pollutants (Omil 2014). The interaction between the microbes and the contaminants takes place after the dispersion of the contaminants in the liquid phase. Therefore, the liquid phase flow rate and the recycling rate are known to be acute parameters for biotrickling filter procedure.

The biotrickling filter has the benefit of having the capacity to react with acidic degradation entities of volatile organic compounds, acidic or alkaline compounds, and acidic odorous gases; small operating and capital costs; and lower pressure drop throughout continuous operation (Lebrero et al. 2012). On account of this, when combining this advantage with its cost-efficacy, biotrickling filter technique could be an excellent choice to manage VOCs and odor emissions from various industrial operations (Zehraoui et al. 2012). In spite of all, there are also some constraints with BTF methods such as complex in construction and operation, plenty of biomass accumulation, and low mass-transfer rate that may impact the contaminant elimination efficiency of BTFs. The design, trickling recycling rate to guarantee improved mass transfer, nutrient enrichment, packing materials, operating conditions, and biodegradation of pollutants by microorganisms play a crucial role during biotrickling filter operation (Prachuabmorn and Noppaporn 2010). The degree of degradation of pollutants by microorganisms may vary according to a particular pollutant to be treated. As distinct microbes have their own pros and cons, it becomes crucial to select an appropriate microbial consortium (Wu et al. 2018). The biofilms in biotrickling filters are generally composed of a high amount of bacteria than fungi; thus, most of the researchers have been the focus on the analysis of bacterial communities for their potential (Zhao et al. 2014). Bacterial members of the genera Pseudomonas, Bacillus, Staphylococcus, and Rhodococcus are frequently used in the BTF system. Pseudomonas has been recognized as the superior species of the bacterial community in various bioreactors employed to eliminate H₂S and the number of VOCs (Giri et al. 2014; Li et al. 2014; Zheng et al. 2016). Staphylococcus has the capacity to reduce nitrate to nitrite whereas Bacillus can be found simultaneously under aerobic nitrification and denitrification processes; Rhodococcus has the capability to degrade lethal environmental contaminants comprising naphthalene, toluene, herbicides, and other compounds (Baltrenas et al. 2015). BTF method plays a crucial role in the exclusive treatment of VOCs and odorants that present in large volumes and lesser concentrations (Wu et al. 2018). To the author's knowledge, nearly all of these studies have been focused on the elimination of VOCs (Chen et al. 2010; Zhang et al. 2010; Lebrero et al. 2012; Yang et al. 2013), hydrogen sulfide (H_2S) (Montebello et al. 2013; Chen et al. 2014), and trimethylamine (Schiavon et al. 2016).

In another study, four biotrickling filters have been packed with polyurethane foam to determine the reaction amid four aromatic compounds (xylene, toluene, benzene, and styrene). The 90% removal efficiency is reported for distinct toluene, styrene, and xylene (Treesubsuntorn and Thiravetyan 2018). The complete elimination capabilities for binary, ternary, and quaternary gases considerably lowered largely in all biotrickling filters. Almost all samples were predominated either by the genus *Achromobacter* or *Burkholderia*. Samples of biotrickling filters treating single and binary gases were dominated by the genus *Achromobacter* with little *Burkholderia* inside. The rest of the samples drawn from biotrickling filters treating ternary and quaternary gases were dominated by the genus *Burkholderia* with little *Achromobacter* detected inside. These genera were involved in the breakdown of the benzene series in biotrickling filters (Liao et al. 2018). Elimination performance for trichloroethylene and H₂S was estimated to be in the range of 50–90% and 95–98%, respectively (Vikrant et al. 2017).

Biofilm

Biofilm is a group of microbes (protozoa, fungi, algae, bacteria) or biological film or a thin film of a viscous, gelatinous complex in which microbes adhere themselves on the surface of the packing with the help of several forces like electrostatic properties, covalent bond formation, and hydrophobic forces. The strength and the combination of forces are relying on diverse environmental factors that are oxygen supply, gas flow rate, type of microorganisms' species and their surface characteristics, nutrient availability, and pollutant concentration (Kumar et al. 2011; Gafri et al. 2019). The formation of biofilm might take certain days to months depending upon the microbe's concentration. There are three major biological methods that take place in the biofiltration systems; those are (1) adherence of microbes on the surface, (2) growth of microbes, and (3) decomposition and detachment of microbes. In a biofilm, organics or food to the microbes is provided by the bulk and substrate transport methods as the microbes have adhered to the surface. The substrate is metabolized after diffusion onto the outer facet of the biofilm. There are mainly three attributes that affect the rate of substrate utilization within a biofilm which are (1) transport of substrate mass to the biofilm, (2) substrate distribution over the biofilm, and (3) utilization kinetics of the biofilm (Durgananda et al. 2003). Microbes attached to the biofilm decompose the organic compounds in liquid biofilm, where water-soluble contaminants dispersed into the biofilm. Microbes form slim layers upon un-rough surfaces; each treatment process has a standard thickness of biofilm. Biofilm thickness ranges from 10 to 10,000 mm; usually, it averages around 1000 mm (Fulazzaky et al. 2014). The thickness of the biofilm increases during the biofiltration operation and above particular thickness, it is called active thickness (Malakar et al. 2017). Nevertheless, the activity of the biofilm enhances with the thickness up to a level termed the "active thicknesses" but the entire biofilm is not active. Above this level, the distribution of nutrients becomes a limiting factor to differentiate an "active" biofilm from an "inactive" biofilm (Kumar et al. 2011).

Aggregation of microorganisms in sessile or nonsubmersed (activated sludge) atmosphere has a great benefit of enhanced resistance towards exposure to lethal chemicals contaminants in higher concentration, atmospheric stress environments like change in temperature, pH, and salt concentration and change in environmental conditions viz. nutrients and predation. Hence, these characteristics and stiffness of biofilm can be exploited to come up with approaches for bioremediation of organic contaminants (Edwards and Kjellerup 2013). A multi-species association of Pseudomonas strains amplifies the biofilm development in comparison with pure cultures. During the biodegradation process, it also performs 100% and 78% elimination of phenanthrene and pyrene, respectively, after 7 days of progression (Isaac et al. 2017). Recently, in the occurrence of secondary carbon sources, for instance, glucose, starch, sucrose, and L-arginine, biodegradation of naphthalene was made. It was deduced that the Pseudomonas putida KD9 strain improves the biofilm development in the presence of sucrose (0.5% wt) during the naphthalene degradation. It has been observed that sucrose serves as a biostimulating agent for the breakdown of naphthalene (Dutta et al. 2018). In another study, employing a moving bed biofilm reactor biodegradation of polychlorinated biphenyls (PCBs) carrying wastewater was accomplished with the elimination efficiency of PCB77 in aerobic and anaerobic portions were 73% and 84.4%, respectively (Dong et al. 2015). The integrated approach of activated sludge and biofilm method along with a moving bed biofilm reactor decomposes the pharmaceuticals adequately (Gaur et al. 2018).

Consistent with these observations, it has been observed that Zn was uniformly distributed across thin biofilms (approx. 12 µm) but passes through less than 20 µm into thick biofilms (approx. 350 µm) (Hu et al. 2005). According to previous studies, the interactions amid biofilm and heavy metals have chiefly concentrated on the absorption of heavy metals. Many investigators have investigated the use of biofilms to eliminate heavy metals from contaminated water owing to the capability of biofilms in the elimination of metals from bulk liquid (Labrenz et al. 2000). Electron microscopic study of *Pseudomonas* aeruginosa biofilm has been reported that it has the capability to separate heavy metals while Hg-declining Pseudomonas putida biofilms were observed to store elemental Hg on the extrinsic of the biofilms. Burkholderia cepacia biofilms were also found to accumulate Pb (Meliani and Bensoltane 2016).

The bacteria of the phylum Chloroflexi (*Dehalococcoides*, *Dehalobium chlorocoercia*) can be exploited for the biodegradation of halogenated hydrocarbons due to the presence of organohalide respiration (Löffler et al. 2013). Moreover, bacteria of the genus *Dehalococcoides* have been reported to show the reductive dechlorination of trichloroethene in a biofilm reactor (Chung and Rittmann 2008). Selenium (Se) has been accumulated in biofilms on nutrients incorporating tubes (Williams et al. 2013). As and Fe (iron) at gold-quartz mining sites have been passively oxidized by biofilms (Edwards and Kjellerup 2013). The packed bed bioreactor (PBBR) was chiefly devised for the successful removal of organic and nutrient employing a biofilm complex. The maximum adsorption potential of Cu, Ni, and Cd ions onto activated sludge is in the following order Cu > Ni > Cd, which was documented by Ong et al. (2013); that is, Cu and Zn are more easily removed than Cd and Ni (Cu > Zn > Ni > Cd). It is therefore deduced that PBBR is capable of removing heavy metal contamination from industrial wastewater outflows (Azizi et al. 2016).

The mixed-species biofilm has more tolerance capacity against disinfectants, antibiotics, heavy metals, etc., than the single-species biofilm (Golby et al. 2014; Jahid and Ha 2014). To the writers' knowledge (Golby et al. 2014), one of the first observations on the impact of heavy metals on mixed bacterial biofilm was published. Besides bacteria, the yeast biofilms have also been studied for the efficient elimination of heavy metal (Basak et al. 2014). The mixed-species biofilms of *Rhodotorula mucilaginosa* and *Escherichia coli* show efficient elimination of heavy metals like Cd, Zn, Ni, Cu, Pb, and Hg from polluted environments. Basak et al. (2014) have observed a decrease in the concentrations of the heavy metal ions in the substrate during the removal of Zn using the *Candida rugosa* and *Cryptococcus laurentii* biofilms (Grujić et al. 2017).

Bioscrubber

Bioscrubber's basic design comprises two subunits; one is a bioreactor unit and another is an absorption unit (Rene et al. 2012). In the absorption unit, contaminated gases are converted to the gaseous phase to the dispersed aqueous phase (aerosol). In a column which contains a packing material, gas and liquid phases flow cross currently. In the bioreactor present in the aqueous phase, contaminants are aerobically degraded by microorganisms (Schlegelmilch et al. 2005). The addition of inert material (such as ceramic) provides a developed transfer surface area amid the gas phase (VOCs) and the liquid phase (Van Groenestijn and Hesselink 1993). The separated contaminated liquid phase is pumped to an aerated bioreactor for agitation and the washed gas is liberated from the column. This reactor unit contains nutrient solution (media) and the appropriate microorganism suspended in the liquid phase and gets nutrients from the media which is essential for their growth and maintenance. Presently, most of the bioscrubbers are based on the stimulated sludge principle (Delhoménie and Heitz 2005). In some bioscrubber methods, a specific type of degrading microbial strain is introduced into the bioreactor. The residence time for management differs from 20 to 40 days depending on the nature and absorption of VOCs. After complete biodegradation of the pollutants, the medium of bioreactor is filtered and a portion of the waste liquid solution can be recycled through this process again while a part of the sediment biomass re-introduced into the system.

Some research studies illustrate that the accumulation of silicon oil, phthalate to the liquid solution, can expressively improve the removal of less soluble pollutants because they act as emulsifying agents who facilitate the VOC bulk transmission from gas to liquid phases (Mortgat 2001; Artiga et al. 2005; Delhoménie and Heitz 2005). There are some advantages with this process as follows: they have enough control of the biological parameters such as pH, nutrient level, and also good operational stability; relatively lower pressure drops (Rho 2000); and no need for large spaces for their installation. There are also some major limitations with bioscrubbers as follows: adapted to treat VOC which have low Henry coefficients (< 0.01) such as alcohols and ketones (Le Cloirec and Humeau 2013) and at low concentrations (< 5 g/m^3) (Frederickson et al. 2013). It means a narrow band of VOCs is treatable; mass transfer areas available for gas/liquid are quiet less ($< 300 \text{ m}^{-1}$); excess sludge generation; and required two units for the treatment process (Mortgat 2001; Berenjian et al. 2012). There are several forms of bioscrubbers designs available to boost the performance of the VOC treatment are as follows: sorptive-slurry bioscrubbers, anoxic bioscrubbers, two-liquid phase bioscrubbers, airlift bioscrubbers, and spray column bioscrubbers (Mudliar et al. 2010).

Biosorption processes

The biosorption process is based on the metal-binding capabilities of biological materials. The sorption process converts metal ions from soluble form to the solid phase which includes a group of adsorption and precipitation reactions. Generally, this process uses microorganisms to recover or remove heavy metals from the aqueous phase. It is a cost-effective, ecofriendly, efficient new emerging technology. This process uses the physicochemical interactions between metal ions and cellular compounds of biological species. This interaction results in the uptake of heavy metals (Ahalya et al. 2003). It is a metabolic independent passive process. Metals are primarily bound to the functional groups present on the cell wall of the biological species. These functional groups may comprise carboxyl, phosphate, hydroxyl, and amine groups (Sardrood et al. 2013). Some mechanisms which contribute to this process are as follows: ion exchange, adsorption, electrostatic interaction, complexation, and precipitation (Loukidou et al. 2004; Acheampong et al. 2010; Abbas et al. 2014; Li and Yu 2014). Particularly, the cell wall organization of some specific fungi, bacteria, and algae was found responsible for this method. The biosorption method can remove materials (metal ions) by using inactive, non-living or living biomass (materials of biological origin) owing to attractive forces existing amid absorbent and metal (Volesky and Holan 1995; Gadd 2010).

Microbial cells have the ability to bind up dissolved metals but the sorption affinities and capacities may differ from microbial to non-microbial biomass and between the microorganisms themselves as well (Acheampong et al. 2010). The biosorption process comprises two phases: One is a solid phase which may include sorbent/biosorbent/biomass/biological material and another one is an aqueous phase which may include solvent (water), which contain dissolved metal ions to be sorbet. Microorganisms are great sources of biosorbent; for example, algae, bacteria, fungi, and yeast (Kumar et al. 2014; Mustapha and Halimoon 2015; Ayangbenro and Babalola 2017) possess the metal-sequestering property and by using this method, heavy metal ion concentration can be reduced from ppm to ppb level in aqueous solution. It can efficiently eliminate dissolved metal ions from the contaminant solutions; thus, it is an ideal method for the wastewater treatment as well (Chigondo et al. 2013).

Biosorption processes for metal removal using living cells

This process comprises two important steps. In the first step, the metal ions are adsorbed by biological systems (biosorbent) on their surface. The bioadsorption process takes place owing to the presence of interaction amid heavy metal and functional groups of the biological systems. Second, metal ions are absorbed intracellularly because of active biosorption through the cell membrane and metal enters into the cells. This is a metabolism-dependent process which is responsible for metal transportation and accumulation or deposition (Abbas et al. 2014).

Biosorption processes for metal removal using dead cells

Numerous removal studies were performed on dead cells as they are unaffected by metal toxicity, unlike live cells (Chen et al. 2020). In this process, metal is removed mainly by passive mode with non-living cells which means it is independent of the energy process (Mohapatra et al. 2019). It is a simple physicochemical process that shows resemblance with some conventional methods such as adsorption or ion exchange. This process is accomplished by the different chemical groups present on the surface of the dead cells. The biosorption process initiates with metal uptake on the cell surface (extracellular binding) and occurs by the processes that include physical adsorption, ion exchange, van der Waals forces, complexation, or inorganic microprecipitation (Gin et al. 2002; Kotrba 2011; Abbas et al. 2014). Some reported metal-binding chemical groups belong to carboxylates, amines, and imidazoles family with cellulose (algal cell wall), chitin, and chitosan (fungal cell wall) and teichoic acids or lipopolysaccharides (gram-positive and gram-negative bacteria, respectively) (Chen et al. 2019; Hansda et al. 2016). The biosorption capability of dead cells may be less, equivalent, or greater than that of living cells (Gallardo-Rodríguez et al. 2019). Therefore, it is a metabolism-independent process. It rapidly removes metal by anyone or a group of metal-binding mechanisms, for instance, ion exchange, adsorption, physical, and complexation (Gin et al. 2002; Kotrba 2011; Abbas et al. 2014).

Phytoremediation technologies

Plants have been used to eliminate pollutants from the surrounding dates for 300 years. Baumann (1885) first ever reported bioaccumulation of heavy metals by the plant species Thlaspi caerulescens and Viola calaminaria at the end of the nineteenth century. Later, the term "phytoremediation" was introduced in the earlier 1990s (Shackira and Puthur 2019). Phytoremediation employed plants and cooperating soil microbes. Moreover, in situ or ex situ methods are used to eliminate or reduce pollutants in distinct environmental forms like air, soil, and water. In which in situ phytoremediation is most frequently used as it can manage the interference of soil and atmosphere and it also helps in lowering the expansion of pollution through airborne and waterborne wastes (Kumar and Gunasundari 2018). Phytoremediation can be used to deal with nearly all types of pollutants, radionuclides (Dubchak and Bondar 2019), toxic metals (Xiao et al. 2019), and recalcitrant organic contaminants (Cameselle and Gouveia 2019) such as organophosphate insecticides, sulfonated aromatics, nitroaromatics and explosives, chlorinated pesticides, polynuclear aromatic hydrocarbons, polychlorinated biphenyls petroleum hydrocarbons, phenolics, and chlorinated solvents (Wu et al. 2012). Phytoremediation is a rising branch of biofiltration science that utilizes several plants for the degradation, extraction, accumulation, or immobilization pollutants from soil and water. Later, this technique has been recognized as an innovative, cost-effective unconventional treatment method. Figure 3 provides the schematic representation of the phytoremediation of heavy metals and VOCs. This method is usually depending exclusively on the use of microbes which is complementary to conventional bioremediation methods (Abhilash et al. 2009; Thijs et al. 2017). Plants have been efficiently employed not only for soil remediation but also to treat polluted air, industrial, and municipal wastewaters (Zurita et al. 2009).

Phytoremediation for heavy metals removal

Plant species that have a capacity to absorb and store the pollutants in the plant tissues like roots, aerial parts, or shoots can be employed for the phytoremediation of metals in soils. During the process of phytoremediation, it is important to use hyperaccumulator plant species that has the capability to accumulate an elevated amount of concentrations of heavy metals a hundred times higher than non-hyperaccumulator

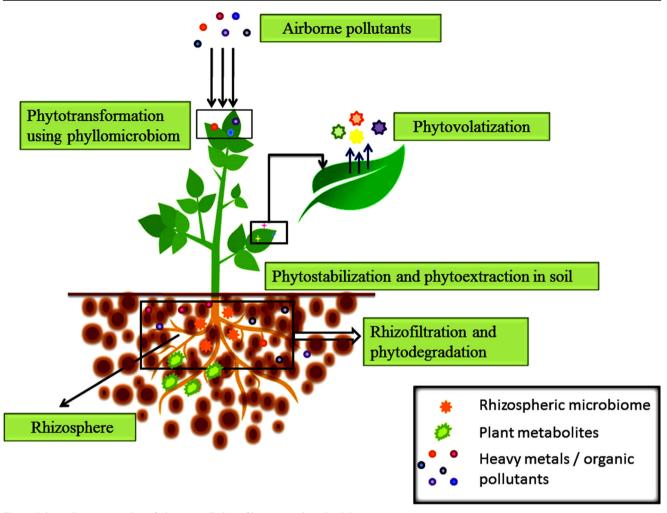


Fig. 3 Schematic representation of phytoremediation of heavy metals and VOCs

plants with no considerable adverse effect on their growth and development. Hyperaccumulators have greatly pronounced metal removal mechanisms and, occasionally, higher internal needs for specific metals, and mobilized and solubilized heavy metals and converts into low-soluble forms than the non-hyperaccumulating plant species (Rascio and Navari-Izzo 2011; Hesami et al. 2018).

Nevertheless, their efficacy also relies upon the kind of heavy metal. Different metals have different types of activity and mobility within plant tissues such as Cd, Ni, and Zn which are more readily translocated to the aboveground plant parts, whereby Pb, Cr, and Cu immobilized and translocated in the root system (Pulford and Watson 2003; Xu et al. 2019). After uptake of metals by the plant, metals commonly accumulated in vacuoles where they are attached to organic acids or tend to bind to cell wall constitutes or to sulfur ligands in the cytosol (Callahan et al. 2006). In addition to this, it may also form precipitates with carbonate, phosphate, or sulfate and accumulates within intracellular or extracellular spaces of cells (Chirakkara et al. 2016).

Phytoremediation of VOC removal

Phytoremediation of volatile organic compounds is principal element of the environment, chiefly as the precursor of ground-level ozone and secondary organic aerosols. Hydroxyl radicals serve as the superior VOC sink; at the same time, volatile organic compounds may also nucleate to very fine particulates through the moderate procedure of oxidation (Singh et al. 2017). Various plants liberate VOCs into the environment; hence, only those plants should be selected for phytoremediation, which have low VOC-emitting capacity. Various plant species have been identified to have the capability to eliminate VOCs from the air (Teiri et al. 2018). The elimination of VOCs comprises the incorporation of direct and indirect methods, which may be obtained either by growing medium, leaves, shoot system, root system, or by microbes existing in the rhizosphere. Both stomata and cuticles play a vital role during the removal process of VOC. The stomatal uptake of VOCs is predominantly depended upon types of VOCs. Benzene passes readily through the cuticle whereas formaldehyde passes more readily through stomatal apertures (Cruz et al.

2014). After entering into the plant body, VOCs undergo breakdown, accumulation, or excretion either at the place of penetration or after translocation to vacuoles of the cell. Certain volatile organic compounds, like xylene, toluene, and formaldehyde, are occupied by plants leaves and are eventually transferred to the root system where microbes are capable to digest them. Ornamental plants are reported as an efficient system for decomposition of volatile organic compounds and as well as lower the volatile organic compound concentration for indoor atmosphere (Kim et al. 2010). Volatile organic compounds are one of the most indoor air pollutants and there are so many predominant sources within the indoor environment with high concentrations than outdoor conditions. The most often volatile organic compounds are ethyl-benzene, formaldehyde, naphthalene, benzene, toluene, xylene, and polycyclic aromatic hydrocarbons (PAHs) including trichloroethylene and benzo $[\alpha]$ pyrene. Hanging pot plants also help in lowering the carbonyl concentration in the indoor atmosphere (Pegas et al. 2012). Other researches have been recommended that Spathiphyllum and Dracaena deremensis successfully eliminate toluene, even though Dracaena marginata, D. deremensis, Spathiphyllum floribundum "Petite", S. floribundum "Sensation," and Schefflera actinophylla "Amate" were identified to be beneficial for the elimination of benzene (Orwell et al. 2006). Moreover, D. marginata, S. floribundum, and D. deremensis have been employed to eliminate xylene and ethylbenzene from indoor air (Wood et al. 2006). In addition to this, the greater removal capacity has been investigated in Chrysanthemum morifolium and Calathea rotundifolia cv. "Fasciata" out of 94 studied potted plant species for the removal of benzene and toluene (Yang and Liu 2011). Some plants have been identified to lower the formaldehyde concentration in the range of 47-70% than the controlled atmosphere. Some plants such as Chlorophytum comosum L. consume formaldehyde as a carbon and energy resource. Industrial, traffic, and commercial activities are the prime sources of outdoor pollutants as they liberate the number of air contaminants. Later these contaminants, either through primary conversion or gas-to-particle conversion, might react with plant bodies and their microbiomes where they have the capabilities to alter the future of pollutants (Agarwal et al. 2019). There are distinct methods used for the phytoremediation of heavy metal and VOCs like phytoextraction, phytodegradation, rhizofiltration, phytotransformation, phytovolatilization, and phytostabilization.

Phytoaccumulation or phytoextraction

Phytoextraction is the process acquired by the plants to store contaminants into their aboveground plant parts like shoots or leaves and the root system. It comprises the absorption, translocation, and accumulation of heavy metals by the aboveground and belowground plant parts along with other nutrients. In this direction, plants are capable of storage of heavy metals. These plants are grown in contaminated places where heavy metal accumulated aboveground plant parts are collected for the elimination of traces of the heavy metal. Phytoextraction is also defined as phytoabsorption, phytoaccumulation, or phytosequestration. Contradictory to the degradation procedures, this method generates a chunk of plants and pollutants that can be transferred for discarding or reprocessing (Sharma 2012). The benefits of the phytoextraction are high tolerance to heavy metals, excessive biomass, rapid growth rate, and great root system (Suman et al. 2018). There are two methods that have been recognized for the phytoextraction based upon the plant properties. The first method is the utilization of natural hyperaccumulator plants that have a greater capacity to store heavy metals. These hyperaccumulators are successfully accumulating many of the heavy metal that is 10-500 times higher than ordinary plants (Chibuike and Obiora 2014). However, in the second method, chelates or soil amendments are used with the high-biomass plant to boost the capability to store heavy metals from the atmosphere. Few plants have the capabilities for the storage of more heavy metals than one in the same respective plant such as the hyperaccumulation of Zn and Cd by Sedum alfredii. Frequently available plants for the hyperaccumulation of metals are Haumaniastrum robertii (Co), Aeollanthus subacaulis (Cu), Lecythis ollaria (Se), Agrostis tenuis (Pd), Streptanthus polygaloides (Ni), Maytenus bureaviana (Mn), Pteris vittata (As), Thlaspitatrense, Thlaspi caerulescens (Zn), etc. Nonetheless, the phytoextraction method also has some constraints such as the utilization of hyperaccumulators which include the possibility of polluting the food chain. In spite of such limitation, the hyperaccumulators of metal of the family Brassicaceae have more amounts of thiocyanates that make them unappetizing to animals, and therefore, these plants can reduce the chances of availability of metal ions in the food chain.

Phytostabilization

This process is relying upon the immobilization of metal ions in the soil by the plant rather than their degradation. Leachable components are uptaken by the plants. These components are attached to the plant structures so that they build a solid mass of plants that taper of the bioavailability of heavy metals in the surroundings through erosion and infiltration from which the pollutants will not turn back into the environment. Phytostabilization of heavy metals using plants can be accomplished through precipitation, absorption, and metal valence reduction. This phytostabilization is more advantageous for the rapid immobilization of heavy metal from soil and groundwater, although the entire elimination of heavy metals from the environment is not unachievable (Kumar and Gunasundari 2018). Phytostabilization is an unsophisticated, economical process that employs plants to restrict the movement of toxic metal contaminants within the root tissues and in the rhizosphere. In spite of the physical elimination of the pollutants, this process involves the deactivation and immobilization of the contaminants, consequently ceasing the further transfer of contaminants to the same food chain. The microbial community that has been associated with roots and rhizospheric regions of plants engaged in performing many functions such as recycling of nutrients, detoxification of toxic pollutants, and sustainment of soil. It has been studied that bacteria namely Sphingomonas macrogoltabidus, Microbacterium liquefaciens, Microbacterium arabinogalactanolyticum, and Alyssum murale upon incorporation into the soil promote the phytostabilization by reducing the pH of the soil, thereby remarkably enhancing the phytoavailability of heavy metals together with Ni too (Shackira and Puthur 2019). Phytostabilization is a highly appropriate approach for the immobilization of the noxious pollutants in a heavily contaminated site. It abruptly stops the movement of potentially harmful pollutants by acting as a strong barrier for the filtration of water within the soil; thus, contaminants remain in the soil (Ali et al. 2020). It has been proved that it is truly efficient in the rapid immobilization for the preservation of ground and surface waters; also it is a pertinent process for the removal of Cd, Cu, As, Zn, and Cr (Ekta and Modi 2018).

Rhizodegradation: phytoremediation using root system

This method comprises the degradation of pollutants. The specific activity in the rhizospheric region is responsible for the breakdown of contaminants which is present in the plantand microbe-derived proteins and enzymes. Rhizodegradation is an outcome of the symbiotic association between plants and microbes. Rhizofiltration is a type of phytoremediation, which is used to purify extracted water with a lower concentration of pollutants by using root system. It can also be termed as phytostimulation as degradation of pollutants being stimulated by rhizospheric microflora (Lee et al. 2020). This method can be used for other metals like Cd, Cu, Pb, Zn, Ni, and Cr that are voluminously accumulated into the roots. Sunflowers, rye, tobacco, corn, Indian mustard, spinach, and pulse are broadly used for the elimination of Pb from water or soil (Luciano et al. 2013). Basically, both terrestrial and aquatic plants engaged in the rhizofiltration for in situ or ex situ purposes. The bigger disadvantage of this method is the pH settlement required for a regular time span (Pinto et al. 2016).

Phytovolatilization

In this method, plants absorbed water and carried organic contaminants from the soil. These organic contaminants are transformed into volatile components after being dispersed into the aboveground plant parts. Hence, the degraded volatile compounds were released into the environment via aerial parts of the plant (Lee et al. 2020). Later, these organic pollutants are transformed into volatile skeletons and are liberated into the air through their leaves. The phytovolatilization can be employed for the elimination of organic contaminants as well as some heavy metals such as Se and Hg. This method could not completely eliminate contaminants. It only transformed the lethal form of contaminants into the least toxic form. The limitation of this method is the productions of additional products that may re-accumulate into the water bodies. For this process, genetically modified plants are predominantly used for the absorption of pollutants; particularly, Brassica juncea and Brassica napus have been employed for the phytovolatilization of Hg and Se from soil (Chibuike and Obiora 2014). Since, Hg and Se are considered most convenient to be remediated through phytovolatilization, it has been reported that Indian mustard and canola are very helpful in the phytovolatilization of Se (Ali et al. 2020). Mercury is the foremost metal contaminant that has been phytoremediated by using phytovolatilization process together with trichloroethene and volatile inorganic chemicals like Se and As (Bisht et al. 2020). This method extremely relies upon the physical state of the pollutant itself and the availability of the contaminant in rhizosphere of the plant to be absorbed by the roots (Gupta et al. 2020).

Conclusions

This review gives a thumbnail sketch of the biological-based methods for the elimination of VOCs and heavy metal from water wastes. Throughout the last few decenniums, tremendous heed has been paid to control the environmental pollution that is attributed to the excessive amounts of lethal heavy metals and VOCs. Here, we emphasize that upcoming endeavors are required to explicate methods for the decontamination of heavy metals and volatile organic compounds from the environment which is becoming very much necessary for the maintenance of a healthy and safe environment. Nevertheless, physical-chemical methods are often used for the same purposes; biological processes namely biosorption/ bioaccumulation, biofilters, phytoremediation, and bioscrubber seem to be a promising alternative method from the perspective of pollutant removal efficiency, costs, technology requirement, environmental impacts, and energy efficiency. Although, all the above methods can be employed for the management of heavy metal and VOCs, it is pivotal to declare that the adoption of the most suitable treatment techniques relies upon the initial contaminant concentration, capital investment and operational cost, the component of the wastewater, environmental impact, utility of the treated water, etc.

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Author's contributions MM, PS, and GY conceived the idea of the review, provided the general concept and inputs for each specific section, and drafted part of the manuscript. MM, PS, and GY wrote the review after collecting the literature. MM edited, compiled, and finalized the draft. Finally, all the authors read and approved it for publication.

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Compliance with ethical standards

Competing interest The authors declare that there is no conflict of interest.

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