

Volatile Organic Compounds (VOCs) in China: Progress and Prospects of Research on Treatment Technologies and Policy Provisions

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Abstract

Volatile organic compounds (VOCs) are an atmospheric pollutant with a boiling point of 50°C - 260°C at room temperature and pressure. They are precursors of sulfur dioxide and ozone, which can seriously pollute the atmosphere and endanger human health. After the “14th Five-Year Plan”, VOCs, instead of SO₂, became one of the five indicators of China’s atmospheric governance. As a result, the government’s efforts to control VOCs have increased significantly. VOCs governance mustn’t be delayed. This paper provides a comprehensive summary and analysis of VOCs governance, covering the classification of VOCs, analysis of VOC governance technology (with a focus on end-of-pipe governance technology), national policy regulations, current governance shortcomings, and a forward-looking perspective on the future direction of VOCs governance, emphasizing healthy and sustainable development.

Keywords

Volatile Organic Compounds, VOCs, End-of-Pipe Treatment Technology, Policy Regulations

1. Introduction

Volatile organic compounds (VOCs) are air pollutants with a boiling point of 50°C - 260°C at normal temperature and pressure [1]. VOCs directly contribute to photochemical smog and worsen haze pollution. They are also a significant

source of PM_{2.5} and O₃, which can chemically react with atmospheric substances like SO₂ and NO_x, leading to secondary pollution [2] [3]. Long-term exposure to VOCs can impact human health, causing respiratory diseases, sick-building syndrome (SBS) [4], and even cancer.

Statistically, the most polluted areas of VOCs are mainly in Asia and Africa [5]. It has been demonstrated that anthropogenic volatile organic compound (VOC) emissions in China increased by 11 percent between 2010 and 2017. Industrial VOC emissions saw a significant rise, with a 21 percent increase in concentration, while emissions from other sources are decreasing [6]-[10]. Without treatment of volatile organic compounds (VOCs), the generation of VOCs is projected to increase by 22.91% from 2019 to 2025 [11] [12]. As a result, research on VOC pollution control has become a significant global issue, particularly in China. During the “14th Five-Year Plan” period, China has incorporated volatile organic pollutants (VOCs) as binding indicators of atmospheric environmental quality, replacing sulfur dioxide. Preventing and controlling VOCs pollution will be a key focus of air pollution control. To align with the state’s objectives, protect the environment, and ensure human health, increasing the treatment of VOCs is imminent.

Volatile organic compounds (VOCs) come from a wide range of sources and have a complex structure, which makes managing them difficult and complex. The main sources of VOCs are classified into two categories: natural sources and anthropogenic sources. Natural sources mainly include emissions from green vegetation, which are uncontrollable. Anthropogenic sources, on the other hand, are caused by human activities and are the main source of VOCs emissions. These sources are further divided into industrial sources, transport sources, and domestic sources, with industrial sources accounting for the largest proportion of emissions, at about 43 percent [13]. The main industries that produce VOCs include petrochemicals, printing, machinery coating, and rubber processing. It is important to effectively control these industries to manage VOCs.

This review aims to provide the latest advancements in VOC management technologies. It classifies VOCs and then summarizes and analyzes recycling technology, destruction technology, and reduction technology. It also highlights the current hotspot of VOC management, which is combination technology. The review also covers China’s policies and standards in VOC management. Finally, it emphasizes the challenges and prospects of VOC management.

2. Classification of VOCs

To carry out comprehensive control and management of VOCs better and more comprehensively and effectively, a specific classification of VOCs is needed. According to the differences in the structure of VOCs, VOCs are classified into oxygenated VOCs, aromatic VOCs, halogenated VOCs, and other VOCs [14]. As shown in **Table 1**, VOCs are categorised, and each VOC contains the main substances and the main sources and hazards.

Table 1. Comparison of different types of VOCs

Category Name	Common substances	Main sources	Threaten
OVOCs	Construction materials, industrial solvents, oil and gas coal chemical industries, etc.	Natural sources, indoor decoration, vehicle exhaust, industrial emissions, etc.	Atmospheric environmental and human hazards
Aromatic VOCs	Toluene, benzene, and ethylbenzene are typical representatives.	oil and gas industry	Serious harm, carcinogenic
HVOCs	Chlorinated, brominated, and fluorinated volatile organic compounds.	Chemical production of halogenated solvents and halogenated compounds, electronics manufacturing, metalworking, metallurgical industries, printing, and ink industries.	Most damaging, destroying the ozone layer, causing biological crises
Other	Alkanes, olefins, etc.	Automotive exhaust, asphalt applications, biomass combustion, oil refining, agricultural products, and chemical processes	Harmful to the environment and the human body

2.1. Oxygenated VOCs (OVOCs)

These volatile organic compounds are known as volatile oxygenated organic compounds (OVOCs), a class of volatile organic compounds containing oxygen functional groups, OVOCs are one of the most important sources of free radicals, and the concentration of OVOCs in the atmosphere varies greatly from region to region [15] [16]. They mainly comprise aldehydes and ketones, alcohols, ethers, low molecular organic acids, organic esters, and extremely reactive compounds such as enols and eons [17].

The sources of these volatile organic compounds (VOCs) are mainly divided into three categories. First, there are natural sources, including biological sources and forest fires. Biological sources are the main contributors to this category. Second, there are anthropogenic sources such as indoor decoration, automobile exhaust, and industrial emissions. With the improvement of human living standards, automobiles have become a common means of transport, leading to automobile exhaust emissions, which are the primary man-made VOC emissions. These emissions contain high concentrations of aldehydes and ketones, with formaldehyde having the highest concentration, followed by acetaldehyde, acetone, benzaldehyde [18], etc. Third, there is the secondary conversion of atmospheric photochemical reactions and the release of hydrocarbons by plants, leading to the secondary conversion of atmospheric organic pollutants.

Some OVOCs show strong polarity among VOCs, which act as intermediates during the oxidation process to affect the oxidative capacity of the atmosphere,

i.e., some low-carbon OVOCs (formaldehyde and acetaldehyde) can produce OH radicals and hydroperoxyl radicals (HO₂) that can affect the oxidative capacity of the atmosphere through photolysis [19]-[21], and OVOCs can also be involved in the photochemical reaction to accelerate the production of O₃ and SO_A [22] [23]. Karl *et al.* [24] confirmed this with direct VOC flux measurements based on the vorticity covariance technique.

OVOCs are primary as well as secondary pollutants, which are harmful to both the atmospheric environment and human health. Firstly, OVOCs are important precursors of free radicals, ozone and PANs in the atmosphere [25]; moreover, formaldehyde, acetaldehyde, etc., can indirectly cause acid rain [26]-[28]; moreover, most of the OVOCs are highly water-soluble, and they can be absorbed by the human body and irritate the eyes, skin and respiratory tract, thus endangering human health, and they are also carcinogenic, teratogenic and mutagenic [29].

2.2. Aromatic VOCs

The text focuses on aromatic VOCs, including benzene, toluene, and xylene (BTX), and their impact on atmospheric chemical reactions, pollution, and human health. Studies have shown that BTX can contribute to photochemical pollution [30] and pose hazards to human health through various means of exposure [31]. Benzene, a component of BTX, is classified as a group 1 carcinogen, and the harmful effects of toluene and xylene on humans have also been established.

Aromatic compounds mainly originate from the oil and gas industry, including oil refining, flaring, and natural gas extraction and processing; the chemical industry involving the production and use of solvents, chemical raw materials, etc.; the automotive industry, where aromatic VOCs are contained in the exhaust emissions; the construction and decorative materials industry, such as the production and use of paints, coatings, and adhesives; and the manufacturing of daily necessities, such as the production of cleaners, personal care products, and so on. products such as paints, coatings, adhesives, etc. Transport petrol evaporation, biodegradation of solvent use and waste and industrial processes are the main sources of outdoor VOC emissions [32]. The solvents used are the most important source of aromatic VOCs, and this class of solvents is mainly used in thinners, glues, adhesives, and printing inks.

This class of VOCs are the most toxic VOCs and pose a significant risk to human health [33].

2.3. Halogenated VOCs

Halogenated volatile organic compounds, or HVOCs, are a class of VOCs that contain halogens. These VOCs are the most common in the environment. Halogenated VOCs mainly include chlorinated, brominated, and fluorinated VOCs. Halogenated VOCs mainly include chlorinated, brominated, and fluorinated VOCs. Among the halogenated VOCs, Poly chloromethane is the most common and widely used. Common Poly chloromethane mainly includes chloroform,

dichloromethane, trichloromethane, and carbon tetrachloride.

Halogenated VOCs mainly originate from the chemical production of halogenated solvents and halogenated compounds, electronics manufacturing, metal processing and metallurgical industries, and printing and ink industries. Halogenated VOCs mainly include chlorinated, brominated, and fluorinated VOCs. PCMs mainly include chloroform, dichloromethane, trichloromethane, and carbon tetrachloride, and their main source is waste from water purification and evaporation systems [34]. This class of VOCs is highly destructive to the ozone layer because halogenated VOCs are the main source of Cl ion radicals in the atmosphere. Most of the halogenated hydrocarbon pollutants have high Henry's constants and therefore high gas-liquid partitioning capacity. The mobility of halogenated hydrocarbon pollutants in soil is mainly influenced by the soil's organic carbon content, including organic carbon composition, such as humus, which has a high adsorption capacity [35]. In general, the possible exposure pathways of halogenated hydrocarbon pollutants are as follows: contact with contaminated soil, dust ingestion; groundwater migration and thus contamination of rivers, drinking water sources, etc.; volatile gas invasion indoors, pipelines, etc.; and food chain transmission [36], HVOCs are highly toxic, difficult to degrade, difficult to manage, and untreated emissions into the atmosphere can cause ecological crises [37] [38].

2.4. Other VOCs

Volatile organic compounds (VOCs) encompass various types including alkanes and olefins, such as ethane, butane, propylene, and cyclic vinyl. For instance, aliphatic hydrocarbons are derived from sources like vehicle exhaust, asphalt applications, biomass combustion, oil refining, agricultural products, and chemical processes [34], Hexane is a common contaminant in the workplace and can damage the human body with prolonged exposure.

A study showed that 99 types of VOCs were monitored in the atmosphere of Haikou District, Beijing in 2016. The average value of the volume fraction of VOCs during the observation period was 20.02×10^{-9} , of which alkanes accounted for the highest percentage of 38.48%, followed by oxygenated volatile organic compounds (OVOCs) accounting for 28.28%, and halogenated hydrocarbons, aromatic hydrocarbons, olefins, and alkynes and acetonitrile accounted for a smaller percentage [39]. Atmospheric VOCs and their contribution to the generation of O_3 and SO_A in the summer in Haikou, Beijing can be seen that in addition to the three types of VOCs mentioned above, other classes of VOCs do not contribute much to the atmospheric VOCs, and they also have different degrees of hazards to the atmospheric environment and human health.

3. VOCs Management Technologies

The control and management of VOCs are usually achieved through three routes: source containment, process control, and end-of-pipe management. Source containment refers to the selection of process routes and raw materials, as far as

possible, the use of VOCs-free raw materials for production; process control refers to the existing production process for the generation of VOCs in the transformation of the links to improve the sealing of each link is one of the effective measures; the end of the governance is the use of physical or chemical means of VOCs emitted from the production process for the collection, governance.

As an important part of VOCs treatment, end-of-pipe treatment is one of the hotspots. End-of-pipe treatment is generally divided into three technologies: one is recycling technology, that is, VOCs gas using physical means into a special device to separate and simplify the components; the second is destruction technology that is, VOCs gas using chemical means to make it degraded to H₂O, CO₂ and small molecules and other non-toxic and odorless substances; the third is the reduction of technology, is through a series of chemical and physical processes, volatile organic compounds will be transformed into harmless substances or reduce their concentration. **Figure 1** shows three ways to control and manage VOCs.

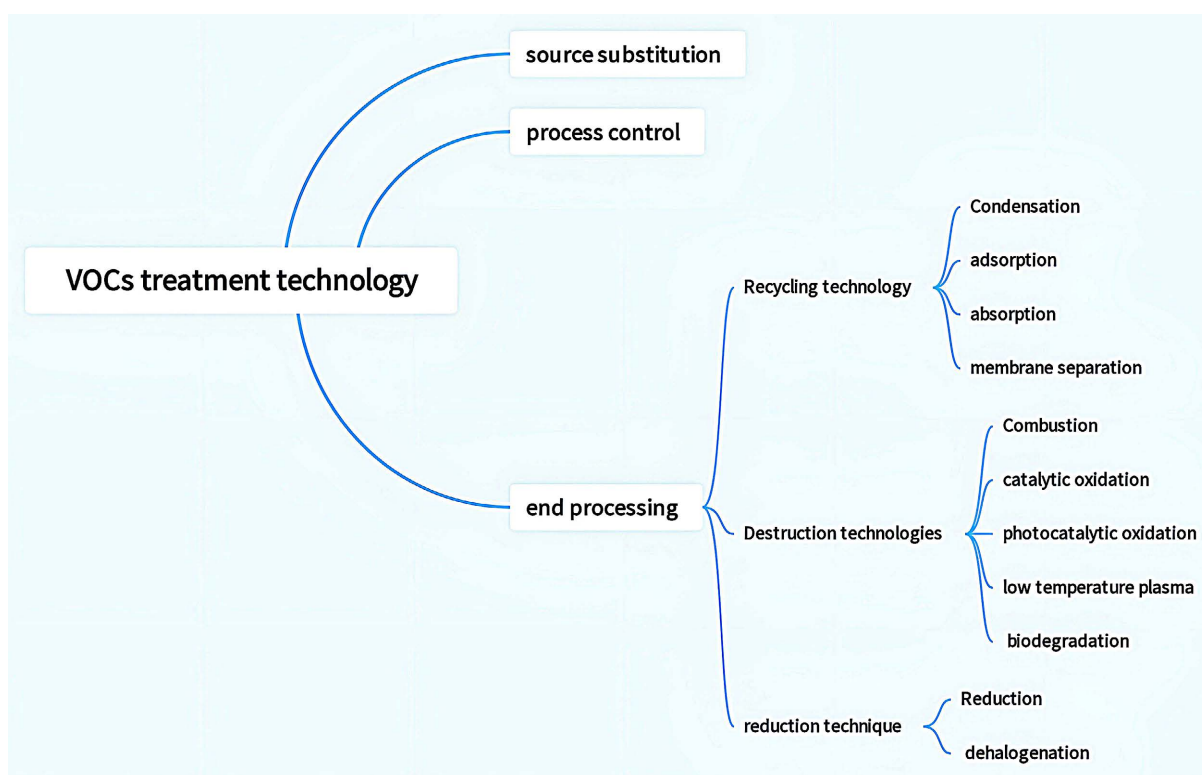


Figure 1. Classification of end-of-pipe treatment technologies for VOCs.

3.1. VOCs Recovery Technology

Volatile organic compounds (VOCs) recovery technologies are crucial for environmental and health protection, resource utilization, and regulatory compliance. These technologies play a significant role in ensuring a cleaner, healthier, and more sustainable future by recovering VOCs with recycling value. The main recovery technologies for VOCs include condensation, adsorption, absorption, and membrane separation.

3.1.1. Condensation

The condensation method is based on the nature of different substances at different temperatures that have different saturated vapor pressure, the use of pressure or cooling to achieve the saturation of the exhaust gas VOCs gas volume, and condensation into liquid from the exhaust gas separation, to achieve the organic purification and recycling, the treatment process as shown in **Figure 2** [14].

The process of condensation is divided into two parts: one is waste pre-cooling; the other is waste condensation.

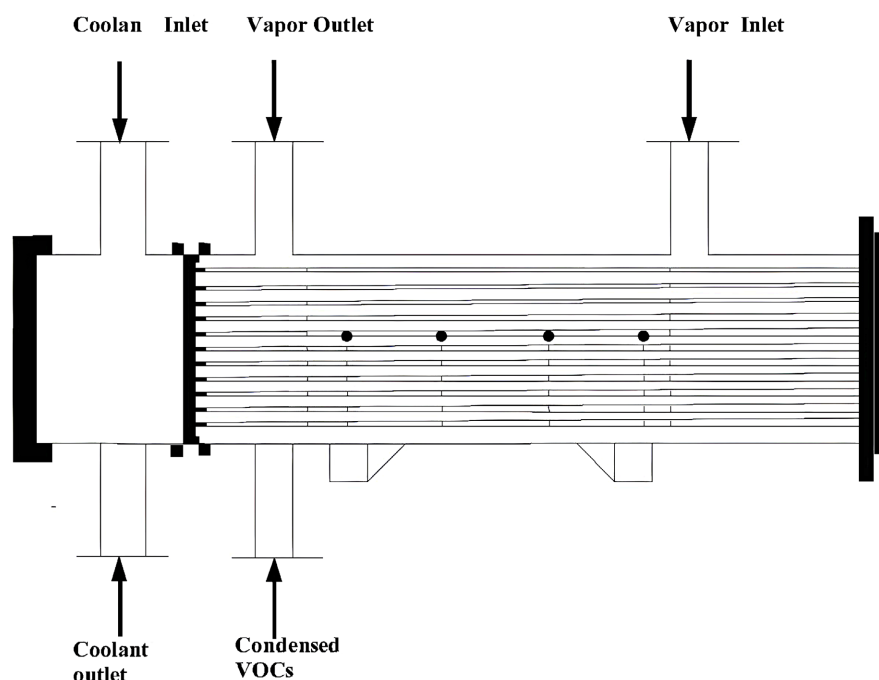


Figure 2. Condensation technology for VOCs treatment process.

Waste pre-cooling is when the waste, condensates with a compressor compression, and is then passed into the condenser; waste condensation is with the condenser cools to a certain temperature, and VOCs gas into liquid. The cooling process has two ways: mechanical cooling and liquid nitrogen cooling. One is the use of compression equipment to VOCs cooling to the liquefaction point, the second is the use of liquid nitrogen cooling and heat absorption principle will VOCs gas cooling to the liquefaction point. The condensation method operates at temperatures ranging from -110°C to -35°C , with -70°C to -35°C being the shallow cooling temperature and -110°C to -70°C being the deep cooling temperature [40].

In summary, there are advantages and disadvantages of using condensation to recover VOCs. The advantage is that condensation is suitable for the recovery of industrial exhaust gases with high VOCs concentration and small flow rate [5]; the effect is ideal for VOCs exhaust gases with higher boiling point, higher concentration, and recovery price; the disadvantage is that the recovery effect is not good for VOCs exhaust gases with low boiling point and lower concentration. Recovery of the latter by condensation is not commonly used, because to improve

the optimization of the recovery of such VOCs by condensation, it is necessary to use a lower temperature condensation medium or higher pressure, which inevitably increases the complexity of the condensation equipment and technology.

3.1.2. Adsorption

The adsorption method uses the differences in selectivity of various components of VOCs exhaust gas on adsorbents (solid porous substances) to separate pollutants in the exhaust gas by changing the temperature or pressure. The adsorption equipment can be chosen from fixed bed, fluidized bed, and air flow bed. Adsorption technology uses adsorbent materials to interact with the VOCs physically and chemically in the exhaust gas. It is an effective method for enriching and separating VOCs, and the adsorbent material can be reused through thermal or vacuum desorption. Adsorption technology is considered an efficient and economical control strategy because of its potential to recover and reuse adsorbent materials and VOCs [41].

After the adsorption is saturated, the VOCs on the adsorbent are desorbed using steam or hot air flow, and then treated and recovered using combustion, condensation, and other technologies, depending on whether they have recovery value. The process of this method is shown in **Figure 3** [14].

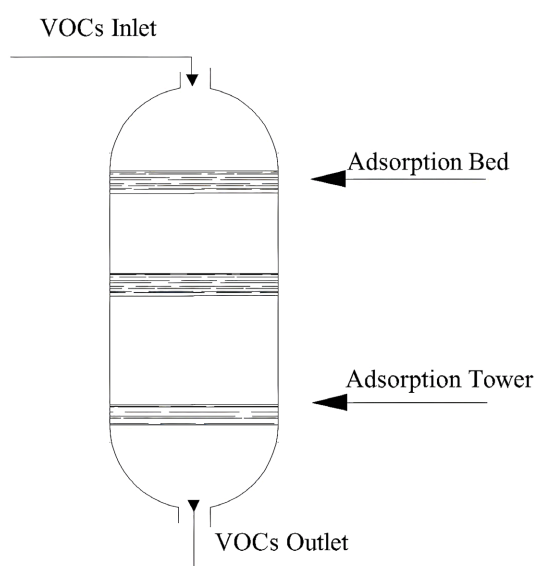


Figure 3. VOCs treatment process by adsorption technology.

The effectiveness of the adsorption method is influenced by three factors. The first factor is the performance of the adsorbent, specifically its specific surface area, pore size distribution, and surface chemical functional groups. The second factor is the performance of the adsorbate, including the molecular structure, polarity of the molecules, and boiling point. The third factor is the adsorption conditions, such as temperature and humidity. The key to the adsorption method lies in the adsorbent. From both technical and economic standpoints, the adsorbent should possess characteristics such as a large specific surface area, high thermal

stability, strong hydrophobicity, low cost, and the ability to be recycled through desorption treatment. Currently, there are many classifications of adsorbents, mainly activated carbon [42], zeolites (molecular sieves) [43], Metal-Organic Frameworks (MOFs) materials [44], and hyper crosslinked polymers (HCPs) [45] have been studied.

Activated Carbons (ACs) are one of the most widely used adsorbents, with the advantage of good acid and alkali resistance heat resistance, and high chemical stability; superior to most adsorbents [46]. However, AC adsorbents also have their shortcomings: 1) ACs have a certain water-absorbing capacity, and when the humidity of the exhaust gas is high, the purification power of organic matter decreases; 2) ACs will burn at high temperatures, with poor safety, the regeneration temperature is limited, and when the regeneration temperature is low, the high-boiling compounds cannot be completely desorbed; and 3) it is not suitable for high-concentration wastes and waste gases that contain water or granular substances.

The modification of molecular sieves began in Japan in 1990. This involved the hydrophobic modification of silica-aluminum molecular sieves, to enable desorption and regeneration at high temperatures. The common fixed bed was replaced with rotary concentration equipment, leading to a significant improvement in the adsorption efficiency of the modified adsorbent [41]. Li [47] and others, on the other hand, investigated the treatment of VOCs-containing exhaust gases with activated carbon and zeolite molecular sieves, respectively, and summarized the experiments to find that zeolite molecular sieves were better than activated carbon in terms of thermal stability and adsorption of exhaust gases when the flow rate was increased, while the equilibrium adsorption capacity was not as good as that of activated carbon. After that, the adsorption of VOC gases went to another height due to the emergence of MOF adsorbent materials. The average specific surface area, pore volume, and VOC adsorption capacity of different adsorbents were MOFs > ACs > Supercrosslinked Polymer Resin (HPR) > zeolite, respectively. The VOCs adsorption capacity of MOFs was 796.2 mg/g, and the maximum adsorption capacity was 1375.0 mg/g, which was 1.73 times higher than that of activated carbon, 5.80 times higher than that of molecular sieves, and 2.07 times higher than that of HPR [48].

In summary, when it comes to adsorbing and removing VOCs, traditional activated carbon and zeolite materials work well. However, their poor water stability limits their industrial use, and their adsorption capacity in high humidity can be enhanced by adjusting the structural properties and functional groups of the material surface. While molecular sieves have a good specific surface area and void ratio, their adsorption capacity for VOCs is low. MOF is a new type of porous material with an adjustable surface and large adsorption capacity, but its high cost and huge pore space restrict its widespread use.

The saturation adsorption capacity of volatile organic compounds (VOCs) increases with the number of functional groups. The relative coefficient of benzene

adsorption is 0.98152. Adsorbent materials improve the adsorption capacity of benzene, toluene, and xylene by enhancing the basic functional groups through ammonification and increasing the acidic functional groups on the surface through oxidation [49]; it is also possible to form a composite material by MOFs-based composites, especially by coating inexpensive micropore materials, such as biochar, clay, and zeolite, which is hopeful to become a current adsorbent material for conventional VOCs as an Alternatives.

The adsorption method is mainly used to treat large volumes of air with low concentrations of VOCs. It has a certain recovery value of VOCs, with a removal efficiency of up to 90%. Adsorption reaches saturation and can be desorbed through condensation to recover part of the organic matter, allowing for the resourceful use of waste. This technology is widely used in China for VOC recycling treatment. The fixed bed activated carbon adsorption process is suitable for dealing with high boiling point organics, while the rotor molecular sieve adsorption process can be used for treating mixed waste gas or high boiling point waste gas.

3.1.3. Absorption

The absorption method is based on the nature of different components of VOCs in the absorbent solubility difference, through the absorption equipment to make the exhaust gas in the VOCs component from the gas phase to the liquid phase, and then use the VOCs and the physical properties of the absorbent differences in the separation of the treatment method, can also be understood as a mixture of gas dissolution and the liquid process. Absorption equipment includes packed towers, spray towers, rotating packed beds, and so on. The absorption method is widely used because of its simplicity, high efficiency, low operation, low investment cost, and absorber regeneration capability [50]. At present, the absorption method of VOCs treatment equipment mainly includes a packed absorption tower and a spray absorption tower. Supergravity rotating packed bed is a newly developed equipment in recent years, gas-liquid mass transfer efficiency, not easy to scale and clogging, has been successfully applied in flue gas desulphurization and dedusting, wastewater waste gas treatment, and other industries.

When using the absorption method, the selection of absorbent is the key, VOC gases are hydrophobic substances, so the choice of absorbent should be based on other types than water. Usually, high boiling point, low volatility, low toxicity, oil organic solvents with high solubility for VOCs, such as diesel fuel, washing oil, etc.; because most of the VOCs are poorly soluble in water, water, the most used absorbent, is not effective in the adsorption of organic gases. In recent years, there have been numerous studies on hotspot absorbents, mainly surfactants, microemulsions, ionic liquid absorbents, and so on.

Organic solvents were the first used for the absorption of VOCs; surfactants also have some adsorption effect on VOCs; microemulsions have better adsorption effect on VOCs but their preparation is more complicated and difficult; and then ionic liquids (ILs) were discovered, which are environmentally friendly and stable solvents, usually consisting of organic cations and organic or inorganic

anions with very low volatility, which can be designed by choosing suitable anions and cations to design the structure [51] [52], ILs have wider applications in gas separation and for the removal of VOCs, especially as absorbents for benzene, toluene, and sulfur-based VOCs as well as acetone [50] [53] [54]. However, ionic liquids are not as perfect as imagined, most of them are toxic and highly viscous, poorly biodegradable, and complicated to synthesize [55]. Classification of DES according to the HBA component in the structure of eutectic mixtures can be divided into four categories [56], as shown in **Table 2**.

Table 2. Classification of DES according to HBA composition in the structure of eutectic mixtures.

Category Name	Main Substances Contained
Ion DES	Quaternary ammonium salt (QAS) or phosphine salt (QPS) composition
Non-ionic DES	Monoterpenes, polyphenols, or carboxylic acids
SUPRADES	Cyclodextrin (CD)
DES based on ILs	Ionic liquids, organic compounds

The regeneration of the absorber can be achieved using thermal degradation, thermal desorption, adsorption using common adsorbents, distillation, or pasteurization using inert gases [57]. However, some DES with poor thermal stability is not suitable for VOCs treatment due to the high temperatures involved. Reusing the absorber after saturation can reduce costs and allow for the recovery of valuable components from the exhaust gas.

Overall, the absorption method has low recovery efficiency and is primarily used for treating mixed gases with higher concentrations and lower pressures and temperatures. It is especially suitable for recovering oil and gas in chemical plants and refineries and can also be used for absorbing low-concentration exhaust gases in combined technologies.

3.1.4. Membrane Separation and Recovery Methods

Membrane separation treatment for recovering VOCs involves utilizing the differences in dissolution and diffusion rates of different components in the membrane. This allows organic molecules dissolved in the membrane to rely on the concentration gradient formed on both sides of the membrane to diffuse to the other side, while the residual gas is discharged into the atmosphere. This process separates volatile organic compounds from the air [58]. The method involves enriching various gaseous components of VOCs exhaust gas on a permeable membrane by pressure, ultimately resulting in the separation of VOCs exhaust gas [59].

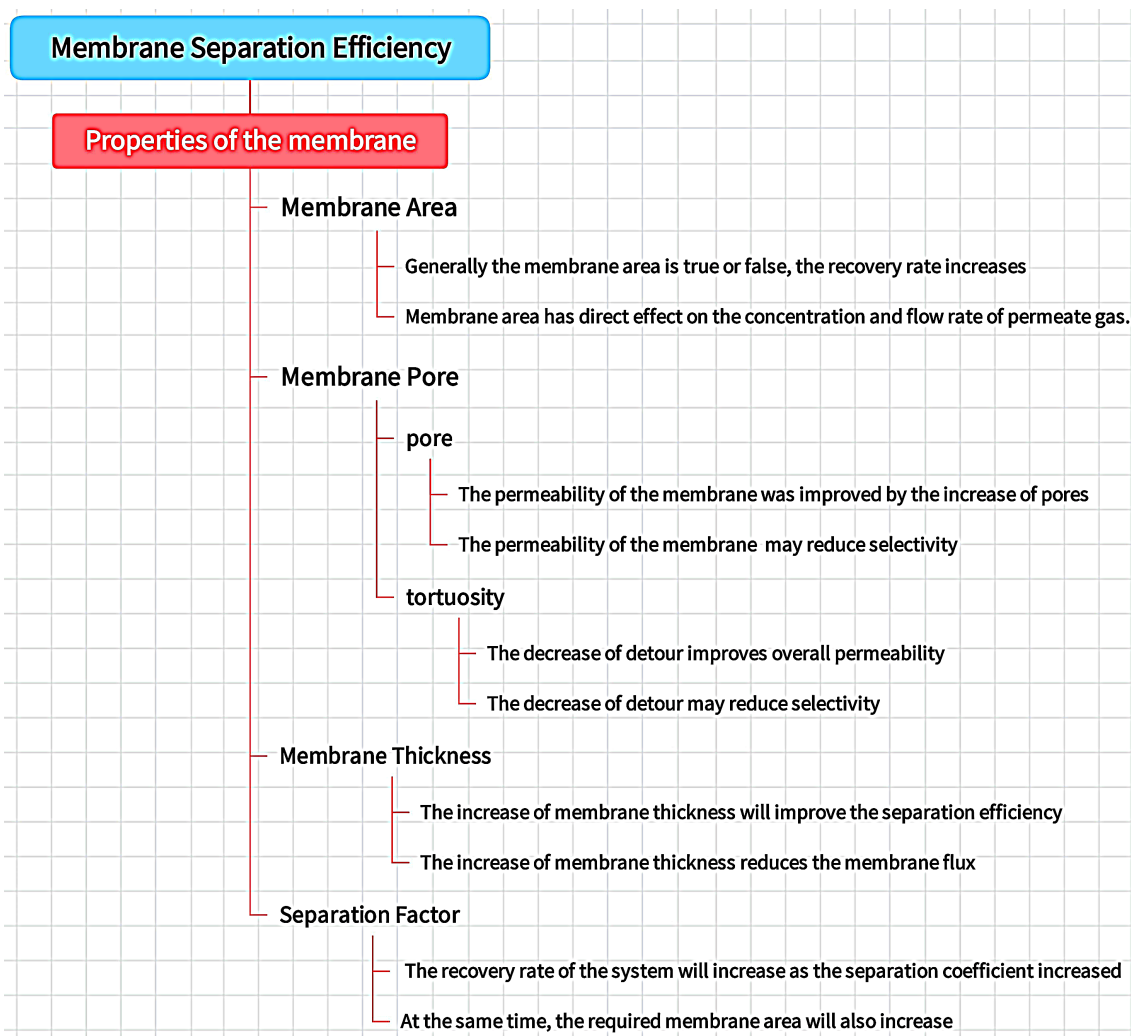
Suitable membrane materials are a key issue in membrane separation and recovery [60]. Different membrane structures result in different gas transport and diffusion processes, leading to distinct separation mechanisms. Currently, membrane separation operates through the microporous diffusion mechanism of

porous membranes and the dissolution-diffusion mechanism of non-porous membranes [13]. Microporous diffusion involves selective permeation through the membrane’s micropores. In contrast, dissolution diffusion entails the desorption of gas molecules from the downstream surface of the membrane after they are adsorbed and dissolved on the upstream side, followed by diffusion through the membrane driven by a concentration difference, and then desorption from the downstream surface of the membrane.

The influencing factors of the membrane separation process are primarily the membrane’s nature and the separation conditions, with the membrane’s nature being the main factor affecting the separation effect [61].

Figure 4 shows the factors and influence patterns affecting the recovery efficiency of membrane separation [62]-[65].

Ideal gas separation membranes require good permeability, selectivity, excellent thermal and chemical stability, and high mechanical strength [66]. Typically, gas separation membranes can be categorized as porous or non-porous, and are



(a)

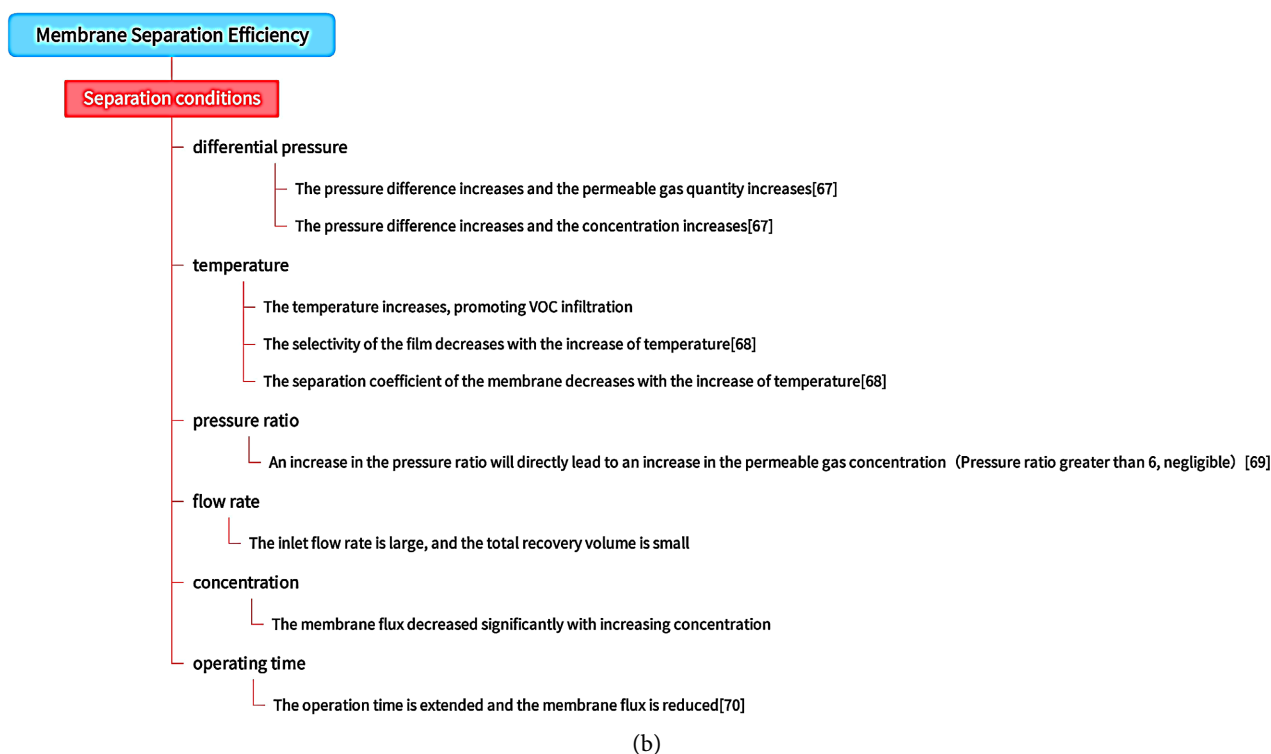


Figure 4. Effect of the membrane separation process. Influence of membrane properties on separation efficiency as (a), Effect of separation conditions on separation efficiency as (b).

made from inorganic materials and organic polymers, respectively, Below I have summarized the types of membranes that are more commonly used for the separation and recovery of VOCs.

Membrane separation and recovery is a well-established technology that has been used since the 1950s in the United States, Japan, and other countries for recovering volatile atmospheric oil and gas molecules. It has been widely adopted for recycling organics such as ethane, dichloromethane, and toluene in the petroleum industry, as well as for separating aromatic compounds and oxygen-containing organic compounds [67]. In the late 1970s, vacuum-based membrane technology began to be explored to improve the separation efficiency of volatile organic compounds (VOCs). The liquid membrane process is particularly promising due to its high permeability and selectivity [68]. This process involves trapping the absorbing liquid in the membrane's pores, creating a stationary liquid membrane that achieves separation through liquid permeation.

Ozturk *et al.* [69] conducted experimental studies on the separation of mixtures of VOCs such as benzene, carbon tetrachloride, and methanol with N₂ using immobilized liquid membranes. The results demonstrated the effectiveness of liquid membranes in separating highly volatile organic compounds.

Membrane separation is a promising technology for recovering volatile organic compounds (VOCs) due to several advantages [60] [70] [71]:

1) High selectivity and separation efficiency: VOC removal rate from the feed is over 80%.

2) Simple process operation, low initial investment, low energy consumption, and small footprint.

3) Direct obtainment of condensable VOC gases without any need for a reaction, change in molecular structure, or secondary contamination.

4) Operation at ambient temperature and pressure, no consumption of organic solvents, and simple operation.

5) Easy coupling with other technologies.

However, membrane contamination, instability, high equipment investment, and limitations in industrial implementation are notable drawbacks. **Table 3** shows the various recovery techniques for end-of-pipe technologies and their advantages and disadvantages.

Table 3. Comparison of common VOCs recovery technologies.

Technical name	Principles	influencing factors	applicable environment	advantages	disadvantages
condensation	Conversion of VOCs from gaseous to liquid form through thermal energy recovery	Gas composition, gas temperature and pressure, cooling medium, condenser design, ambient conditions, exhaust gas flow rate	High concentration, high boiling point VOCs	High recovery for high boiling point VOCs	Unsuitable for low concentration VOCs, high operating costs, secondary treatment required
adsorption	Separation of VOCs by selective adsorption of VOCs using adsorbents	Properties of adsorbents, properties of adsorbents, adsorption conditions	High removal efficiency and easy operation	Complexity of desorption problems	Adsorption of low-concentration VOCs
absorption	Transfer to absorbent using absorbent	Properties of the absorbing mass, properties of the absorber, conditions of absorption	simple and feasible	Secondary treatment is complex and may result in secondary contamination	VOCs with high solubility in the absorbent
Membrane Separation Recovery	Separation of VOCs from other gases using their different ability to pass through separation membranes	Membrane properties, separation conditions	Good results for medium-concentration VOCs	separable	Complex and costly membrane selection

3.2. Destruction Technologies

Destruction technologies are specialized methods that transform volatile organic compounds (VOCs) into non-toxic substances, such as CO₂ and H₂O, or simple small molecules. These technologies include catalytic oxidation, low-temperature plasma, biodegradation methods, and photocatalytic oxidation. In destruction-based methods, volatile organic compounds are converted to CO₂ and H₂O. The

destruction process can be thermal, catalytic, or biological oxidation.

Combustion methods

With strong applicability and high efficiency, the combustion method is the most widely used VOCs treatment technology in China. It should be mentioned that if VOCs produce inorganic exhaust gas containing sulfur, nitrogen, chlorine, etc., during various combustion processes, resulting in secondary pollution, they should be further treated to meet the standards before being discharged.

3.2.1. Direct Combustion Method

Combustion is the traditional method for controlling VOCs, and the direct combustion method involves spraying VOCs-containing exhaust gases and auxiliary fuels into a combustion furnace for direct combustion. This method is simple in terms of equipment and process and has a removal rate of more than 95% for high concentrations of VOCs, with a combustion temperature of around 1100°C [72].

Comprehensively this technology is suitable for treating VOCs waste gas with high concentration, high calorific value, and no recovery value. However, due to the complexity of the composition of VOCs, some of the components will form toxic or irritating gases during the combustion process. If the direct combustion method is to be applied, it is necessary to carry out compositional testing and harmless treatment of hazardous gases before combustion, and the high concentration of exhaust gases must be mixed with air before combustion to avoid the production of dioxins and other harmful substances [73].

3.2.2. Catalytic Combustion

The catalytic combustion method involves preheating the VOCs exhaust gas to the ignition temperature, which leads to the catalyst's oxidative decomposition of VOCs molecules into CO₂ and H₂O at low temperatures [74]. The catalyst plays a crucial role in the reaction by adsorbing the reactant molecules and reducing the reaction activation energy.

Compared to non-catalytic thermal oxidation processes, catalytic combustion is more thermally efficient and can be more energy efficient when used in heat exchange mode, coupled to a heat exchanger after the catalytic combustion chamber. This technology operates at lower temperatures than direct combustion methods, resulting in lower combustion costs, improved equipment safety, and reduced generation of toxic substances.

The selection of the catalyst is crucial for catalytic combustion. If the exhaust gas contains components that can poison the catalyst, pretreatment is necessary to control the content of sulfides and halogenated hydrocarbons, or it may be necessary to switch to thermal combustion [75].

The catalyst is the most critical part of this method, including precious metal catalysts and non-precious metal catalysts. The technology can be improved by enhancing the catalyst's performance at low temperatures and developing high-quality catalysts with chlorine, SO₂, and water resistance to improve the treatment.

3.2.3. Regenerative Combustion Method

The thermal regenerative combustion method is based on thermal and catalytic combustion methods, installing a thermal regeneration system using high-heat capacity ceramics as a heat accumulator, which is characterized by the possibility of storing the heat of the combustion exhaust gases to heat the high-temperature accumulator to treat the VOCs exhaust gases [76].

In essence, the VOCs exhaust gas is preheated and then combusted under the action of a small amount of combustion aids, and then the heat released from the cooling of the purified gas after combustion is used to preheat the front-end VOCs exhaust gas. Advantages: self-heating system, high utilization of waste heat, low energy consumption, processing efficiency of more than 95%, can effectively reduce the use of auxiliary fuels [77].

Regenerative combustion technology is divided into Regenerative Catalytic Combustion (RCO) and Regenerative Thermal Combustion (RTO). RCO is a regenerative catalytic oxidation technology that uses a catalyst to promote the oxidation of VOCs at high temperatures compared to RTO. This reduces the temperature and energy consumption required to operate the system. It is usually used for the treatment of low-concentration VOCs and may have a slightly lower heat recovery efficiency compared to RTO. RCO has a fast cold start and low cost and is suitable for intermittent treatment of exhaust gases from production conditions. The exhaust gas must not contain S, P, AS, halogens, and other components that poison the catalyst, and the trace dust in the exhaust gas needs to be deeply filtered, otherwise, it will affect the effectiveness of the catalyst [77]. RTO is a thermal oxidation technology, which oxidizes the VOCs into carbon dioxide and water vapor through high temperatures. Ceramic or metal packing is usually used to store heat between high and low temperatures for efficient energy recovery and recycling. It is suitable for treating VOCs exhaust gases with low to medium concentrations and high continuous emission concentrations. Corrosive exhaust gases containing S, CL, etc. cannot be treated in RTO and RCO.

The regenerative combustion method is adaptable to low, medium, and high concentrations of organic waste gas, expanding the use of combustion technology. The removal efficiency of VOCs is high, but the consumption of energy is also high.

3.2.4. Porous Media Combustion Method

The principle of the porous media combustion method is the same as that of the thermal storage combustion method, which uses porous media as heat storage material. The principle is that in the presence of high temperature and oxygen, VOCs are mixed with air and then catalytically combusted through porous media to oxidize the organic matter into harmless CO₂ and water vapor, thus achieving the effect of purifying the air.

Porous media have excellent thermal storage and thermal conductivity, and the residual heat generated by downstream combustion can preheat the upstream exhaust gas by solid heat transfer the porous media increase the contact area between the material surface and the VOCs, which is the most ideal for the application,

and the removal rate can reach more than 98% [77].

3.2.5. Catalytic Oxidation of VOCs

Catalytic oxidation refers to the use of catalysts to reduce the activation energy of the reaction so that the VOCs at a lower temperature degrade into CO_2 and H_2O and some of the hazards relative to the VOCs of smaller substances. To achieve the purpose of harmless treatment of VOCs. This technology is also one of the most effective and economically feasible ways. Its process diagram is shown in **Figure 5** [40].

The goal of catalytic oxidation is the destruction of VOCs; the key to catalytic oxidation also lies in the choice of catalyst. There are three main types of catalysts: precious metal catalysts, non-precious metal catalysts, and mixed metal catalysts. Researchers have searched for efficient, stable, and selective catalysts by optimizing catalyst configurations, elemental doping, acid-base modification, and other modifying media. **Table 4** shows the main catalysts used for VOCs and their advantages and disadvantages.

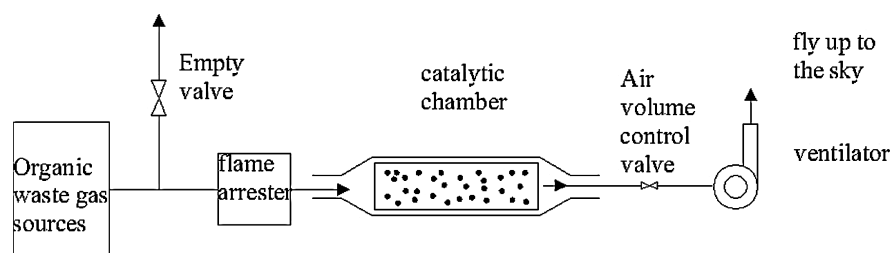


Figure 5. Catalytic oxidation process for VOCs treatment.

Table 4. Comparison of different catalysts.

Types of catalysts	names of commonly used catalysts,	advantages	disadvantages	ways of improvement	suitable types of VOC
Precious metal catalysts	Pd, Pt, Rh, and other precious metals	High activity, good catalytic effect.	High cost, easy to sinter, easy to poison [78]	Improvement by adjusting loadings, surface modification, alloying, etc.	VOC removal at low temperatures (active in catalytic oxidation of hydrocarbons [34])
non-precious metal catalysts	Oxides of transition or rare earth metals [79]	Easily available and inexpensive, shielding resistance, and stability [80]	Lower activity than precious metal catalysts	can be improved by combining two or more oxides [81], adding specific cations	Catalytic oxidation of Cl-VOCs with high activity and good stability, anti-neutral toxicity [82] [83]
mixed metal catalysts	Calcite catalysts, spinel catalysts [84]	High catalytic activity and selectivity, can make use of the catalytic activity and properties of different metals, and suitable mixing ratios and catalyst formulations can improve the stability of the catalyst and anti-neutral toxicity [85]	Preparation complexity, poisoning problems, catalyst selectivity	This can be achieved by adjusting metal ratios, optimizing carriers, surface modification, etc.	Mixed metal catalysts are generally suitable for all types of VOCs

Precious metal-loaded catalysts, such as Pd, Pt, and Rh, are commonly used for removing volatile organic compounds (VOCs) at low temperatures due to their high efficiency. However, these catalysts are expensive, prone to activity loss from sintering, and unstable in the presence of chlorides.

Non-precious metal catalysts can be either loaded or unloaded. Loaded catalysts show better activity and performance in VOC oxidation due to better dispersion of the active components. Common non-precious metal catalysts include transition metal oxides and rare earth metal oxides. Some commonly used metal oxide catalysts are copper oxide, manganese dioxide, iron oxide, nickel oxide, chromium oxide, and cobalt oxide.

Manganese-based catalysts have high catalytic activity, low cost, and high stability. However, they have drawbacks such as weak surface electron transfer capacity, low specific surface area (SSA), and susceptibility to chlorine poisoning [86].

Chlorine can lead to the poisoning of manganese-based and cerium-based catalysts, which are typically used in catalytic oxidation in environments without chlorine. Copper-based catalysts are less stable. Co_3O_4 has good catalytic activity, but its catalytic temperature is high, and its thermal stability is poor at high temperatures. TiO_2 is mainly used as a photocatalyst, but its light utilization efficiency is low, so it needs to be modified by semiconductor recombination, noble metal deposition, photosensitization, and ion doping.

The performance of metal oxide catalysts can be enhanced by combining two or more oxides to achieve a synergistic effect. Bastos [87] *et al.* found that the reducibility of the metal and the rate of oxygen removal by the metal are crucial for catalytic oxidation. Experimental evidence suggests that adding another cation can improve the reducibility of the metal, thereby increasing catalytic efficiency.

The current development on the catalytic oxidation of VOCs is mainly developed by optimizing or working on the preparation of a new type of catalyst. Wang [88] *et al.* prepared noble metal-free mixed aluminum valence substituted CeCuOx dioxide and NiO-modified $\gamma\text{Ni}/\text{CeCuOx}$ ternary mixed-metal oxide catalysts at the molecular level. Through the optimization of the microstructure and grafting of octakis-trichlorosilane (OTS), the catalysts successfully achieved excellent catalytic selectivity of the catalyst for low concentrations of VOCs. The researchers also successfully induced lanthanum referenced CoMn_2O_4 catalysts, which improved the oxidation rate by modulating the oxide species activity of CoMn_2O_4 [89].

Catalytic oxidation is commonly used for treating medium and high-concentration VOCs (concentration > 5000 mg/m). While it can effectively treat exhaust streams with varying VOC concentrations and flow rates, it is most suitable for medium flow rates and low concentrations of VOCs [90].

3.2.6. Low-Temperature Plasma Method

The low-temperature plasma method achieves a high-voltage pulsed discharge using an applied electric field, where the high-energy electrons generated by the

discharge are used to bombard the molecules of the VOCs, generating a large number of reactive molecules (active particles such as hydroxyl radicals and reactive oxygen radicals) that interact with and oxidize the components in the VOCs, degrading the VOCs into CO₂ and H₂O or simple small molecules. It is a combination of the advantages of NPT and catalysis to increase retention time by placing the catalyst in or near the discharge zone and adsorbing the target molecules to favor complete oxidation to CO₂ and water [91].

Low-temperature plasmas can be generated by corona discharges, dielectric barrier discharges (DBDs), glow discharges, pulse discharges, microwave discharges, and other high-voltage discharges [92]-[94].

Depending on the reactor structure and the type of power supply, the technology is realized by three different methods: electron beam irradiation, dielectric barrier discharge, and corona discharge of these three methods, current research, and industrial applications in treating VOCs are mainly focused on the dielectric barrier discharge method [95]-[97]. **Table 5** shows the influencing factors of low-temperature plasma of VOCs and their influence patterns.

Table 5. Influencing factors of low-temperature plasma method.

Influences	Regulation	Mechanism
Temperature	Generally, higher temperatures result in higher removal rates [98] [99]	The heat-absorbing behavior of the reaction increases the rate of reaction of O and Oh radicals with VOC [100]-[108]
Initial VOC concentration	High initial VOC concentrations are detrimental to the removal	High initial VOC concentrations are detrimental to removal High initial VOC concentrations are detrimental to removal
Humidity	The presence of water is detrimental to VOC removal	Electronegative properties of water limit electron density and burst reactive chemicals
Oxygen content	Small increases in oxygen content can enhance removal rates; higher oxygen concentrations can reduce removal rates.	High oxygen concentrations tend to initiate electron attachment reactions, allowing excited nitrogen molecules and nitrogen atoms used for VOC removal to be consumed by oxygen with its free radicals [109]-[111].
Air velocity	Lower gas flow rates increase VOC removal.	The effect of reducing the gas flow rate increases the collision probability of electron collision reactions and reactions between volatile organic compounds and plasma-generated radicals and substates

Low-temperature plasma technology can operate at room temperature and be adjusted by the electric field to meet the treatment needs of different VOC emissions. It is suitable for lower concentrations of VOC gases and is highly efficient in treating benzene, formaldehyde exhaust gas, odors, and other fields. However, there are some disadvantages to the low-temperature plasma method: 1) it has high cost and high energy consumption, making it expensive to operate; 2) the plasma generation process may lead to spark discharge, posing safety hazards; 3) the work process produces nitrogen oxides, O₃, and other by-products, leading to secondary pollution; 4) the technology usually has less than 70% efficiency in treating VOCs, and the purification efficiency is not high. Current national policies do not recommend using this technology for VOC treatment other than for

malodor and odor treatment [96] [97].

The degradation of VOCs using plasma technology alone is not very effective. As a result, researchers have combined plasma technology with some existing mature technologies.

3.2.7. Biodegradation

Biodegradation was initially used for the deodorization of exhaust gases, but in recent years, it has gradually emerged in the field of degradation of volatile organic compounds (VOCs) [112]-[114]. The biodegradation method is to provide energy and nutrients for microorganisms in a suitable environment with organic matter in VOCs exhaust gas as a carbon source, and use screened microbial strains to convert inorganic substances such as CO_2 , H_2O , and microbial cytoplasm in the exhaust gas through their metabolic process [77]. The mechanism of biodegradation is the mass transfer of VOCs exhaust from the gas phase to the bioreactor and then decomposed by microorganisms [115]. Depending on the mode of operation, biodegradation consists of three main processes: bioscrubbing, biofiltration, and bio-drip filtration [116].

1) Bioscrubbing method

The method is based on the principle that microorganisms and their nutrients are placed in a liquid to change the VOCs from the gas phase to the liquid phase in contact with the suspension, and then decompose them through the metabolism of the microorganisms. Typical realizations include spray towers and bubbling towers. A schematic of the principal process flow is shown in Figure 6 [77]. This method is suitable for the removal of VOCs that are small, high in concentration, easily soluble, and slow in biological metabolism.

The biological washing device operation process is stable, the parameter control is more convenient, and the operation process pressure drop is low, but it will

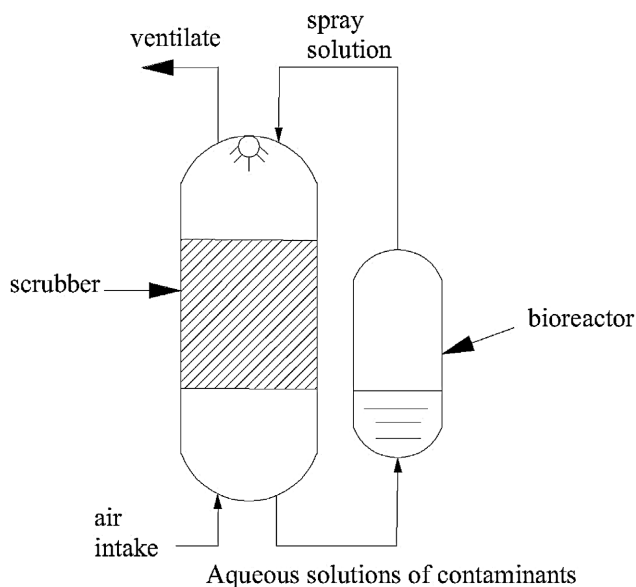


Figure 6. Schematic diagram of the process of the biological washing method.

produce more activated sludge, which needs further treatment, and at present, the application of this method is not much.

2) Biofiltration

On a solid media surface, attached microorganisms grow and degrade the exhaust gas as it passes through the fixed bed. The fixed bed is made up of a filter media, typically a porous material that adsorbs gaseous compounds and supports microbial growth using common biomass like peat, wood chips, and soil. This method is suitable for volatile organic compounds with large volume and low concentration. It is often used in filtration towers and is depicted in **Figure 7** [77].

While biodegradation is a simple process, it is dependent on many factors that influence biodigester operation, including temperature, pH, moisture content, packing, air consumption rate oxygen demand, residence time, and more. **Table 6** shows the influencing factors and influence pattern of VOCs removal by biodegradation method.

Biofilters generally perform poorly at temperatures below 20°C. Sun *et al.* [117].

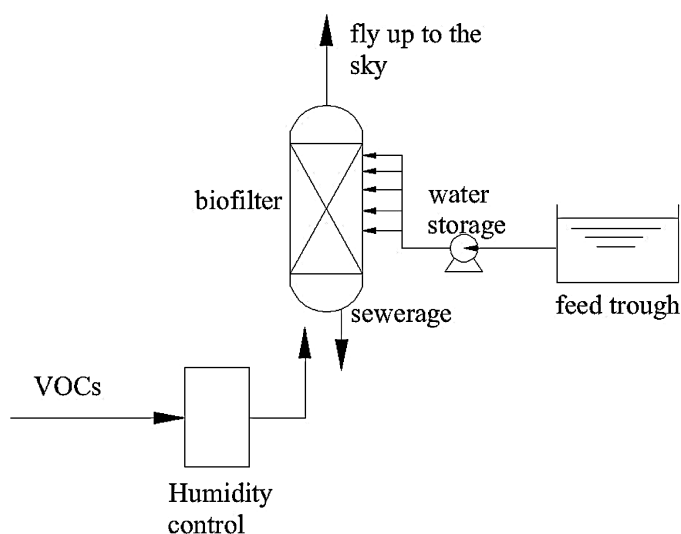


Figure 7. Schematic flow diagrams of the biofiltration method.

Table 6. Factors affecting the biofiltration method.

Influencing factors	Appropriate choices
Packing	Needs to have a large specific surface, excellent gas mass transfer efficiency, large porosity
Ph	The degradation efficiency of VOCs is highest when the PH is about 7.
Temperature	A temperature of 30°C - 40°C is suitable
Water content	The water content in biofiltration is 20% - 30%.
Oxygen content	Aerobic microorganisms at 0.003 - 0.05 mol/L
Inlet flow rate	The larger intake flow rate will result in incomplete degradation; a smaller flow rate will increase the input cost.

used two quorum sensing (QS) enhancement methods to improve the removal of gaseous toluene in a biofilter at a low temperature of 12°C. These methods involved adding exogenous N-acyl-homoserine lactones (AHLs) and inoculating AHL-producing bacteria. The enhancement techniques effectively improved toluene removal at 12°C.

To address the limitations of biofiltration in degrading volatile organic compounds (VOCs) with poor water solubility, researchers are exploring innovative bioreactor configurations, such as membrane bioreactors or capillary bioreactors, to overcome mass transfer limitations during indoor air treatment. Additionally, the use of biofiltration based on biologically active coatings can help minimize equipment costs and mass transfer issues, thereby partially addressing the limitations of biofiltration [115].

Biofiltration is considered environmentally friendly, cost-effective, and safe, but it does have some drawbacks. These include uneven distribution of biomass, volatile organic compound (VOC) loading, excessive accumulation of nutrients and biomass, and applicability only to low concentrations of VOCs [118]. To improve the degradation of high concentrations of VOCs, two-phase biofilters can be used. However, the management of hydrophobic VOCs remains the biggest challenge for biofiltration.

3) Bio-drip filtration

At the same time with the characteristics of washing bed, filter bed. The top is equipped with a spraying device, solid media generally inert filler (without biomass) bed composition, compared with the filtration tower, has a lower pressure drop and a more effective way of nutrient control. Process characteristics: biological phase fixed, aqueous phase flow, equipped with a top spray. The principal process flow is shown schematically in **Figure 8** [38]. Fillers are commonly used as volcanic rock, activated carbon, and ceramic materials, and drip filter beds are suitable for VOCs that produce acidic substances after degradation.

The biological method is more suitable for the treatment of volatile organic

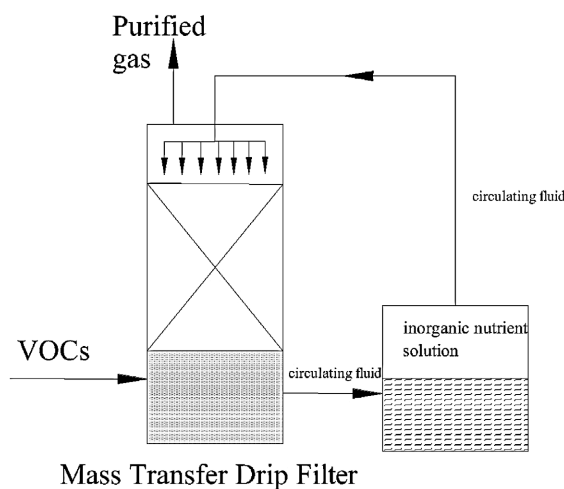


Figure 8. Schematic diagram of biological trickling filtration method.

compounds in malodorous gases, and the technological development trend is the screening and cultivation of efficient microbial flora.

3.2.8. Photocatalytic Oxidation Method

The basic principle of photocatalytic degradation is that VOCs will be oxidized to H_2O , CO_2 , or any inorganic harmless substances under ultraviolet (UV) irradiation by photocatalysts (e.g., TiO_2) [119].

Photocatalysts are the key to photocatalytic oxidation, and in recent years titanium dioxide (TiO_2) has been known as the most widely studied photocatalyst due to its excellent stability, high photoactivity, and suitable bandgap structure; however, traditional photocatalytic materials (e.g., titanium dioxide) can only respond to UV irradiation, so scholars have done a lot of digging into the photocatalysts based on titanium dioxide, and have found that two of titanium dioxide's crystalline phases, Anatase and Rutile can also be used in PCO for indoor air pollutants. It also includes TiO_2-xN_x [120] [121], C- TiO_2 [122] [123], Fe- TiO_2 [124] [125].

Although the photocatalytic decomposition method is characterized by mild reaction conditions, low energy consumption, and low cost, many experiments have shown that photocatalytic treatment of VOCs generates intermediates [126] [127]. For example, photocatalytic oxidation of toluene can generate benzaldehyde and benzoic acid intermediates in relatively dry conditions, and compounds such as esters, aldehydes, acids, and ketones are generated during the degradation of VOCs, and these intermediates will be Adsorption on the catalyst surface will generate a series of problems, such as 1) reducing the photocatalytic efficiency, 2) leading to secondary pollution.

Strengthening the study of degradation mechanisms and final products to solve the problem of secondary pollution has become a key topic for photocatalytic VOC treatment technology in the future [128]. Photocatalytic treatment of aldehydes and benzenes is the majority of studies, and it is more suitable to be applied deodorization and deodorization of malodorous gases; however, the degradation effect of this technology on gases of VOCs and their mixtures of gases of higher concentration is not ideal, and the future needs the scholars to continue to make efforts in the optimization of the catalysts and the solution of the undesirable effects of the intermediates produced as a result of the photocatalysts. **Table 7** shows a summary of the various treatment technologies for destruction technologies in end-of-pipe treatment of VOCs.

3.3. Reduction Technology

Reduction technologies aim to convert volatile organic compounds (VOCs) into more stable or non-volatile compounds through different methods. These include thermal reduction, catalytic reduction, and dehalogenation reduction.

3.3.1. Thermal Reduction, Catalytic Reduction

Thermal reduction involves using VOCs at high temperatures to undergo

Table 7. Advantages and disadvantages of various destruction technologies and types of VOCs used.

Destruction technology	Principle	Advantages	Disadvantages	Applicable conditions
Direct combustion method	Direct degradation of VOCs by high-temperature combustion	Simple operation	high operating costs at high temperatures	Usually flammable and volatile organic compounds, such as hydrocarbons, alcohols, ethers, ketones, etc.
Catalytic combustion method	Utilizes a catalyst to burn VOCs at a lower temperature.	No secondary pollution, low operating temperature, low cost, good results	Lower-concentration VOCs need external supplementary energy.	Usually, high molecular weight organic compounds that are difficult to burn completely under conventional conditions
Regenerative Combustion (RTO, RCO)	utilizes thermal oxidation reaction at high temperatures to oxidize VOCs into carbon dioxide (CO ₂) and water vapor (H ₂ O).	High efficiency, no secondary pollution, heat energy can be recovered, adaptable.	High cost, high operational stability requirements	VOCs without special components such as sulfur and chlorine compounds
Regenerative combustion (RTO, RCO)	Both RTO and RCO utilize the principle of thermal regeneration to treat VOCs, but RCO reduces the temperature of oxidation through a catalyst	High efficiency, no secondary pollution, heat energy can be recovered, adaptable	High cost and high operational stability requirements	VOCs without special components such as sulfur and chlorine compounds
Catalytic oxidation method	Under the action of a catalyst, VOCs are degraded to H ₂ O and CO ₂ by oxidation reaction with oxygen (O ₂).	High degradation efficiency and low operating temperature.	Catalyst selection and lifetime issues	Best suited for medium flow rates and low concentrations of VOCs
Low-temperature plasma method	Degradation of VOCs by plasma bombardment.	High degradation efficiency, no need for a catalyst, no secondary pollution, a wide range of application	Complex equipment and operation	Suitable for treating various types of VOCs, especially for high molecular weight, difficult-to-degrade organic compounds have better treatment effects.
Biodegradation	Utilizing microorganisms to degrade VOCs.	Simple equipment, low investment and operating costs, no secondary pollution, etc.	For VOCs with poor water solubility or high Henry's law coefficients, gas-microbe mass transfer is limited [129]-[131].	Low-concentration VOCs, water-soluble VOCs.
Photocatalytic oxidation	Utilizes light energy and catalyst to degrade VOCs.	Low energy consumption, high purification efficiency, and no secondary pollution [132].	Strict light conditions, poor efficiency at low VOCs concentration, toxic intermediate products	VOCs that can be degraded by photocatalysis

decomposition, reorganization, and other chemical reactions to form more stable compounds or simple molecules. This method is commonly used to treat organic solvent vapors and other high-temperature volatiles.

Catalytic reduction is a method that utilizes a catalyst to facilitate the chemical reaction, reducing the temperature and energy requirements of the reaction. Commonly used catalysts include metal oxides and precious metals such as platinum, palladium, and rhodium. Catalytic reduction allows for the conversion of VOCs at lower temperatures, resulting in energy and cost savings.

However, it is different from combustion and catalytic oxidation in destruction technology, which mainly destroys VOCs by converting them into carbon dioxide and water through oxidation reactions. In contrast, thermal reduction and catalytic reduction mainly convert VOCs into other more stable or non-volatile compounds through reduction reactions.

3.3.2. Dehalogenation Technologies

The classification of VOCs shows that Cl-VOCs can cause serious damage to the environment and human health. As a result, they have been categorized as priority pollutants by the U.S. Environmental Protection Agency (EPA), the European Commission, and China [133]-[135]. Consequently, the management of Cl-VOCs has garnered global attention. One of the most promising remediation technologies for detoxifying organ halogens is the reductive dehalogenation of chlorine-containing compounds using non-homogeneous catalysts [136]-[138]. **Table 8** summarises some examples of dehalogenation reductions in VOCs reduction technologies.

Table 8. Technologies on the removal of Cl-VOCs.

reduction technique	Pros	Cons	Ref
Zero-valent metal reduction, bimetallic reduction Catalytic Dehalogenation	Excellent dichlorination efficiency and capacity	Limited by stringent reaction conditions of metal catalyst passivation and loss or catalyst activation	[139]-[143]
Electrochemical reduction	Effectively avoids metal corrosion and surface passivation problems. The electrolytic reduction of chlorinated substances is much higher than the reaction of zero-valent metals.	Higher costs and by-products	[144]-[146]
Electrocatalytic Hydro dehalogenation	Environmentally friendly, easy to operate. Requires	stable electrocatalyst, high technical requirements	[147] [148]

The processes of zero-valent metal reduction, bimetallic reduction, catalytic dehalogenation, and electrochemical reduction may have different effects and

capabilities on the removal of chlorinated compounds, but they all follow similar dehalogenation pathways [149]. Additionally, aside from these reduction techniques, there are also microbial electrochemical systems and electrochemically mediated reduction methods [150]-[152].

Bioremediation of sites contaminated with Cl-VOCs shows great promise through reductive dehalogenation, which is primarily driven by microorganisms directly or indirectly using electrons from solid-state electrodes in bioelectrochemical systems.

3.4. Combined Techniques

The governance of VOCs is quite complex, and each method has its drawbacks. The use of combined processes and equipment is constantly evolving and gradually improving the effectiveness of governance in engineering applications. The following represents a common combination of VOC governance technology.

3.4.1. Adsorption-Combustion Technology

When dealing with low concentrations of VOCs, RTO/RCO is not applicable. Adsorption can be used to first increase the concentration of VOCs, and then coupled with combustion technology as a proven means. For example, using zeolite rotor adsorption concentration + regenerative thermal oxidation technology (KPR + RTO) for direct combustion of VOCs treatment equipment is beneficial but it requires high operating costs. For low concentrations and large air volumes of VOC organic waste gas, the use of zeolite rotor adsorption concentration + regenerative thermal oxidation technology can transform a large air volume of low-concentration waste gas into a small air volume of high-concentration waste gas for combustion treatment. This combined purification technology can effectively reduce energy consumption.

3.4.2. Activated Carbon Adsorption + Catalytic Oxidation Technology (AC + CO)

The technology of using activated carbon adsorption/desorption for enrichment treatment and then introducing it into the catalytic oxidation system for purification treatment can be applied to working conditions where the exhaust gas has poor continuity and low average concentration.

3.4.3. Condensation-Adsorption

Condensation technology is used to recover valuable components from high concentrations of volatile organic compounds in the exhaust gases and then adsorption technology is used to treat the non-condensable gases. The condensation technique reduces the components in the exhaust gas and lowers the temperature of the exhaust gas, thus minimising the damage caused by high temperatures to the adsorbent and activated carbon adsorption process, which can lead to combustion. Low temperature can improve the adsorption capacity of adsorbent carbon. Hao [153] *et al.* proposed a new VOCs recovery system based on low-temperature condensation and low-temperature adsorption, *i.e.*, the low-temperature

exhaust gas treated by low-temperature condensation equipment was introduced into the adsorption bed, which resulted in a lower temperature of the adsorbent bed and a higher adsorption capacity, which not only effectively increased the recovery rate of VOCs, but also solved the spontaneous combustion caused by the adsorption thermal effect of the traditional room temperature adsorption method. The problem is solved.

3.4.4. Adsorption-Photocatalysis

The photocatalyst is applied to the adsorbent material, and it absorbs the low concentration of VOC exhaust gas, enriching it on the surface of the photocatalyst. This allows for the full implementation of the photocatalytic reaction and improves the degradation efficiency.

The development of synergistic adsorption-photocatalysis systems is important to achieve efficient removal of pollutants with recycling properties [154].

The adsorption process can be efficiently enriched with organics, and the elimination of organics after saturation is more complicated [155].

Photocatalysts were applied as adsorbent materials to absorb low concentrations of VOC exhaust gases and enrich them on the surface of the photocatalysts. This allows the full realisation of the photocatalytic reaction and improves the degradation efficiency.

The combination of photocatalysis and adsorption can effectively enrich and degrade organic pollutants. The adsorbent promotes the transfer of pollutants to the catalyst surface, which leads to rapid degradation of the catalyst, thus preventing the decrease of the photocatalytic rate. At the same time, the photocatalyst degrades the adsorbed pollutants to achieve the recycling of adsorption [156].

Translated with DeepL.com (free version) Synergistic degradation of VOCs by plasma and catalyst can combine their advantages to effectively improve the degradation efficiency of VOCs, EE, and CO₂ selectivity, and reduce toxic by-products [157].

3.4.5. Adsorption-Condensation

Low concentrations of VOCs gas are most suitable for adsorption recovery technology. The condensation method is suitable for high-concentration conditions. The first adsorption method is used to concentrate the VOCs, and then the condensation process is used to recover and utilize the valuable VOCs components. The combination of these two technologies can complement each other. This method is suitable for the disposal of VOCs waste gas with large air volume, low concentration, and high recovery value.

As conditions continue to mature in all aspects, combined technologies will play a more important role in VOCs management in the future, promoting environmental protection and sustainable development.

4. China's Policy Regulations on VOCs

The governance of VOCs is essential globally, and in China as well, the state has

issued a series of policies and regulations, from industry-wide VOCs governance to various industries, from the national to the local provincial level, there are strict policies and regulations, as summarized in the table below. **Table 9** shows the regulations in the development of VOCs treatment in China.

The state has also introduced relevant standards for key VOCs industries, and **Table 10** shows some of the standards for VOCs management.

Table 9. China's atmospheric governance policy regulations.

Name of policy	Content	Issuing Department	Issuing time
Guidance on Promoting Joint Prevention and Control of Air Pollution to Improve Regional Air Quality	Early policy requirement to carry out VOC pollution prevention and control' for the first time at the national level	State Council Office of the People's Republic of China	May 2010
Twelfth Five-Year Plan for Prevention and Control of Air Pollution in Key Regions	The aim is to carry out comprehensive work on the prevention and control of VOCs pollution in 2015, to establish a regional mechanism for joint prevention and control of air pollution, and to significantly improve the regional air environment management capacity.	Ministry of Environmental Protection National Development and Reform Commission Ministry of Finance	October 2012
Volatile Organic Compounds (VOCs) Pollution Prevention and Control Technology Policy	It is the first policy issued specifically for VOCs management in China. This policy sets out the general principles of VOCs management and the control of sources and processes.	PRC Ministry of Environmental Protection (MEP)	December 2012
Air Pollution Prevention and Control Action Plan	Aims to promote VOCs pollution control. Implement comprehensive remediation in typical industries	State Council (PRC)	September 2013
Comprehensive Remediation Program for Volatile Organic Compounds in the Petrochemical Industry	Orientation to the productive enterprises with crude oil for VOCs pollution sources to be investigated; strict environmental access for construction projects; sound supervision and management system of VOCs; whole-process pollution control of VOCs; and construction of VOCs management system.	Ministry of Environmental Protection	December 2014
Work Program for the Prevention and Control of Volatile Organic Compounds Pollution in the 13th Five-Year Plan	Improvement of ambient air quality as the core, with key areas as the focus, key industries, and key pollutants as the main control object, to promote VOCs and NOx synergistic emission reduction.	Ministry of Environmental Protection National Development and Reform Commission Ministry of Finance Ministry of Transport General Administration of Quality Supervision, Inspection and Quarantine National Energy Administration	September 2017
Program for the Integrated Management of Volatile Organic Compounds in Key Industries	Completion of the 10 percent reduction in VOCs emissions as planned in the 13th Five-Year Plan.	Ministry of Ecology and Environment (MEP)	June 2019

Continued

Implementation Program on Pollution Reduction, Carbon Reduction, and Synergistic Efficiency Enhancement	It points out the need to promote synergistic control of air pollution prevention and control, optimize treatment technology routes, and increase synergistic emission reduction of nitrogen oxides (NO _x), volatile organic compounds (VOCs), and greenhouse gases (GHGs).	Ministry of Ecology and Environment Development and Reform Commission Ministry of Industry and Information Technology Ministry of Housing and Urban-Rural Development Ministry of Transport Ministry of Agriculture and Rural Development Ministry of Energy Bureau	June 2022
Action Plan for Sustainable Improvement of Air Quality	Improving air quality is centered on reducing the concentration of fine particulate matter (PM _{2.5}), with a strong push to reduce emissions of nitrogen oxides (NO _x) and volatile organic compounds (VOCs). Targets By 2025, the total emissions of NO _x and VOCs will each be reduced by more than 10% compared to 2020.	State Council	November 2023
Guidance on Further Optimizing the Response Mechanism for Heavy Pollution Weather	Points out the strengthening of daily supervision of volatile organic compounds (VOCs) and nitrogen oxides (NO _x) emission sources.	Ministry of Ecology and Environment	January 2024

Table 10. VOCs management standards.

Standard Name	Standard No.	Publishing organ	Implementation time
Guideline for the Determination of Volatile Organic Compound Leaks and Uncovered Liquid Surface Emissions	HJ 733-2014	Ministry of Environmental Protection	February 2015
Emission standard of pollutants for petroleum refining industry	GB31570-2015	Ministry of Environmental Protection General Administration of Quality Supervision, Inspection and Quarantine	July 2015
Emission standard of pollutants for petroleum chemistry industry	GB 31571-2015	Ministry of Environmental Protection General Administration of Quality Supervision, Inspection and Quarantine	July 2015
Standard for fugitive emission of volatile organic compounds	GB 37822-2019	Ministry of Ecology and Environment, State Administration for Market Supervision and Administration	July 2019
Emission standard of air pollutants for pharmaceutical industry	GB 37823-2019	Ministry of Ecology and Environment, State Administration for Market Supervision and Administration	July 2019
Emission standard of air pollutants for paint, ink, and adhesive industry	GB 37824-2019	Ministry of Ecology and Environment, State Administration for Market Supervision and Administration	July 2019
Limit of harmful substances of vehicle coatings	GB 24409-2020	State Administration for Market Supervision and Regulation, China National Committee for Standardization	December 2020

Continued

Limit of harmful substances of industrial protective coatings	GB30981-2020	State Administration of Market Supervision and Administration (SACMA) Standardization Administration of China (SAC)	December 2020
Limits of volatile organic compounds (VOCs) in printing ink	GB 38507-2020	State Administration of Market Supervision and Administration (SACMA) Standardization Administration of China (SAC)	December 2020
Limits for volatile organic compounds content in cleaning agents	GB/T38508-2020	State Administration of Market Supervision and Administration (SACMA) Standardization Administration of China (SAC)	December 2020
Technical requirement for low-volatile-organic-compound-content coatings product	GB/T 38597-2020	State Administration of Market Supervision and Administration (SACMA) Standardization Administration of China (SAC)	February 2021
Emission standard of air pollutant for gasoline filling stations	GB 20952-2020	Ministry of Ecology and Environment, State Administration for Market Supervision and Regulation	April 2021
Emission standard of air pollutant for petroleum transport	GB 20951-2020	Ministry of Ecology and Environment, State Administration for Market Supervision and Regulation	April 2021
Limits for volatile organic compound content in adhesives	GB33372-2020	State Administration of Market Supervision and Administration (SACMA) Standardization Administration of China (SAC)	April 2021
Technical guide for leak detection and repair of volatile organic compounds in industries	HJ 1230-2021	Ministry of Ecology and Environment (MEP)	April 2022

5. Challenges and Difficulties in the Management of VOCs

5.1. VOCs Themselves are More Difficult to Treat

Volatile organic compounds (VOCs) come from many sources and have complex compositions. VOCs come from a variety of sources, including industrial production, transport, and building renovation. Their complex and varied composition makes it difficult to treat them. It is necessary to adopt different treatment technologies for different sources and types of VOCs. Certain efficient treatment technologies for VOCs are costly and may be unaffordable to some small enterprises or regions.

5.2. China's Treatment of VOCs Is Not Yet Mature Enough

Whether it is the technology itself, the choice of technology, or the policies and standards for treatment, there is still much room for progress in the treatment of VOCs in China.

Through research and on-site monitoring, it has been found that VOCs (volatile organic compounds) control in many industries in China does not effectively meet the requirements of national standards. The methods used to control VOCs have various defects, resulting in VOCs not being effectively controlled. High-efficiency combustion and other technologies used to control VOCs have high economic costs and certain safety risks. In addition, there are problems such as inappropriate choice of VOCs control technology, irrational process design, lack of attention to pre-treatment, and irregular operation.

The lack of unified emission standards for VOCs and treatment technology standards has led to inconsistencies in treatment measures in different regions and industries, as well as uneven results.

5.3. Lack of Awareness of VOCs Treatment among Some Enterprises and the Public

The lack of an effective regulatory mechanism for VOCs emissions and stringent enforcement measures in some regions has resulted in some enterprises not paying enough attention to emission control. The most easily overlooked point is that the public is relatively unaware of the VOCs pollution problem and lacks concern and support for the control work, which affects the promotion and implementation of the control work.

6. Conclusions

Volatile organic compounds (VOCs) management in the final treatment stage is crucial. It involves recovery technology, destruction technology, and reduction technology. A combination of these technologies is required to meet VOCs management needs. Recovery technology options include condensation, adsorption, absorption, membrane separation, and catalytic oxidation. Destruction technology includes low-temperature plasma, biodegradation, and combustion. Reduction methods include thermal reduction, catalytic reduction, and dehalogenation reduction.

The key adsorbents, absorbents, and catalysts for important recovery technologies, such as adsorption, absorption, and catalytic oxidation, are highly developed, aiding in the removal of VOCs. An in-depth understanding and exploration of the desorption phenomenon are needed for adsorption technology to maximize its advantages. Development of emerging VOCs treatment technologies, such as membrane separation and biodegradation, is crucial for achieving efficient end-of-end treatment of VOCs by overcoming technological bottlenecks.

Efficient removal of VOCs often requires the combination of various technologies due to the limitations of a single treatment method. Therefore, the future direction of VOCs treatment lies in the appropriate combination of various technologies for efficient and safe VOCs removal.

China is currently facing a serious air pollution situation caused by VOCs. During the current and future “14th Five-Year Plan” period, VOCs governance and

control will be China's top priority in managing the atmospheric environment. In this period, VOCs have replaced SO₂ as one of the five important indicators of atmospheric governance, indicating the importance of VOCs management. As a result, China has introduced numerous governance policies and standards, but there is still room for improvement in the relevant provisions of VOCs governance.

Data Availability

The data used and/or analyzed during the current study are available in the supplemental materials or from the corresponding author on reasonable request.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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