Inventum Biologicum, 2021, Vol. 1, Issue 1, pp. 31-37

Inventum Biologicum

Journal homepage: www.journals.worldbiologica.com/ib

Review paper

Volatile Organic Compounds as Environmental Pollutants

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ARTICLE INFO

Article history

Received 11 October 2020
Revised 20 November 2021
Accepted 28 November 2021
Published 09 December 2021

Keywords

VOCs
Impact
Mitigation
Pollution
Health

ABSTRACT

Volatile organic compounds (VOCs) comprise various organic chemicals which are released as gases from different liquids or solids. The nature and impact of the health effects are dependent on the VOCs concentrations and, also, on the exposure time. VOCs are present in different household, industrial or commercial and products, but their accumulation in air and water has primarily gained attention. Among VOCs, trichloroethylene and vinyl chloride are the most toxic and carcinogenic compounds. In order to improve the indoor air and water quality, VOCs can be removed via efficient approaches involving nanomaterials, by using techniques such as adsorption, catalysis or photocatalysis. In the recent years, the development of manufacturing procedures, characterization techniques and testing processes has resulted in the growth of nanomaterials obtaining and applications, creating great possibilities and also a tremendous provocation in applying them for highly efficient VOCs removal. This review is intended to contribute to the improvement of awareness and knowledge on the great potential that nanomaterials have in VOCs removal, in order to improve indoor and outdoor environment, but also the worldwide water sources.

1. Introduction

Volatile organic compounds (VOCs) are gases that are released by some solids or liquids. VOCs include a wide range of compounds, some of which may have short- and long-term negative health consequences. Many VOC concentrations are continuously greater inside (up to 10 times higher) than outside. VOCs are released by a diverse range of thousands of goods.

Organic chemicals are widely used in household products as ingredients. Organic solvents are found in paints, varnishes, and wax, as well as many cleaning, disinfecting, cosmetic, degreasing, and hobby products. Organic compounds are used to make fuel. All of these products can emit organic compounds while in use and, to a lesser extent, while being stored. The increased global agricultural operations (the use of fuels, agricultural waste burning, and the use of VOCs as inert components in pesticides) resulted in the widespread diffusion of VOCs in the environment (Liang and Liao, 2007). Furthermore, many studies identified VOCs as indoor air pollutants, with the sources of pollution being tobacco smoke, chlorinated water, the use of perfumes, paint removers, adhesives, new clothing, plastics, or kerosene heaters (Abdullahi et al., 2014).

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DOI 10.5281/zenodo.7514138

Some studies discovered VOCs in bottled water Spengler and Yan 2002 while others discovered microbial volatile organic compounds (mVOC) in the air, which were most likely produced by airborne microbial metabolites or fungal spores Diduch et al., 2011. Composting has been discovered as a significant producer of VOCs Fischer and Dott, 2003. VOCs may be produced by ionic liquid-containing solvents Fischer and Dott, 2003. Until present, the USEPA has classified about 189 air contaminants, 97 of which are VOCs (Komilis et al., 2004; Escudero et al., 2013).

Certain VOCs have been discovered as greenhouse gases Lelieveld et al., 2009, which are capable of absorbing radiated energy from Earth, and their quantities in the atmosphere, have been linked to global warming (Murrells, 2007; Grodowska and Parczewski, 2010; Attia et al., 2019). Furthermore, VOCs in wastewater reduce the possibilities of water reuse, such as irrigation, putting a greater strain on the limited available primary water resources Fischer and Dott, 2003.

The pharmaceutical business is one of the most major consumers of organic solvents (such as ethanol, isopropyl alcohol, toluene, or xylene), with large VOC emissions occurring from chemical synthesis or extraction operations Dimotakis et al., 1995.

Efficient methods are required to lower VOC concentrations by carefully creating materials that may chelate, adsorb, or chemically change them, while also taking into account the efficacy, reuse, and costs of acquiring. Traditional VOC mitigation approaches include burning Guerra et al., 2018, biological oxidation Williams and Koppmann 2007, chemical oxidation Guerra et al., 2018, and adsorption on different carbon materials Pichersky and Gershenzon, 2002. One of the most recent advances in VOC reduction is the use of nanomaterials to reduce environmental pollution Sindelarova et al., 2014.

2. VOCs Impact

VOCs have a wide range of direct and indirect effects on people and the environment. The main issues include toxicity, carcinogenicity, and other negative effects; material damage; the formation of photochemical oxidants in the troposphere, which depletes the stratosphere and causes ozone to be lost; global climate change; and odors released into the atmosphere. (Reimann and Lewis, 2007; Yeoman and Lewis, 2021; Holøs et al., 2018; Heeley-Hill et al., 2021; Ahmed et al., 2017).

Owing to their oxidizing or corrosive qualities, many volatile organic compounds (VOCs) may harm objects in close proximity to their release point. Because VOCs produce ozone, a potent oxidizing agent that may destroy materials like rubber both natural and synthetic textiles, resins, and surface coatings, among other things, they can indirectly cause material degradation. Building deterioration is accelerated when protective layers are compromised (Stoye et al., 2000; Wang et al., 2007; Langer et al., 2021; Yli-Juuti et al., 2020). However, in the presence of sunshine, interactions between volatile organic compounds (VOCs) and nitrogen oxides (NOx) produce photochemical oxidants, such as ozone, peroxyacyl nitrates, peroxides, etc. Guo et al., 2020. These substances have an adverse effect on human health and the environment. When NO is oxidized to NO_2, it becomes much more detrimental to the environment.

By absorbing infrared radiation from the earth's surface, almost all volatile organic compounds (VOCs) directly cause global warming. The more complex a VOC is, the more capable it is of doing so, but most VOCs have a short atmospheric lifetime and break down, which reduces their impact (saturated light hydrocarbons and halogenated compounds are the exceptions to this rule). By altering the quantity of ozone, a potent greenhouse gas, volatile organic compounds (VOCs) indirectly contribute to global warming Heeley-Hill et al., 2021.

The bulk of particle development in a variety of media including an organic precursor gas source has been shown to be caused by organic vapours; nevertheless, their complexity makes it difficult to identify and assess how much of a contribution they make to nanoparticle formation Zhao et al., 2011. It is easy to infer that a compound's volatility must be reduced the smaller the particles in order for it to condense Zhao et al., 2011. The process of VOC oxidation yields a large amount of organic acids, which are thought to be responsible for aerosol nucleation Qiu et al., 2012. Additionally, as was previously shown Qiu et al., 2012, the photooxidation of vehicle exhaust that contains aromatic volatile organic compounds (VOCs) produces a large amount of precursors for the nucleation and development of ultrafine particles in the air.

Numerous VOCs have a distinct smell, and in some cases, unpleasant odor issues may also be caused by VOC emissions Langer et al., 2021. The concentration at which half of the population is unable to perceive a certain compound's odor is known as the odour threshold, and it is often used to describe the strength of an odor. Since complex and nonlinear synergistic effects can change both the intensity and quality of the perceived odor, it is challenging to predict the odour threshold of a VOC mixture. In these cases, the odour threshold emitted by the VOC mixture must be determined by practical measurement.

Indoor air contains a wide range of volatile organic compounds (VOCs). The concerns are with permissible air concentrations and the duration of safe exposure for humans. One technique to identify increased levels and prevent exposure to these substances is by using sensors to monitor VOC concentrations and assess air quality.

3. VOCs Mitigation by Nanomaterials Use

Nanomaterials with different physicochemical properties, such porosity, size, electrostatic interaction, surface functionality, or chemical composition, have been created for VOCs mitigation. In an attempt to reduce environmental pollution, several studies have demonstrated the successful use of nanomaterials for VOCs reduction. Nanomaterials may be anything from carbon Ateia et al., 2019 to metals and metal oxides (Arkas et al., 2006; Lu et al., 2008) to polymer nanocomposites (Su et al., 2010; Liu et al., 2004). Researchers have shown success in removing volatile organic compounds (VOCs) from air and water using nano- and micro-scale materials.

BTEX VOCs (benzene-B, toluene-T, ethylbenzene-E, and p-xylene-X) are widely used solvents across many industries, with significant amounts of BTEX effluent being released into the environment, where they pose threats to ecosystems and human health Peng et al., 2003. Carbon nanotubes (CNTs) and other nanomaterials were employed to remove BTEX from polluted water Peng et al., 2003.

For adsorption of BTEX from water, for instance, multiwall carbon nanotubes (MWCNTs) produced through catalytic chemical vapor deposition and oxidation with sodium hypochlorite (NaOCl) were used Peng et al., 2003. The affinity of BTEX toward the prepared carbon nanotubes followed the order: X > E > T > B. this may be explained by the interaction of various factors, such as the molecular weight variation (B < T < E, X), the solubility decrease (B > T > E > X) and the increase in boiling point (B < T < E, X).

BTEX adsorption from aqueous solutions Li et al., 2020 has also been achieved using a variety of CNTs oxidized by different chemical agents, including HCl, HNO_3, H_2SO_4, and NaOCl. NaOCl-oxidized multi-walled carbon nanotubes (MWCNTs) demonstrated the highest adsorption, followed by HNO3- and H2SO4-oxidized CNTs. The mechanism of the adsorption was associated with a π–π electron donor acceptor mechanism, in which the carboxylic oxygen atom of the MWCNTs acted as the electron donor and the BTEX aromatic ring acted as the electron acceptor, similar to the BTEX adsorption mechanism on powdered activated carbon Li et al., 2020.

MWCNTs were also applied as solid-phase extraction (SPE) sorbents for chlorobenzenes removal and compared the adsorption with SPE adsorbents such as activated carbon or C18 silica Li et al., 2016. The adsorption capacities of MWCNTs were similar with the ones of the classical adsorbents, showing that MWCNTs can be efficiently used both for chlorobenzenes and other VOCs determination from natural or polluted waters. Carbon nanotubes were used for 1,2-dichlorobenzene adsorption from aqueous solutions, a maximum sorption capacity of 30.8 mg/g being reached in 40 min Diduch et al., 2011.

The final goal of nanomaterials synthesis is to obtain an efficient adsorbent for the selective mitigation of VOCs with different functionalities. Accordingly, periodic mesoporous organosilica nanoparticles (MO SiNPs) were synthesized by an efficient one-pot condensation process, the resulted nanomaterials (with approximately 400 nm diameter) having high surface areas (977 m^2/g) and large pore volume (0.92 cm^3/g) Guerra et al., 2018. They were applied for the capture of hexanal and butyric acid vapours using a GC capture assay, the

PMO SiNPs exhibiting mitigation efficiency higher than 99% for both VOCs even at low adsorbent dose. The study showed also that the nanomaterials can be reused for several cycles Guerra et al., 2018. An organic inorganic hydrophobic mesoporous silica has been successfully obtained by a co-condensation method with tetraethoxysilane (TEOS) and vinyltriethoxysilane (VTES) under acidic condition Diduch et al., 2011. This nanomaterial, denoted as v-SiO_2 has been used for the adsorption of p-xylene. Adsorption experiments showed that the nanomaterial is much more hydrophobic than pure silica (56.2%) when tested against p-xylene (85.2% adsorption).

Nanostructures based on noble metals have recently gained a lot of attention because of how well they work as VOC catalytic oxidation catalysts.

In addition to contributing to the overall rate of pollution and even causing climate change Arkas et al., 2006 the chemical transformation of VOCs produces highly reactive volatile substances that play a significant role in the formation of ozone, acid deposition, organic aerosols, and photochemical smog in the atmosphere. The ease with which VOCs may be released is used to categorize them. The World Health Organization (WHO) has identified the following 34 types of organic indoor contaminants: Hexanal, formaldehyde, ethyl alcohol, D-Limonene, isopropyl alcohol, toluene, and acetone are all examples of volatile organic compounds (VOCs), whereas methyl chloride, propane, and butane are examples of very volatile organic compounds (VVOCs). Higher levels of volatility are associated with greater potential for environmental release from consumer items Sindelarova et al., 2014. As gases rather than contained in parts or on surfaces, VVOCs and hazardous air pollutants (HAPs) such certain alkanes, alcohols, aromatics, ethers, aldehydes, ketones, esters, and amines may be difficult to measure. The percentage of VCs found in the air within a building is low, compared to the amount found in solids/liquids containing those or only on interfaces, such as dust, building materials, and furniture. Many VOCs serve as ozone generation precursors, and as a result, they are often blamed for contributing to or even worsening air pollution. Moreover, ozone subsequently becomes a secondary precursor that tends to promote a spectrum of photochemical interactions between numerous primary oxidants and pollutant chemicals, leading to the production of gaseous molecules with a highly reactive character. Since high concentrations of ozone and its byproducts have the potential to significantly interfere with the fundamental physiology of plants, this is adding a great deal of complexity to the atmosphere near the ground. In reality, forest VOCs emerge from a wide range of metabolic activities within the plant system, with isoprenoids being the most abundant and diverse class of metabolites. Human exposure to such volatile derivatives is also a major reason for worry because of the numerous reports that they pose a variety of hazardous effects, including skin and lung-related ailments Li et al., 2016.

Carbon dioxide, nitric oxide, and even many volatile organic molecules primarily perform their chemical reaction with light's assistance in the presence of atmospheric radiation Li et al., 2020. Two times the rate of temperature increase may be attributed to the continual emission of volatile organic compounds (VOCs) from a variety of biological and non-biological sources. In addition, polar ecosystems' VOCs emissions have been predicted to increase significantly. Researchers have shown that global warming has a major and growing effect on VOCs emissions. In addition, plant communities, biomass modification processes, and non-biological processes are all affected by changes in temperature and soil moisture. According to yet another study, the indirect consequences of global warming due to VOCs production were significant, but less severe than the direct effects. In addition, changes in vegetation cause shifts in the chemical development of VOC emissions levels. There are large regional differences in the response of VOC emissions to global warming because of direct and indirect implications related to regional vegetation and climate interactions.

In addition, the oxidation of volatile organic compounds in different conditions results in the release of many low and semi-volatile derivatives into the atmosphere, which are a major contributor to the formation of both primary and secondary organic aerosols. More unique volatile compounds are produced as a result of this chain reaction, and several of these molecules have been shown to possibly contribute to climate change and changes in environmental health. Accelerated oxidation of volatile organic molecules was also linked to the increased concentration of carbon dioxide and halocarbons in conjunction with carbon monoxide stress. Recent research has linked the increased global warming impacts to the breakdown of volatile organic compounds through incineration aided by the burning of fossil fuels Wang et al., 2007.

Increased time spent in significant indoor areas including workplaces, workstations, homes, and similar places has increased human exposure to a range of volatile organic chemicals, according to approximated data from several researches. Since many people spend their days in close quarters, they are more likely to be exposed to the many volatile organic compounds that may be found in building materials and decorative finishes. Regular activities, the intensity of regular activities, the time of year, and other factors are shown to affect the exposure levels in the aforementioned settings. It has been shown that the chemical load caused by volatile organic compounds (VOCs) within the home seems to be higher in the winter than in the summer Diduch et al., 2011.

Environmental exposure is the most often cited chemical source as the origin of possible health consequences to human and animals, despite the fact that toxicological studies of common chemicals continually claim a diversified source as the reason. The health effects of volatile organic compounds were studied, and although the topic is not entirely addressed, it was shown that VOCs have a wide-ranging influence on a variety of groups, particularly when exposure increases year after year Komilis et al., 2004. In addition, human observational and biomonitoring studies have repeatedly revealed many novel types of volatile organic chemicals in each fresh investigation. The most worrying discovery was that VOCs had the same negative effects on children as they did on adults, regardless of age. Specifically, kindergarteners were shown to be more vulnerable than their elementary and secondary school counterparts Heeley-Hill et al., 2021. Since their schools are often located in areas with a high pollution rate as a result of high levels of traffic exhaust pollution and residential heating activities, etc., these findings have shown some correlation with their vulnerability towards early lung ailments such as bronchitis.

4. Conclusions

Problems arise when actually collecting and analysing VOCs from the environment, making their detection and analysis a significant irritant. Adsorption, catalysis, and photocatalysis are only few of the traditional methods that have been proposed for the theoretical removal of these VOCs.

The operating costs and feasibility for industrial purposes are heavily influenced by the adsorbent's or catalyst's capacity to be regenerated and reused. Nanocatalysts and photocatalysts are attracting increasing attention as potential tools for reducing VOC emissions. TiO2's inexpensive price, good chemical stability, and low toxicity make it the material of choice for use in the catalytic removal of VOCs from buildings. More catalyst nanomaterials are needed because mixing metal oxides with hybrid adsorbents increases their photocatalytic efficiency. More research is needed to increase removal effectiveness under certain circumstances like visible light in order to enhance indoor VOC removal. Catalyst deactivation during actual process operation is a major problem. To achieve this goal, it is essential to age catalysts under severe pre-treatment to guarantee their longevity and stability.

The creation of highly effective and stable catalysts with fascinating design and specific functionality may benefit from a knowledge of the catalytic processes, such as the interface boundary sites and the synergetic effect. Most intermediates in the catalytic oxidation of volatile organic compounds (VOCs) by means of small molecules have been discovered, thanks to extensive study of the underlying processes. However, owing to the complexity of the reaction pathways, the mechanisms for catalytic oxidation of VOCs with big molecules are currently being investigated. New and better characterisation methods, particularly for in situ analysis, will be inspired by the discovery of the underlying chemical processes. The performance and mechanism of catalytic oxidation of mixed VOCs from real-world industrial processes and from indoor settings are quite different from those accomplished in the lab employing single VOC. Therefore, further study is needed in both academia and industry before nanomaterials may be widely used to VOCs abatement. In an effort to aid in the development of more effective technological ways for the removal of the pollutant from the environment, this study sought to emphasize the foundations of VOCs mitigation utilizing nanomaterials. The population should be screened for potential health problems on a regular basis, and education should be spread on proper waste management and ways to reduce indoor air pollution in order to lessen the likelihood of accidental or deliberate VOCs contamination.

Funding Information

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors

Declaration of Conflict

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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