ARTICLE IN PRESS

Catalysis Today xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Abatement of gaseous volatile organic compounds: A process perspective

Anirudh Krishnamurthy, Busuyi Adebayo, Teresa Gelles, Ali Rownaghi, Fateme Rezaei*

Department of Chemical and Biochemical Engineering, Missouri University of Science and Technology, Rolla, Missouri 65409-1230, United States

ARTICLE INFO

Keywords:
VOCs
Abatement
Adsorption
Catalysis
Thermal oxidation
Catalytic oxidation

ABSTRACT

Volatile organic compounds (VOCs) are a class of liquid compounds with low saturation vapor pressures, which enables them to change phases even at ambient conditions. This causes a huge problem when it comes to emissions. A large portion of VOCs cause catastrophic health effects such as cancer or liver damage even at very low concentrations (ppm), and the control of these compounds is vital in ensuring good air quality. Many VOCs are used in common household implements such as wood finishes or paints and can even be emitted off improperly ventilated cooking. This significantly alters indoor air quality, and as such, a large portion of research into these compounds have focused on indoor air. On the other hand, their widespread use as solvents in most industries along with their emission rates from vehicular exhausts results in contamination of outdoor air as well. The combination of these VOCs and NO_x pollutants tends to cause ground level ozone formation, which has a large bio-toxicity and causes the formation of a smog. Densely populated cities have also seen a sharp rise in VOC emissions due to the increase in both vehicular traffic and industrialization. A myriad of options is available for the abatement of VOCs, and they are similar to other pollution control strategies. These methods can be broadly be classified into destruction, separation and hybrid methods. This review discusses the different perspectives to be considered for this scenario, along with descriptions of the different methods available to the industry, along with some novel technologies that have been introduced recently. The influential parameters for each method have been investigated, along with optimum catalyst/material selection. In addition to this, a mathematical modeling perspective has also been examined, with significance to simulation studies performed for the control of VOC emission technologies.

1. Introduction

Volatile organic compounds (VOCs) are a diverse group of chemicals with the unique property of vaporizing to the atmosphere at ambient conditions. According to EPA, VOCS are defined as “any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates and ammonium carbonate, which participates in atmospheric photochemical reactions”. The significance of VOC emissions extends beyond their exhaust from common sources and their reactions with other pollutants result in biological and environmental consequences such as photochemical smog, which is responsible for tropospheric ozone formation with carcinogenic properties. The 18th century brought about the industrial revolution, which was accompanied with quantitatively large emission rates that have been progressively increasing. While the largest emission rates are from biological sources, human contributions from automotive and industrial sources have resulted in unprecedented levels of VOCs [1]. Among anthropogenic sources, industrial processes dominate emission rates, as seen from Fig. 1.

The sphere of influence of VOC emissions can broadly be classified into biological, environmental and a direct effect on human health. While anthropological emissions result in degraded soil quality, smog formation and ozone imbalances, indoor emissions have a more direct effect on human health because of its carcinogenic nature due to higher concentrations. Some commonly emitted VOCs in the indoor environment are benzene, toluene, and xylene (BTX) compounds, acetone, and formaldehyde [2,3].

Reducing the emissions of VOCs to the atmosphere is usually carried out by the use “add-on” equipment which recover or destroy off-gas VOC pollutants and the change in processes and/or raw materials to reduce or destroy VOCs generation. Over the years, different “add-on” techniques have been developed for VOCs abatement. Prominent of these are absorption [4–7], adsorption [8–12], thermal oxidation [13–15], catalytic oxidation [16–22], photocatalysis [23], non-thermal plasma oxidation [24], membrane technology [25–30]. The choice of abatement method depends on factors such as concentration, capital and operating costs, operation environmental impacts, energy consumption, etc. Dilute streams of VOCs will require long contact times

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* Corresponding author.
E-mail address: rezaeif@mst.edu (F. Rezaei).

https://doi.org/10.1016/j.cattod.2019.05.069
Received 1 March 2019; Received in revised form 16 May 2019; Accepted 24 May 2019

Please cite this article as: Anirudh Krishnamurthy, et al., Catalysis Today, https://doi.org/10.1016/j.cattod.2019.05.069

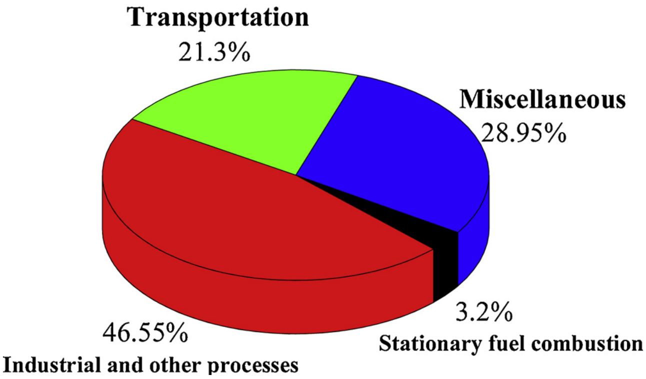


Fig. 1. Anthropogenic VOC emission rates (Adapted from [1]).

and large volume of absorbent for effective removal thus making absorption ineffective for dilute streams separation. Thermal and non-thermal plasma oxidation require high energy, while thermal and catalytic oxidation can lead to production of harmful byproducts like CO, SO_x, NO_x, etc. through incomplete/partial oxidation. High cost of catalyst inventory coupled with catalyst fouling and coking also have caused some setbacks to the use of catalytic oxidation. All these shortcomings have necessitated the development of a hybrid methods of abatement of VOCs. Hybrid systems of abatement are a unique method of abatement that involves synergistic contributions from two or more mono-operation systems, e.g., sequential adsorption and destructive technique [31–34], and alternate adsorption and plasma-assisted regeneration [35].

Credence goes to the specific works that have been done on the abatement methods of individual VOCs. However, this review focusses on the categories of methods of abatement (capture, destruction or hybrid capture and destruction) of VOCs in the industry (outdoor) and also its indoor counterpart.

2. Commonly encountered VOCs

The molecular structure of the VOC to be destroyed is an important factor in any abatement method. Depending on what kind of molecules are present of what structure the VOC takes will determine the type of method we select. In terms of biological toxicity, both concentration levels and duration of exposure are also important factors to consider. VOCs are a varied species and have a few basic categories that they are broadly classified under.

2.1. Carbonyl compounds

Including aldehydes and ketones, this classification is the largest type of VOC emitted in both indoor and outdoor scenarios. Carbonyl compounds are frequently responsible for causing ozone imbalance [36] by forming tropospheric ozone [37] due to their ability to form free radicals. They are found in largest concentrations in indoor environments [38,39] and are responsible for a large number of health effects such as allergies, respiratory illnesses, and cancer. This makes them particularly important when it comes to the investigation of VOC capture methods in indoor environments. Formaldehyde has been identified as one of the most harmful carbonyl compounds in terms of toxicity and emission rates in the indoor environment [40–43].

Formaldehyde can be produced through the degradation of other higher VOCs [44]. This is important to note when considering solvent use or ethanol based bio-fuels [45]. The EPA and the American lung association recommends a maximum threshold concentration for 0.1 ppm in air to maintain acceptable indoor air quality. While ambient concentrations are around 0.03 ppm [46], industrial workers are commonly exposed to much higher levels of formaldehyde for extended durations, which can cause adverse health effects [47]. In a study done by Jordan et al. [48], formaldehyde levels of 30 ppm or more caused allergic reactions in patients in short durations. Ethyl acetate (EA) and acetone are two ketone-based VOCs that are commonly emitted, although recently acetone has gained VOC exempt status form the EPA. Ketone based VOCs are dangerous, and have the capacity to cause CNS depression, according to the US Department of Health and Human services. They are present in smaller concentrations compared to their aldehyde counterparts.

2.2. Aromatic compounds

This category includes the largest anthropogenic VOCs detected and some of the most commonly encountered VOCs. They are the most significant category to consider when assessing outdoor air quality. BTX compounds fall under this category, and toluene has been identified to be present in large quantities relative to other VOC types [49]. These types of VOCs are responsible for a large portion of groundwater [50] and soil contamination [51] through the process of vapor sorption.

Automotive exhaust is one of the largest contributors to aromatic VOC emission, resulting in higher than normal concentrations in the outdoor environment. Aromatic VOCs also undergo photochemical oxidation with nitrogenous pollutants (NO_x compounds), another common type of vehicular pollutants, to form tropospheric ozone. This leads to smog formation [52] and potentially mutagenic effects [53]. Concentrations have also been shown to be at elevated levels near urban landfill sites [54,55]. These class of compounds have been studied extensively, toluene in particular [56–61].

2.3. Halogenated compounds

Halogenated VOCs (X-VOCs, where X is the halogen) are frequently studied due to their elevated toxicity levels, and their presence in commonly used products [62]. They are fairly stable, leading to slower degradation rates, and have been shown to contaminate both ambient air and groundwater systems. More commonly, lower level halocarbons are encountered, however, studies have indicated higher level compounds as well [63].

Water purification systems have also been identified to be a source of polychloroalkanes, PCMs in particular [64]. Their large atmospheric lifetime causes some to remain in the atmosphere for as long as 100 years, according to the Agency for Toxic Substances and Disease Registry (ATSDR). Common VOCs of this type include chloroform, carbon tetrachloride and dichloromethane (DCM). Due to their presence in relatively dilute concentrations, a highly selective process must be used for the abatement of these compounds. They also have a very strong bioaccumulation potential. Chlorine containing VOCs (C-VOCs) are the most abundant of this category. There are multiple challenges when dealing with C-VOCs when compared to other types of VOCs, including catalyst deactivation, harmful byproduct formation, such as HCl, and higher energy requirements. They are frequently used in cleaning agents, chemical extractants, paint additives, and as raw materials in a number of industrial processes [65]. To overcome these issues, various strategies are employed, such as the incorporation of an alkali earth metal/metal carbonate [66] to counter poisoning effects of HCl during the abatement of CVOCs (Figs. 2–4).

3. Current abatement technologies

VOC emission control can be carried out in different ways depending on separation or destruction. The former is classified under prevention methods, which involves the capture of the pollutant before process introduction, or ‘end-of-pipe’ methods, which abates the VOC at the exhaust of the process. The latter is the more common type of solution used. Capture methods include operations based on recovery, such as absorption, adsorption, or membrane technology. Biological

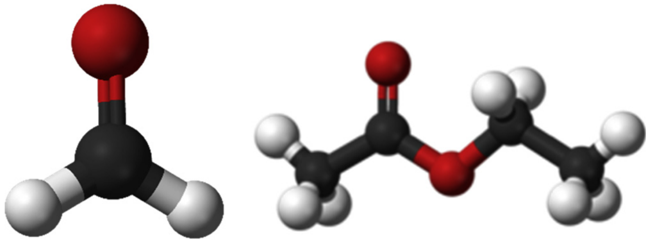


Fig. 2. Carbonyl based VOCs (a) Formaldehyde (b) Ethyl acetate (Red – Oxygen, Grey – Hydrogen, Black – Carbon).

methods, such as biofilters and bioreactors, fall under this category as well. Fig. 5 illustrates the different types of VOC abatement techniques developed so far.

Destruction methods fall under the ‘end-of-pipe’ solution strategy. Among the methods highlighted in Fig. 5, one of the most widely used in industry is thermal oxidation. It is a fairly simplistic process. One of the most significant disadvantages of thermal incineration is the high energy penalty associated with elevated temperatures. As a means to overcome the activation energy gap required to activate a reaction, a catalyst is used to reduce energy requirements. This can reduce the required temperature from 900 °C to as low as 150–250 °C [45]. Among the plethora of catalysts used, some of the most used catalysts are noble metal based [67,68], metal [69,70] and mixed metal oxide based [71,72], fibers [73], and zeolites [74,75].

While these methods include some of the most complete ways to deal with VOC pollution problems, they suffer from numerous disadvantages, such as high energy demands, high cost of materials, and operating conditions. The advent of new technologies has yielded a myriad of VOC capture options. These processes involve the selective capture of a VOC using physical or chemical separations, and can be both preventive and ‘end-of-pipe’. The focus of these methods is the high recoverability of materials. The most commonly used capture methods for VOCs include adsorption, absorption, membrane separation and biofiltration. They include capturing a VOC and then recovering it by means of an entropy change and further recycling for use. These methods generally involve high selectivity and the potential to reuse the pollutant for other uses, such as a solvent. The combination of these processes with successive destruction methods have been a focus recently, and have been discussed further in this paper. Table 1 provides a comprehensive comparison of the different destruction methods discussed herein, as well as representative examples of VOC abatement for each method type.

3.1. Destruction methods

3.1.1. Thermal oxidation

Thermal oxidation, as mentioned earlier, is one of the most straightforward operations used to destroy VOCs. This involves burning the VOC at very high temperatures (900–1000 °C) to facilitate complete oxidation to CO_2 and H_2O in a highly exothermic process. This process is suitable for removing VOCs from flue gas and highly concentrated effluent streams [76]. The combustion of VOCs follows the reaction described in Eq. (1) [77]:

$$C_aH_bN_cO_dS_eX_f + (a + e + 0.25(b - f) - 0.5d)O_2 \rightarrow aCO_2 + 0.5(b - f)H_2O + fHX + eSO_2 + 0.5cN_2 \quad (1)$$

where X refers to a halogen molecule and a, b, c, d, e, and f represent the stoichiometric number for C, H, N, O, and S, respectively.

This is classified as a combustion method. In the case of VOC combustion, thermal oxidizers are used instead of incinerators. This is due to the fact that incinerators generally are involved with dangerous combustion products, such as heavy metals or dioxins. This method is frequently employed in the industry due to the lack of necessary post treatment of the combustion products. It is a reliable method, and the availability of combustion operations in production facilities and factories has supported the use of this process. Halogenated VOCs tend to cause the formation of ‘HX’ compounds, where X refers to a halogen atom. In many cases, however, the amount of hydrogen is not sufficient enough to cause this formation on a sufficient scale, and so, external hydrogen must be supplied to the system. This causes a concern in the emission of acid vapors, and therefore, usually is followed by a scrubbing operation. One of the most important parameters to consider during the design of a thermal oxidation process is the destruction efficiency (DE), or destruction removal efficiency (DRE), of the VOC, and is a mass ratio between the amounts of VOC involved in the reaction with respect to the amount of VOC fed into the thermal oxidizer unit. The DE of a combustion process for a VOC can be defined by Eq. (2).

$$DE = \frac{VOC_f - VOC_s}{VOC_f} \times 100 \quad (2)$$

where VOC_f refers to the amount of VOC fed to the thermal oxidizer and VOC_s refers to the amount of VOC present in the stream to be purified. This is a very important factor, as incomplete oxidation/reaction can cause the evolution of harmful byproducts, such as CO. Modern thermal oxidizers [78] generally have a DE or DRE of 95–99%. Apart from this, other important parameters include temperature, residence time, and oxygen concentration supplied to facilitate the reaction process. On an interesting note, any amount of oxygen present in the VOC molecule can facilitate the oxidation process, and therefore, the amount of

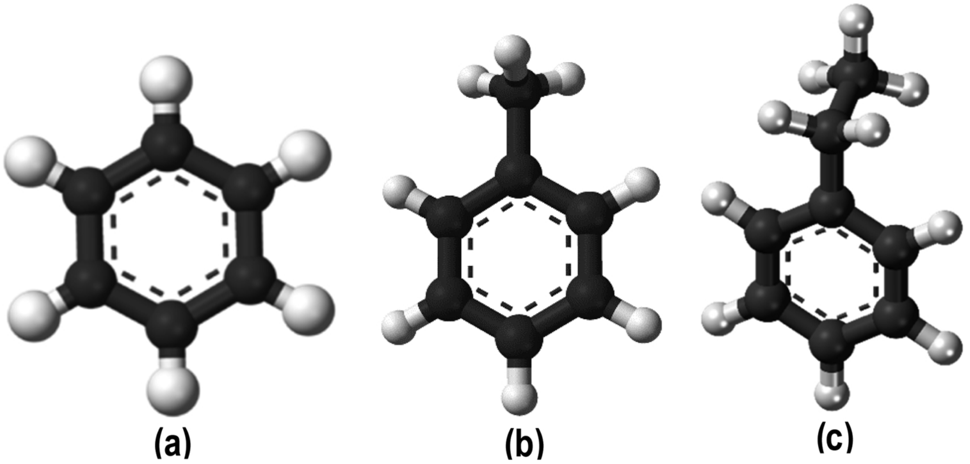


Fig. 3. Aromatic VOCs (a) Benzene (b) Toluene (c) Ethyl benzene (White - Hydrogen, Black - carbon).

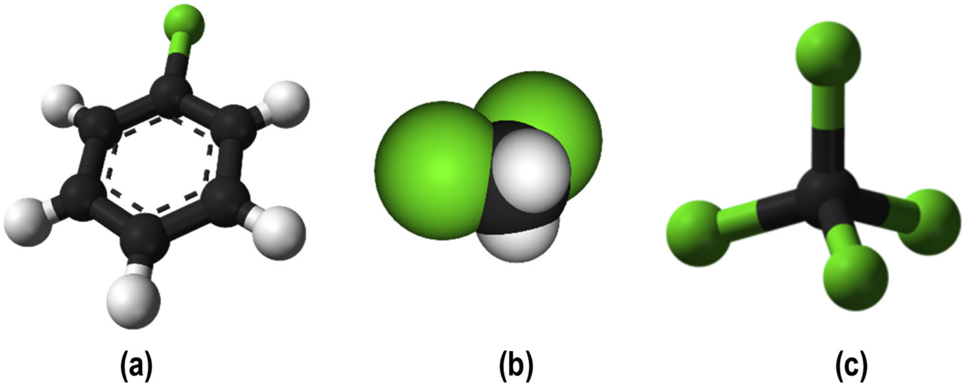


Fig. 4. Halogenated VOCs (a) Chlorobenzene (b) Dichloromethane (c) Carbon tetrachloride (Black - Carbon, White - Hydrogen, Green - Chlorine).

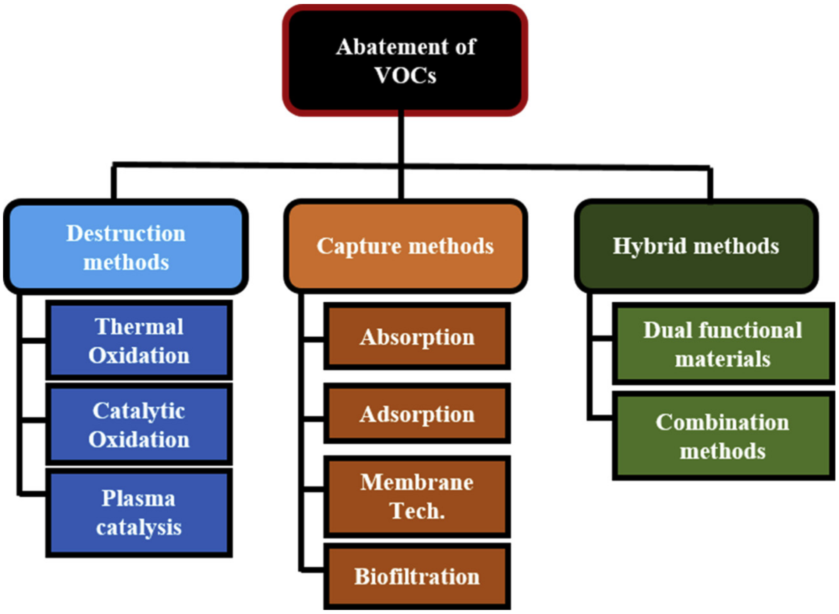


Fig. 5. Types of VOC abatement methods.

oxygen needed to be supplied can be reduced. This is useful when considering the economics of the process. One of the primary disadvantages of this process is the lack of versatility.

Apart from organic molecules, it is very difficult, and in some cases impossible, to treat the contaminated air. This could potentially be an issue due to the myriad of pollutants commonly emitted from the industry, such as GHGs or SO_x/NO_x compounds, which are common pollutants introduced during industrial operations and vehicular exhaust [79–81]. Another disadvantage is that thermal oxidizers are optimal only for VOCs at high concentrations. Such high temperature operations with organic compounds frequently involve the formation of coke, which can be a hindrance in thermal operations. To overcome financial constraints associated with this process, regenerative thermal oxidizer units [82] have been suggested.

3.1.2. *Catalytic oxidation*

The catalytic oxidation of VOCs is a process that is similar to thermal combustion of VOCs. It involves the use of a catalyst in the form of a packed column in order to reduce the activation energy of the otherwise high temperature operation and alter the reaction kinetics of the thermal combustion of a VOC. In general, the catalytic oxidation of VOCs usually follows the deep oxidation pathway, which is the complete conversion of the VOC to carbon dioxide and water/steam. This reaction [83] is given by Eq. (3).

$$C_xH_yO_z + \left[x + \frac{y}{4} - \frac{z}{2}\right]O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O \tag{3}$$

where x, y, and z represent the stoichiometric number for C, H, and O, respectively.

The field of catalysis is a multi-faceted and complex one. Historically, solid based catalysts have been used. The following sections describe the different types of catalytic operations used for the abatement of VOCs. The different types of catalysis are graphically represented in Fig. 6.

3.1.3. *Thermal catalytic oxidation*

The thermal combustion of VOCs using catalysts greatly reduces operational energy requirements. The complete oxidation of VOCs have been achieved at temperatures as low as 150–250 °C [45]. Commonly, this involves the addition of a catalyst in a thermal oxidizer unit, a general process configuration is illustrated by Fig. 7a. This is a very efficient method, as it involves the complete destruction of the pollutant with a high potential for reusability. Catalysts are used to accelerate the degradation of VOCs. Furthermore, unlike thermal oxidizers, this process is capable of treating even dilute [84] VOC streams ($> 1\%$). One of the most important concepts in this process is choosing the right catalyst. Determining operating conditions such as temperature and vapor hourly space velocity (VHSV) has also been found to be crucial in determining or optimizing the conversion of the reactant

Table 1
VOC destruction methods, their associated challenges and advantages, and VOC abatement examples.

Destruction Method	Challenges	Advantages	VOC Abatement	Ref.
Thermal Oxidation	-High thermal energy requirements (900 - 1000 °C) -Requires high VOC concentrations -Coke formation -Acid vapor formation from halogenated VOC oxidation	-Frequently employed due to supported use in production facilities -VOC removal from flue gas – 95 – 99% destruction efficiencies	-Benzene destruction (destruction efficiency of 99% at 730 °C with 2 s residence time) [144] -DCM destruction (destruction efficiency of 99% at 770 °C with 2 s residence time) [144]	[76,77,78,79,80,81]
Thermal Catalytic Oxidation	-Presence of catalyst poisoners in flue gas streams (SO_x/NO_x, humidity) -Process performance optimized with the use of expensive catalysts (noble-metal)	-Low operating temperatures (150 – 250 °C) -VOC removal from dilute gaseous streams (> 1%)	-IPA oxidation (Cu-MMO catalyst, 98% CO_2 yield at 450 °C with 0.37 m/s throughput at 200 ppm concentration) [145]	[45,88,89]
Photocatalytic Degradation	-High catalyst regeneration temperatures (420 °C) -Catalyst poisoning from coke deposition -Harmful byproduct formation from photocatalytic irradiation	-VOC removal at low concentrations (ppbs) -Harmless oxidation byproducts (CO_2 and H_2O) -Supports MMO catalysts -High versatility in VOC type for abatement	-Formaldehyde degradation for indoor air environments (Fe-TiO_2 catalyst, 93% degradation at 300 min under visible light irradiation) [119]	[98,99,100,128]
Non-Thermal Plasma Catalysis	-Limited to lab scale studies -Formation of harmful side-reactions and byproducts -Coke deposition and catalyst poisoning -Complicated operational parameters -High operating temperatures (2200 °C)	-High removal efficiencies (55 – 100%) -Simultaneously oxidizes and destroys VOCs -Use of MMO catalysts	-Benzene oxidation (Mn-zeolite Y catalyst, 100% conversion achieved at 200 ppm at 7 W input power and 250 ml/min gaseous throughput) [140]	[133,134,139,141]

VOC. The rate mechanism has been identified as Mars-van Krevelen (MVK) (Fig. 7b) [85] model for most VOCs, however, a decisive mechanism for all VOCs is still yet to be determined. This mechanism suggests that the oxidation of VOCs is carried out by two successive steps, namely, interaction of organic molecules with surface oxygen and the transfer/consumption of the oxygen molecules. It is a form of a redox reaction. The CO oxidative mechanism is similar, and many of the catalysts used for VOC abatement could potentially be used for CO as well [86]. The Langmuir-Hinshelwood (L-H) mechanism and the Eley-Rideal (E–R) mechanism are also significant when considering the interaction of oxygen [87], with the latter being the controlling step. The validity of application of these mechanisms heavily depend on the type of catalyst used [88].

The performance of a thermal catalytic oxidative unit is dependent on operating temperature, space velocity, VOC composition and concentration, catalyst properties, and the presence of any poisons/inhibitors in the inlet stream [89].

In recent years, metal organic frameworks (MOFs) have been studied as sorption media for VOC abatement [90,91] and have been incorporated as catalyst supports and tested for the thermal catalytic oxidation of a variety of VOC types. Liu et al. [92] investigated the catalytic oxidation of toluene over a ZIF-67 supported rubidium catalyst. They found that the Ru-ZIF-67 catalyst composite can achieve the complete conversion of 1000 ppm of toluene after 6 h at 240 °C at a weight hourly space velocity of 60,000 mL/gh. In a similar study, Chen et al. [93] Pt was incorporated onto a MIL-101(Cr) precursor and tested for the catalytic combustion of toluene. At a weight hourly space velocity of 20,000 mL/gh, the resultant Pt-MIL-101 composite catalyst achieved complete conversion of 1000 ppm toluene at 140 °C.

3.1.4. Photocatalytic degradation of VOCs

Photocatalytic oxidation of VOCs (PCO) is another abatement method for VOCs that has been of great interest due to their high efficiency and low energy costs, with most studies done on titania based materials [94–97]. This method is also of particular focus in indoor air quality due to low temperature conditions [98–100]. This method is frequently used even at very low contaminant concentrations (ppb level). The chemistry of PCO has been greatly explored. In this method, electron and holes form in the semiconductor-based catalyst, followed by the excitation of the electrons from the conductance to the valance band, and the absorption of photons from a selected energy source, such as a UV or germicidal lamp (Fig. 8).

These highly active particles (free radicals) react with the contaminant and molecular oxygen to yield final relatively harmless oxidation products, such as CO_2 and H_2O. It is a redox reaction. Photocatalytic activation of the semiconductor-based catalyst is usually a combination of different steps involving the excitation of valence band electrons and free radical recombination and interactions. The following steps (Eq. (4)a–g) are a summary of this process over a TiO_2 based catalyst [98], while Fig. 9 depicts the possible reaction pathways of PCO for toluene [101]:

$$TiO_2 + h\upsilon \rightarrow TiO_2(e^-_{CB} + h^+_{VB}) \tag{4a}$$

$$TiO_2(h^+_{VB}) + OH^- \rightarrow TiO_2 + [OH^\bullet] \tag{4b}$$

$$TiO_2(e^+_{CB}) + O_2 \rightarrow TiO_2 + [O_2^\bullet]^- \tag{4c}$$

$$[O_2^\bullet]^- + H^+ \rightarrow [H_2^\bullet] \tag{4d}$$

$$[HO_2^\bullet]^- + [HO_2^\bullet]^- \rightarrow H_2O_2 + O_2 \tag{4e}$$

$$TiO_2(e^+_{CB}) + H_2O_2 \rightarrow [OH^\bullet] + OH^- \tag{4f}$$

$$VOC + O_2 + [OH^\bullet] \rightarrow H_2O + CO_2 + Other \tag{4 g}$$

The general scheme for a VOC can be written according to stoichiometry as follows [102]:

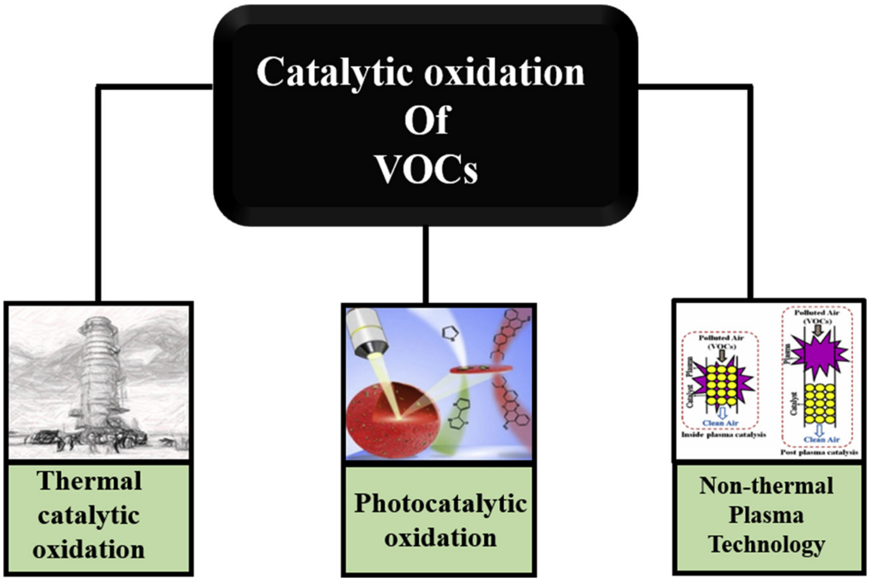


Fig. 6. Different types of catalytic operations for VOCs.

$$C_xH_yCl_z + \left(x + \frac{y-z}{4}\right)O_2 \xrightarrow{hv,TiO_2} xCO_2 + zH^+ + Cl^- + \left(\frac{y-z}{2}\right)H_2O \qquad (5)$$

where *x, y,* and *z* represent the stoichiometric number for *C, H,* and *Cl*, respectively.

In addition to the above phenomena, the charge carriers (e^- and h^+, illustrated by Fig. 8) are constantly undergoing recombination. This is said to cause a decreased quantum efficiency, and consequently a lower degradation potential. This can be overcome in a number of ways. For example, Kim at al [97]. performed a kinetic study on the photocatalytic degradation of several VOCs over a TiO_2 photocatalyst with the aim of determining optimum conditions. It was found that molecular oxygen was a critical parameter in determining reaction rates, as it decreases the recombination of holes and electrons by trapping the generated photoelectrons on the surface. PCO has multiple advantages over conventional methods, namely [99], (i) PCO uses commonly produced metal oxides, most of which can be obtained effortlessly; (ii) molecular oxygen used in this process is a mild oxidant and doesn't share the dangers of commercially used oxidants such as hydrogen peroxide; (iii) high activity rates at ambient conditions; and (iv) high versatility in the type of VOC to be destroyed. All these factors make PCO an optimum choice in abatement of VOCs in the indoor environment. An issue with PCO is the possibility of harmful side products being formed during the irradiation of the VOC and has been identified as one of the challenges of the emergence of this technology. Another common problem faced is catalyst poisoning due to the deposition of carbonaceous 'coke' on the periphery of the catalyst system during the catalysis of bulky aromatics.

The commonly used photocatalysts are primary metal oxides such as TiO_2, ZnO, $ZrO_2$and Fe_2O_3 [102]. While most active metal oxides can be used for PCO, TiO_2 is usually selected due to its electronic properties, physiochemical stability and ease of use [98,99]. The more active anatase phase is frequently employed as opposed to its rutile phase due to a number of reasons [100]. The significance of the phase of titania was investigated by Tellez et al. [101] for the destruction of MEK. UV100 was found to be more active in this case due to a larger production of $OH^\cdot$ radicals due to superior surface characteristics.

UV radiation intensity, type and exposure time are important factors in PCO, especially in TiO_2 based catalysts. Overall quantum yield of the light absorbed by a photocatalyst can be represented by Eq. (6) [103]:

$$\phi = \frac{r_R}{r_A} \qquad (6)$$

Where ϕ is the quantum yield, r_R is the rate of reaction, and r_A is the rate of absorption of radiation. This has an ideal value of 1, which is achieved when all factors, such as e^- and h^+ recombination are taken care of. This suggests that the UV light has just enough energy to activate the catalyst [104]. Vacuum UV lamps (VUV) are another type of light source used in VOC decontamination. It is utility lies in the fact that lower rates of accumulation have been reported [105].

While the phase of titania is crucial in determining photochemical efficiency, the dimension of the structure also plays an influential role. For example, while 3D structures such as monoliths have a highly

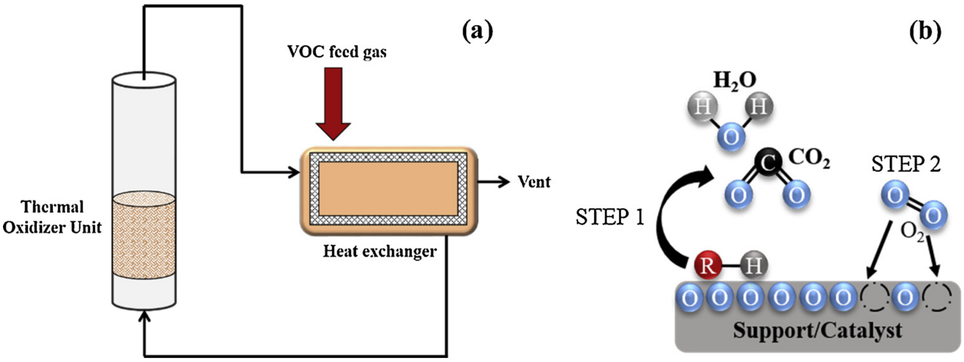


Fig. 7. (a) General scheme for thermal catalytic oxidation (b) Mars-van Krevelen (MVK) mechanism for the total oxidation of VOCs.

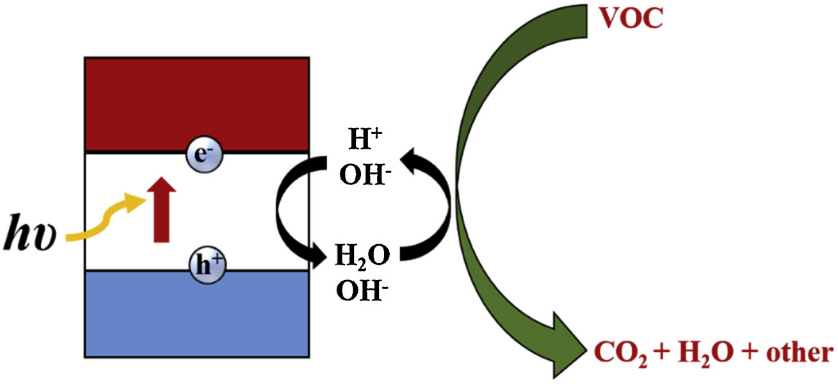


Fig. 8. Primary steps in PCO over semiconductor-based catalysts.

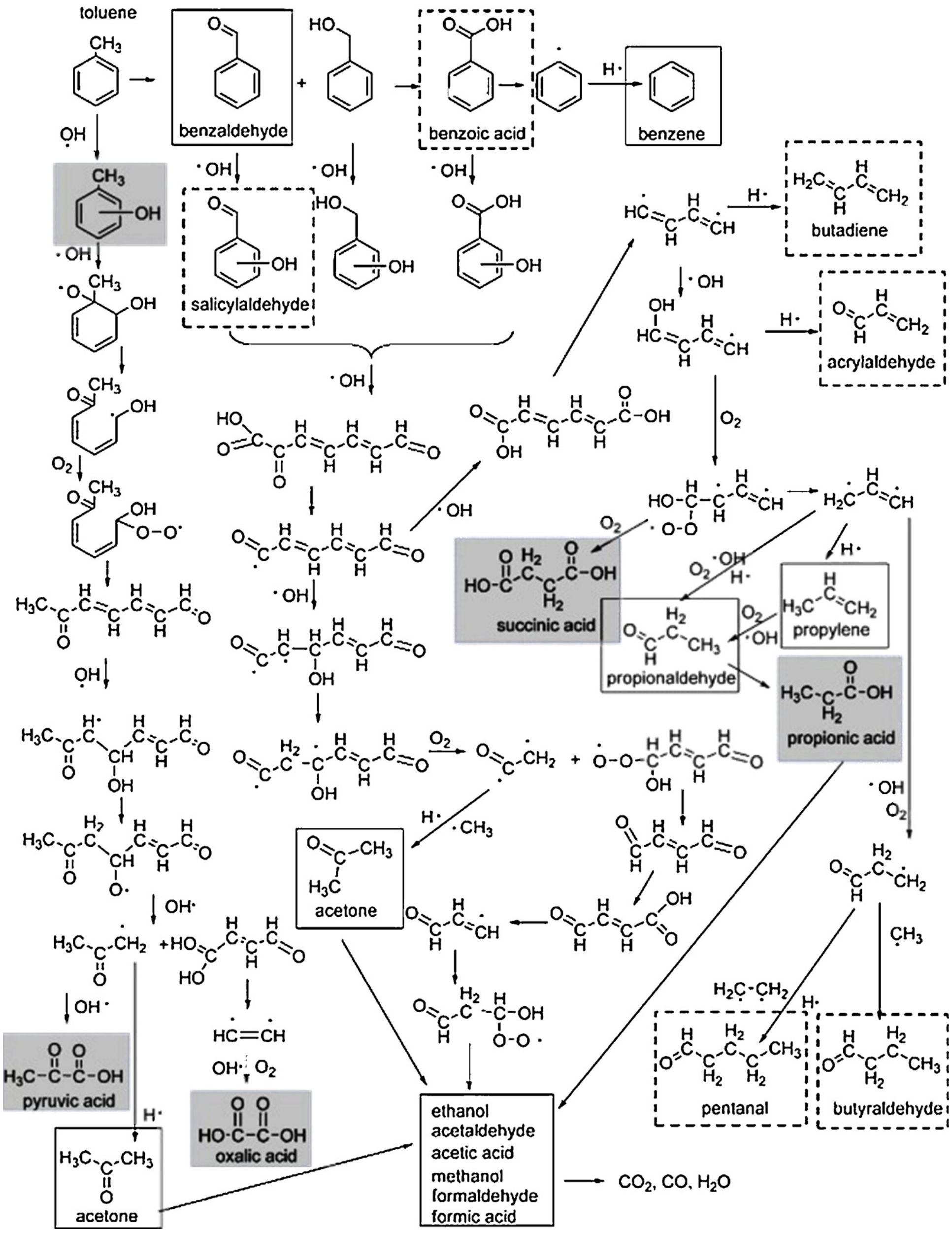


Fig. 9. Possible PCO pathways of toluene under UV irradiation (Reprinted with permission from [101], Copyright 2009 Elsevier B.V.).

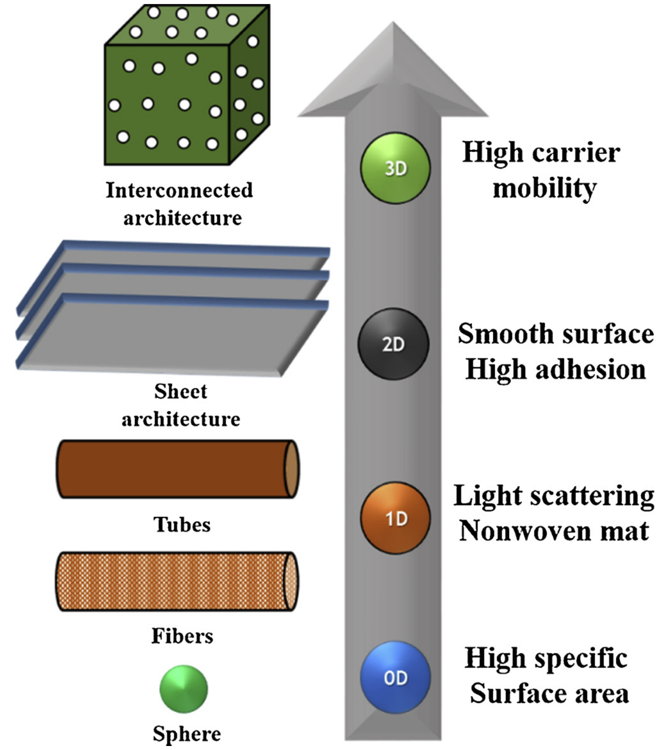


Fig. 10. Effect of dimensionality on photocatalytic activity (Adapted from [112]).

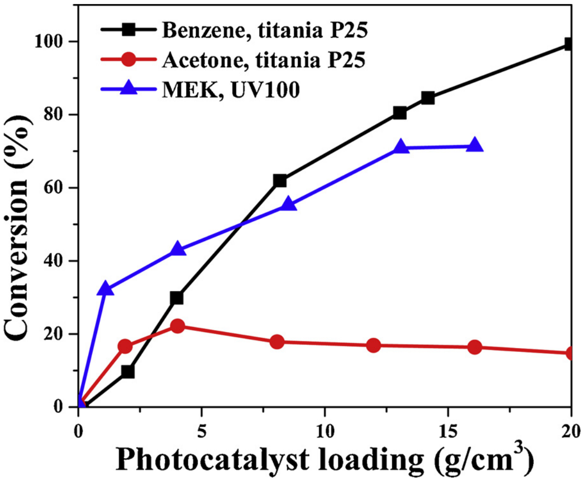


Fig. 11. Effect of photocatalyst loading on the PCO process for benzene [113], acetone [114] and MEK [115] at comparable catalyst loading. (Adapted from [113–115]).

efficient interconnected porous framework resulting in high charge carrier mobility, 1D structures such as rods or fibers have shorter pathways during charge carrier diffusion. These concepts are illustrated by Fig. 10. For example, Weon and Choi [106] prepared TiO_2 NTs by electrochemical anodization on Ti foil for the degradation of various VOCs. Due to its open channels and greater exposure to diffusion and radiation, along with consequent increased oxygen mobility, the geometry/dimensionality played a crucial part in degradation efficiency. Commonly, TiO_2 is used in its nano-size (< 100 nm) [107]. In a study done by Bianchi et al. [108] on the degradation of acetone, acetaldehyde and toluene, the degradation rates over micro and nano-sized TiO_2 were investigated. The adsorption of the pollutant was a deciding factor, along with the higher concentration of Ti−OH-Ti bridged groups for the lower VOCs in particular. While both types of TiO_2 showed the same activity range, micro-sized TiO_2 are more advantageous as nano-sized particles are a health hazard [109]. Other factors, such as the increase in water vapor concentration had also affects VOC conversion, as it lead to a greater availability of free radicals [110]. Some common issues that exist with titania photocatalysts [111] are its wide band gap in the bulk phase (which limits its usage in the UV or IR spectrum), low surface characteristics and high aggregation tendency. Loading of the catalyst is also another important factor to consider. Exemplified by Fig. 11, the influence of loading percentages is a significant one, and can greatly effect VOC conversion in a PCO process.

Recent advances in the field of PCO has given rise to novel materials with respect to this process. For example, by modifying the properties of titania, the efficiency of the PCO process can be greatly enhanced. This is usually done by charge combination reduction, wavelength response range and by further investigation of absorption mechanisms [116]. The easiest way to achieve this is by impregnation of noble metals or other active transition metal elements on titania. This also increases quantum efficiency by offering a larger number of electron-hole pairs. Furthermore, the reusability of the catalyst is enhanced due to the larger number of active sites exposed to radiation. Rare earth metals in specific, such as Pt or Pd can greatly increase PCO conversion rates due to a larger light absorption potential and a decreased electron-hole recombination [117]. Similar to thermal catalysis, this reduces the activation energy required to facilitate the reaction, thereby shifting the spectrum to a lower intensity radiation, such as visible spectrum. This greatly reduces energy costs, as UV and IR radiations require a lot of energy to operate. From Fig. 12, it is inferred that optimum doping percentages of Fe onto titania can enhance the conversion of the VOC by influencing particle growth and agglomeration. In a study done by Grabowska et al. [118], the effect of geometry of the photocatalyst was investigated, and was shown to have an effect on performance of the catalyst in PCO. It was also observed that conversion rates were observed in the vis spectrum with optimal loading of a noble metal due to enhanced absorbance.

Dispersion and particle size were found to be controlling factors in PCO processes. In an investigation performed by Li et al. [119], PCO over Fe doped TiO2 films were shown to be more efficient in HCHO degradation than it's undoped counterpart. This has been attributed to a synergistic effect between the dopant and the TiO_2. The doping of Fe further enhanced the physiochemical properties of TiO_2, along with increasing its radiation absorbance. This gave rise to a higher conversion of HCHO. In a comprehensive study performed by Zeng et al. [120], the potential of PCO combined with thermocatalytic operations were investigated. Compared to conventional PCO processes, an increased benzene conversion was detected, which implied the importance of a synergistic process.

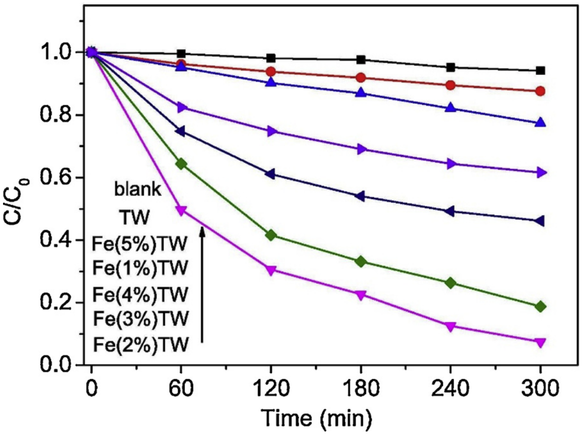


Fig. 12. Effect of dopants on HCHO degradation over TiO_2 based photocatalysts (Reprinted with permission from [119], Copyright 2018 Elsevier Inc.).

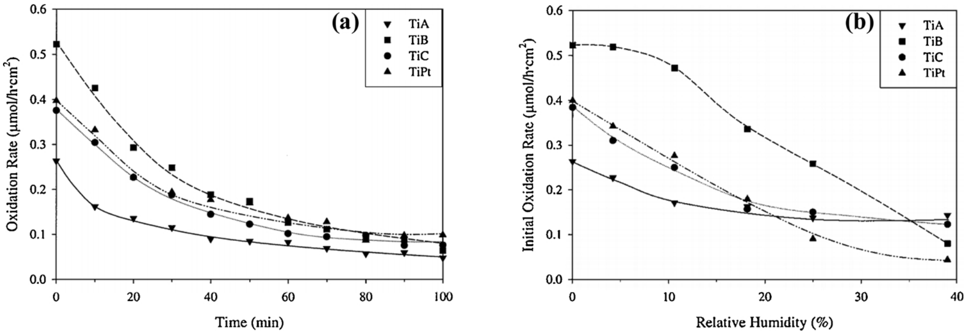


Fig. 13. Photocatalyic oxidation rates of toluene in (a) absence of humidity (b) presence of humidity (Reprinted with permission from [128], Copyright 2000 Academic Press).

In the indoor environment, visible light responsive catalysts are used. By combining titania with a small band gap semiconductor, such as Cr or V, the light absorption extends to the vis-spectrum. This process, however, may decrease the efficiency of this catalyst in the UV spectrum [121]. A plethora of studies have focused on the photo-degredation of formaldehyde due to its significance in indoor pollution control [122–125].

The deactivation of photocatalysts is an important factor to consider when designing a PCO process. Process economics focuses on catalyst lifetime, and potential reusability. For example, the active role of humidity in catalytic performance of BTEX compounds was studied by Li et al. [126], and photocatalytic conversion rates were shown to drastically increase with progressively higher humidity levels (Fig. 13). However, rather than humidity having a negative effect in general, it was shown that an optimum humidity level results in enhanced photocatalytic activity rates [127].

Due to the surface of most common metal oxides being covered by hydroxyl groups, the π-election complex is formed by hydrogen bonding, which results in a competitive adsorption between the VOC and water on the surface of the catalyst. A strong interaction between active sites on the catalyst and the reaction intermediates leads to a sharp drop in destruction capability of the catalyst due to the loss of active sites [128]. Furthermore, the deposition of various coking materials on the surface of the catalyst during the PCO of chlorinated and heavy, aromatic VOCs due to their reaction intermediates [99]. These compounds are chemisorbed onto the surface of the catalyst due to ambient process conditions, and sometimes need very high regeneration temperatures of above 420 °C [128].

3.1.5. Non-thermal plasma catalysis of VOCs

The chemical effect of an electrical discharge has been studied since the 18th century and has been extensively investigated since [129]. Non-Thermal plasma catalysis (NTP) is a fairly new method introduced recently as a means of pollutant abatement, with special focus on VOCs and NO_x based contaminants. Fig. 14 represents the different constituents of plasma. There exist two types of plasma, high temperature plasma and low temperature or quasi-equilibrium plasma. The latter is of particular interest to VOC decontamination, and consists of two further sub-categories, namely, local thermal equilibrium (LTE) and NTP states [130]. To maintain a plasma state, the applied voltage must be quantitatively greater than the breakdown voltage of the discharge gases. This can be assessed using Paschen's breakdown criteria [131], details of which exceeds the scope of this article.

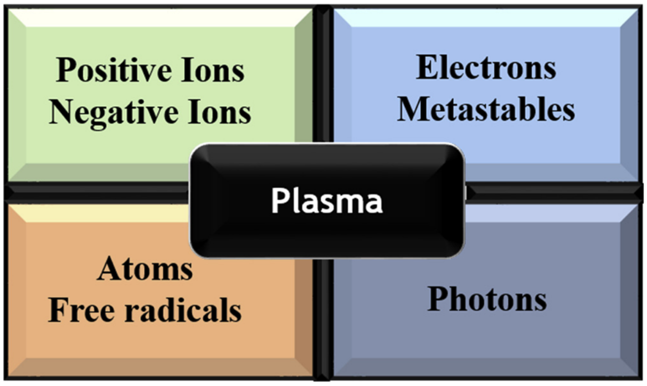
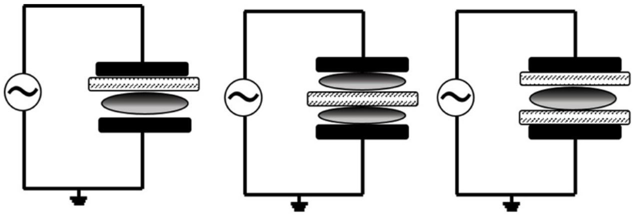


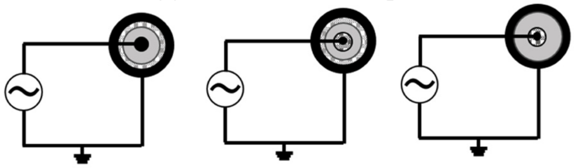
Fig. 14. Constituents of plasma (Adapted from [130]).

This process seeks to simultaneously oxidize and destroy VOCs using a highly active electrons produced from a high discharge voltage [132]. This is achieved by applying an intense electrical field on a neutral gas molecule creating a highly active environment containing ions, free radicals, neutrals and UV photons. This causes electron acceleration, and subsequent excitation while retaining heavier particles through energy exchange with a background gas. During electron bombardment on bulk gas molecules, temperatures can reach 2500 K (20 eV), creating excited gas molecules. The discharge zone subsequently facilitates ionization, disassociation and electron attachment. Similar to PCO, free radical $OH^{\cdot}$ and $O^{\cdot}$ are produced in the channels, which react with the pollutant to yield decomposition products [133]. Different methods exist for creating NTPs, such as corona discharge, pulsed corona and dielectric barrier discharge (DBD) [134]. The different configurations of NTP reactors are illustrated in Fig. 15.

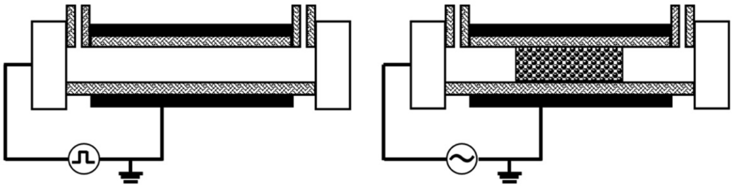
Exploration into the application of NTP reactors for air quality control was primarily introduced by Mizuno et al. [135] for the removal of SO_2 from stack gas using a pulsed corona discharge. Since then, NTP catalysis has been investigated greatly for VOC abatement. The determining factors in NTP reactor performance are the type of discharge (corona, DBD etc.), power supply (AC, DC, radio frequency (RF) etc.). Other factors such as electrode configuration or catalyst can also play a crucial role and are discussed further in this section [130]. Plasma assisted catalysis involves the incorporation of plasma technology in heterogeneous catalytic operations. It can broadly be classified into two types, plasma assisted catalysis (PEC) and plasma driven catalysis (PDC) [136]. The former involves plasma discharge followed by solid phase catalysis in a subsequent operation and is a dual stage operation. This enables the combination of individual optimization techniques being incorporated, which proves to be a significant advantage [35]. The latter involves a single stage operation, where the catalyst is activated by the plasma discharge and the system is then transferred to the reaction zone. This is a much more complex system that requires tedious optimization techniques, along with the variables associated with an uncertain and rarely explored phenomena [137]. Most studies have focused on PEC due to its easier usage and low complexity. PEC also enables relatively accurate assessment on the adsorption properties of the catalyst, which leads to an easier route towards optimization. When considering plasma treatment for air treatment, an important factor to consider is the specific input energy (*SIE*) [138] which can be represented by Eq. (7).



(a) Planar DBD configuration



(b) Cylindrical DBD configuration



(c) Pulsed corona discharge **(d) Ferroelectric pellet packed-bed reactor**

Fig. 15. Different NTP configurations used in pollutant abatement operations (Adapted from [133]).

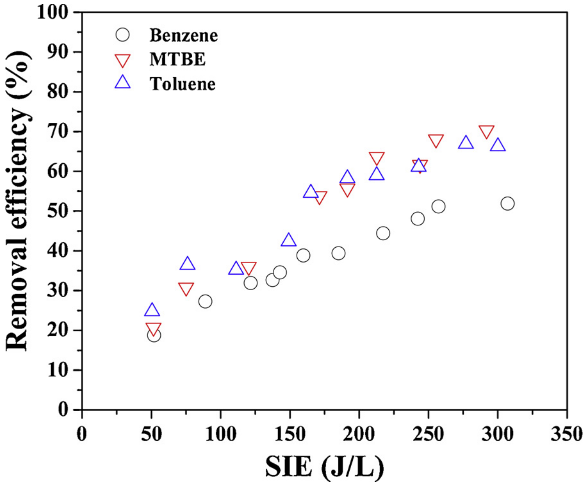


Fig. 16. Removal efficiencies of VOCs as a function of SIE (Adapted from [139]).

$$SIE = \frac{P_{plasma}}{Q_{gas}} \tag{7}$$

where P_{plasma} refers to the plasma discharge power and Q_{gas} is the total gas flow rate. Karatum and Deshusses [139] performed a study on different commonly encountered VOCs in an NTP reactor. Relatively high removal efficiencies (RE) were observed (55–100%) for the VOCs, with a dependence on SIE. This relationship is illustrated by Fig. 16. Other factors such as carbonaceous deposits were also investigated and while didn't change the RE, but did cause blockage of the reactor. Hamada et al. [140] studied the effect of catalyst composition and reactor configuration on the conversion of benzene. The dual stage surface discharge reactor (SDR) configuration was revealed to have a much better CO_2 selectivity. In general, the efficiency of the combined SDR was dependent on formation of ozone within the reactor, with higher ozone concentration corresponding to better decomposition. Different metal oxide loadings also revealed enhanced catalytic activity, with Mn based zeolite Y samples having the highest decomposition rate. This corresponds to Mn being a very good catalyst for VOCs in general. This study also highlights how dual stage systems have greater potential for modifications, with each individual component of the system having an effect in overall conversion.

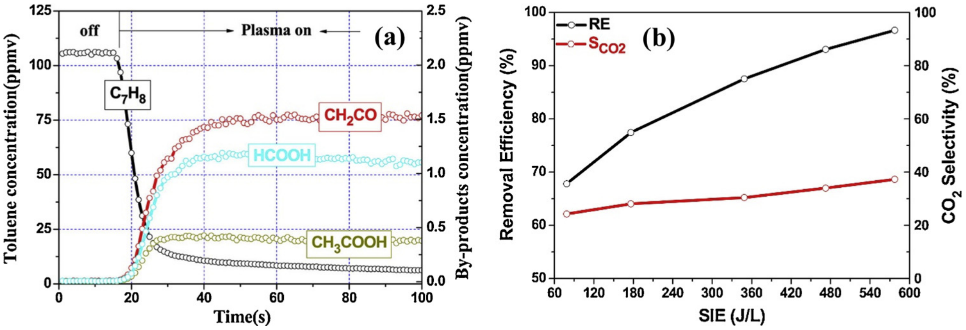


Fig. 17. (a) By-products formed during toluene decomposition and (b) RE and CO_2 selectivity as a function of SIE (Reprinted with permission from [141], Copyright 2018 John Wiley and Sons).

In a more recent study, Guo et al. [141] performed the oxidation of toluene and investigated the products using proton transfer reaction mass spectroscopy (PTR-MS). This provided a real time assessment of all by-products formed, which provided valuable insight into the side products formed during toluene destruction using NTP reactors. This is of concern, as one of the bottlenecks of this technology is the formation of harmful side reactions and products. The results are displayed in Fig. 17a. It was also observed that with the increase in SIE, the removal efficiency of toluene and the selectivity of CO_2, which corresponds to previous studies.

Yet another factor to consider in the design of NTP reactors is the energy efficiency of the system. This can be calculated by Eq. (8). This is an operating parameter that is crucial in designing an optimum process for NTP reactors.

$$\xi = \frac{C_{tol,in} \times \eta_{RE}}{SIE} \tag{8}$$

where ξ the energy efficiency of the NTP reactor system is, $C_{tol,in}$ is the entering toluene concentration, η_{RE} is the removal efficiency w.r.t the pollutant, and *SIE* is the specific input energy. Kuroki et al. [142] studied the decomposition of toluene at 1500-200 mg/m^3 using an adsorptive SDR reactor. A unique flow system was considered, induced by the NTP, comprising of surface discharge and circulation flow. On reducing pressure and injection of a high concentration of ozone (˜2000 ppm), enhanced CO_2 selectivity was obtained. The conversion rate of toluene doubled with the ozone addition. Quantitatively similar results were obtained for the energy efficiency of the system. The relation between energy efficiency and decomposition rates is illustrated by Fig. 18.

In a combination of the two, Li et al. [143] studied the effect of UV rays as a means of assisting in the photocatalysis of xylene. TiO_2 was selected as the catalyst, due to its superior optical and photochemical properties (explained in previous sections). Results indicated that while the UV rays produced from the plasma process was not sufficient to light off xylene, introduction of UV sources increased the RE of xylene when compared to conventional plasma method. While NTP reactor technology is still in its infancy, extensive studies done in the past have assisted in understanding the very complex process. Lab scale NTP studies are common, however, industrial implementation is still not widespread, except for a few studies [134].

4. Hybrid VOC abatement systems

Conventional systems, such as the ones described above, while easier to operate, have their drawbacks due to a myriad of reasons. For example, in catalytic reactors, the inlet flow of VOCs must have a sufficiently high enough concentration of the reactant to achieve optimum conversion rates. Operating conditions also have a crucial part to play in this. It has been found that VOC value must be significantly above the fuel values to consider recovery processes [146]. For example, Fig. 19a describes the dependence of flow rate and concentration when using a certain kind of process [146]. This shows us that for a particular situation, a certain type of process maybe optimum, while others may not be. In this case, the implementation of successive operations can help achieve the required separation and/or destruction rates.

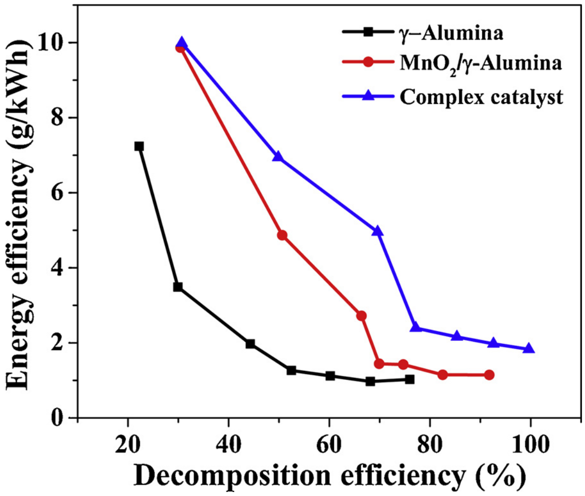


Fig. 18. Relation between energy efficiency and decomposition efficiency (Adapted from [142]).

Another important aspect to consider during the design of different systems is the cost estimation and techno-economic analysis associated with the process selected. While this is fairly straightforward during the use of singular unit operations, it gets a little more complex when using multiple operations successively or in tandem with each other. The cost estimates with respect to flowrates is illustrated by Fig. 19b. An accepted method to determine the economics of a process is the life cycle assessment (LCA) [147]. It is commonly defined as the environmental footprint of a process/material through its lifespan and encompasses everything from raw materials used to waste and disposal. When considering the efficacy of hybrid systems for VOC control, two different perspectives are considered, namely, material and process. The former refers to the selection of a material based off various factors such as surface characteristics or oxygen mobility rates, while the latter involves the selection of a particular process and the optimization of parameters associated with it. Both perspectives are equally important. This section focuses on adsorptiv E-R eactor technology in particular, which is one of the most researched hybrid systems and is a prime candidate for industrial implementation. In this process, VOCs feed is first concentrated by adsorption at low temperature until the breakthrough occurs. Thereafter, regeneration by desorption follows by passing a heated inert gas through the adsorption bed. The desorbed concentrated VOC is then passed through a catalytic combustion chamber and converted to harmless compounds in the presence of suitable catalyst.

The process perspective involves the selection of a hybrid technology for a particular situation in VOC abatement, such as dilute concentrations, or combination with other pollutants. Aziz and Kim [148] used adsorption followed by heterogeneous photo-Fenton catalytic oxidation to capture and destroy benzene, toluene, ethylbenzene and xylene (BTX) from gas and air streams on ultra-violet (UV) pretreated Fe-ZSM-5 adsorbent/catalyst in a batch reactor at room temperature. By revealing that the change in the structure, stability, morphology, and removal efficiency of the catalyst during the experiments is negligible, they established a novelty in sustainable reuse of catalyst with persistent VOC abatement. Moreover, by using residual materials analysis, they showed that there is a complete mineralization of VOC except small amount of acetone as oxidation product. Alsaqoor et al. [149] used a low temperature, quasi-pyrolysis technique of adsorption and catalysis to clean post pyrolysis gases with recovery of post-reaction heat. The research focused on abatement of VOCs from landfills, utilization waste, and oil shale. It was shown that the advantages of the new method over the conventional technology which based on the flame, are that it does not produce additional by-products such as NOx, dioxins, furans, carbon dioxide, methane, etc., the maximum temperature of the process is not higher than 550 °C with a cleaning efficiency by catalytic combustion can reached 99.8%, thereby making it an economically feasible method. Hakan et al. [150] used a microwave-heated adsorbent-reactor system for continuous purification of air streams containing n-hexane at low concentrations. Comparison was made between the performance of a single catalytic bed (PtY zeolite) and a double (adsorptive DAY zeolite + catalytic PtY zeolite) fixed-bed reactor configurations (Fig. 20) under dry and humid conditions.

The operation was especially efficient under realistic humid gas conditions that favored more intense microwave adsorption, producing

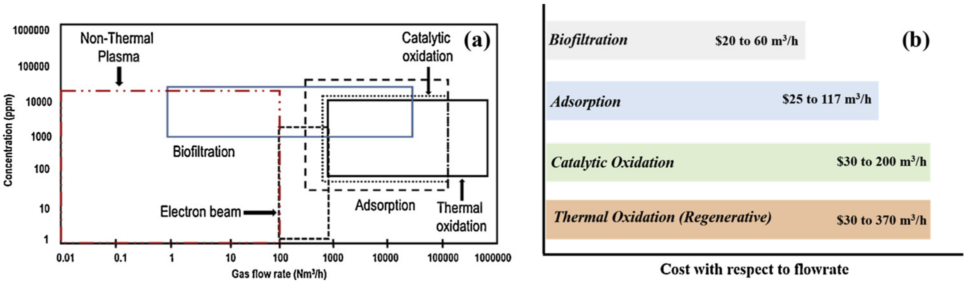


Fig. 19. (a) Optimum Flow rates and concentrations for different VOC abatement processes, (b) cost estimates (Adapted from [146]).

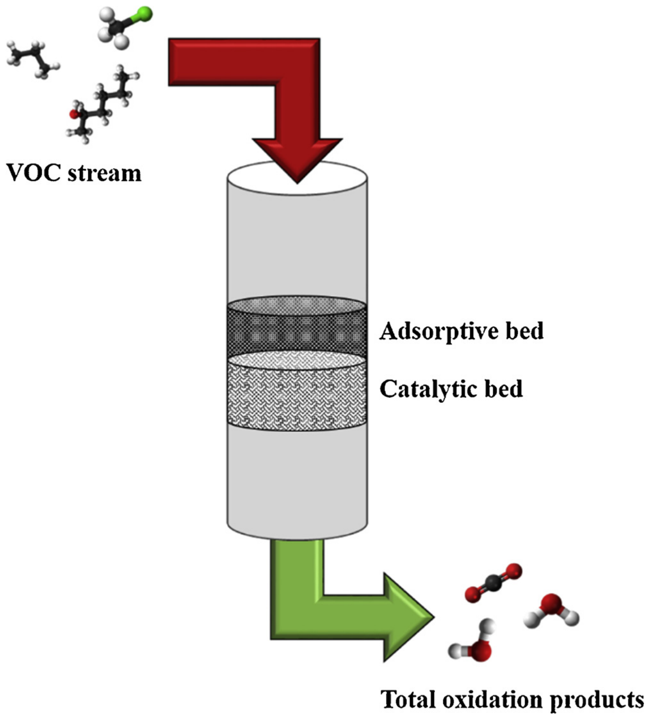


Fig. 20. A Schematic of Sequential Adsorptive and Catalytic System (Adapted from [150]).

a faster heating of the adsorptive and catalytic beds. Parametric sensitivity is another important factor to consider in this perspective. For example, Urbutis et al. [31] shows a cyclic process of decontamination of benzene, toluene and o-xylene (BTX) using a dual function adsorbent-catalyst. Their results indicated that at lower saturation levels (2 mg/g) and air regenerative flow rates (1 L/min), a complete oxidation performance is better. The highest obtained values of the overall conversion of toluene, o-xylene and benzene into CO_2 and H_2O were 99.3, 99.8 and 77.5%, respectively.

While a large number of studies have been done on thermal based hybrid system, the combination of catalysis along with other separation methods as also been investigated. Yet another implementation of the hybrid catalysis concept is the combination of NTP and photocatalysis, described in a study done by Morent et al. [151], which features a pin-to-mesh positive corona discharge with TiO_2 in the discharge gap for the destruction of tricholoroethane (TCE). Various parameters were found to be significant, such as the type of pin system and the implementation of the photocatalyst, which enhanced the removal efficiency of TCE from 67% to 85%. It was shown that the superimposition of the two processes resulted in a synergetic effect, which enhanced the overall VOC conversion. In yet another investigation [152], a multi-stage hybrid surface/packed-bed discharge plasma (HSPBD reactor) for the degradation of benzene was proposed (Fig. 21c). The CO_2 selectivity was shown to dramatically increase on the implementation of the second part in the system, along with an increase in destruction efficiency. Interestingly, the effect of the carrier gas used to carry the VOC was also shown to have a significant effect on the performance of the system, with N_2 showing the best results. Furthermore, this system also manages the harmful side products formed as a result of high corona discharge, which is a big disadvantage of the NTP system.

Two-phase partitioning bioreactors (TPPB) are an expansion upon the traditional liquid scrubbing absorption method. TPPBs couple the absorptive step described in previous section with an additional biodegradation step and have been proposed exclusively for the abatement of hydrophobic VOCs. TPPBs require the use of a biocompatible organic solvent, such as silicone oil or hexadecane, in addition to an aqueous-phase, such as water. Much like the liquid absorption method, a gaseous stream is bubbled into a scrubbing tower where the VOC contacts the organic solvent-water emulsion and transfers from the gas to liquid state. Upon the saturation of the solvent, it is introduced into the bioreactor. Once in the bioreactor, the VOC partitions out of the organic phase into the aqueous phase where it is consumed by organic cells, such as bacteria or fungi, which live in the reactor. As the cells consume the VOCs, disequilibrium is created which causes more VOC to be partitioned into the aqueous phase in an attempt to restore thermodynamic equilibrium. This partitioning occurs until the solvent is completely desorbed of VOC, where it is then recycled to the scrubbing tower for resaturation [153–156]. A simplified schematic of this process is shown in Fig. 22.

Much like traditional liquid scrubbing, the conditions of the TPPB are dependent on the VOC/VOC's in question. A biocompatible organic solvent must be chosen which has both a strong affinity to the VOC and the capacity to facilitate cell life. The optimal solvent-water emulsion ratio must be selected in order to enhance mass transfer in the absorption phase and also yield air/water and air/oil partition coefficients which enhance the transport of VOCs from the non-aqueous to aqueous phase within the reactor. The partition not only informs about the affinity between VOC and emulsion mixture, but also can be used to determine reactor dimensions and operational parameters such as gas and liquid flow rates and pressure drops [157]. The VOC partition coefficients are best represented by Eq. (9):

$$\frac{1}{H_{VOC,mix}} = \frac{1-\varphi}{H_{VOC,water}} + \frac{\varphi}{H_{VOC,oil}} \tag{9}$$

where $H_{VOC,mix}$ represents the partition coefficient (Henry's constant) between the VOC and emulsion mixture (Pa m^3/mol), $H_{VOC,water}$ is the partition coefficient between the VOC and water (Pa m^3/mol), $H_{VOC,oil}$ is the coefficient between the VOC and organic solvent (Pa m^3/mol), and φ is the organic solvent volume fraction of the mixture [154]. A low partition coefficient means that the VOC and emulsion have a strong affinity for one another. Therefore, it is desirable to minimize $H_{VOC,mix}$ in order to find the optimal emulsion ratio. It is also essential to choose an appropriate microorganism that displays a high biodegradation yield.

Within the past 10 years, silicone oil has been extensively researched as an optimal bioorganic solvent for the abatement of toluene. Silicone oil is immiscible in water, non-toxic for microorganisms, non-

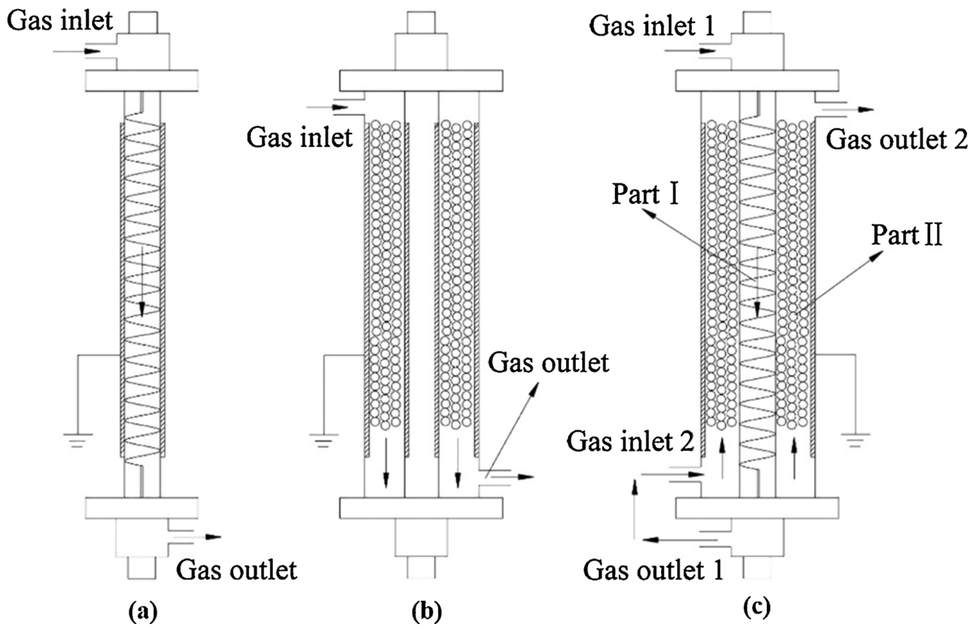


Fig. 21. Schematic of (a) surface discharge reactor, (b) packed bed discharge reactor, (c) HSPBD reactor (Reprinted with permission from [152], Copyright 2013 American Chemical Society).

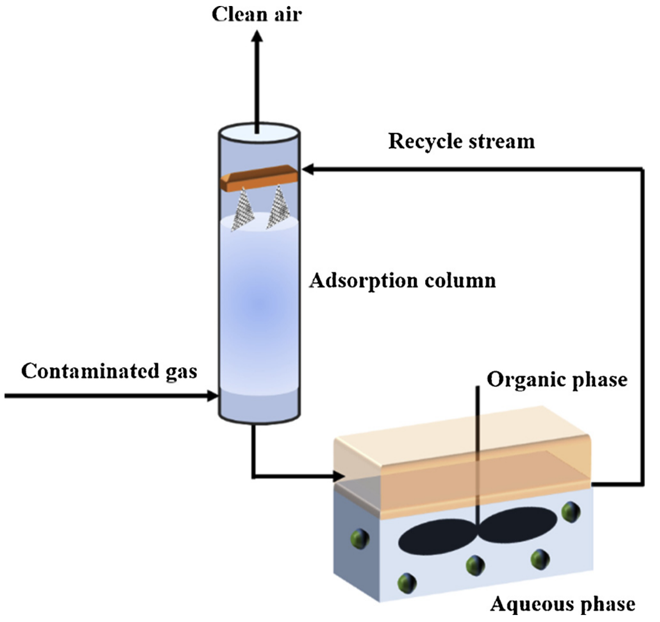


Fig. 22. Simplified TPPB schematic illustrating the scrubbing and biodegradation of VOCs.

biodegradable, and has high affinities for hydrophobic VOCs [155,158]. However, more recent studies have focused on the use of waste oils as a more environmentally friendly alternative to silicone. In a recent study by Lhuissier et al. [157], engine, hydraulic, transformer, and vegetable waste oils were characterized and evaluated for the abatement of isopropanol, EA, n-heptane, and toluene. Exemplified in Fig. 23, it was found that hydraulic oil is an attractive alternative to silicone oil and should be researched further.

In another study by Castillo et al. [159], the use of hydrophobic ionic liquids (ILs) as an alternative to organic oils was investigated. They found that ILs exhibit some success in biodegradation but have shown to be toxic towards several microorganisms. Another study, which focused on ILs' influence on toluene degradation indicated that biodegradation rates were only improved at high toluene concentrations [159,160]. Further investigations are required in order to determine their efficacy for commercial use.

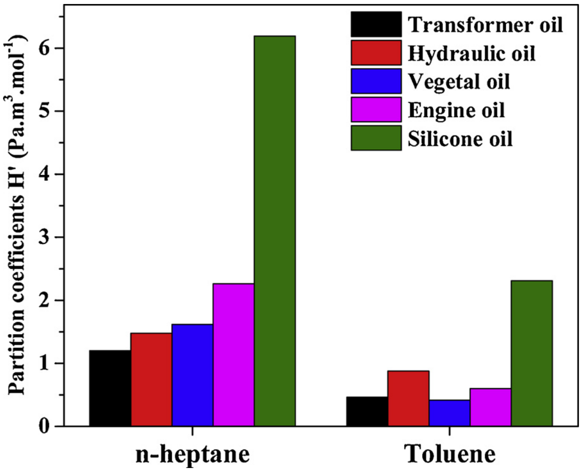


Fig. 23. Partition coefficients of different waste oils for different commonly occurring VOCs (Adapted from [157]).

5. Hybrid adsorptive catalytic fixed-bed reactor modelling

Adsorption is an interior surface phenomenon which occurs at the active sites of an adsorbent. This means that adsorbate molecules are heavily diffusion controlled. Different steps are involved during the aforementioned mass transfer operation and are as follows [161,162]:

(i) Deposition onto active sites in all cardinal directions.
(ii) Particle transfer from bulk fluid to catalyst surface.
(iii) Particle transfer from fluid film to mass transfer zone within pores
(iv) Pore diffusion
(v) Surface adsorption
(vi) Diffusion transfer back into fluid phase.

When considering mathematical modelling for an adsorption-based system, we first select an appropriate adsorption isotherm model that fits the experimental data, followed by choosing an appropriate kinetic model. Using this data, we can model the adsorption process over the dual functional material. Finally, operating conditions are considered for both the adsorption and catalysis, such as temperature, pressure or space velocity and the process can be optimized accordingly. The following sections describe in detail the theory behind these steps, including their significance in VOC removal.

5.1. Adsorption isotherms

Adsorption is usually described through isotherms, and is generally represented as the amount of adsorbate on the adsorbent as a function of its concentration/pressure at constant temperature. These curves provide invaluable information about the mass transfer and molecular mobility within the adsorption system. The quantity adsorbed is usually normalized by the mass of the adsorbent to allow comparison of different materials. These curves are fundamental in our understating of adsorption kinetics. Quite frequently, the shape and hysteresis of the isotherm gives us a good idea about the adsorption of a particular pollutant on a material of choice. The Brauner-Emmet-Taylor perspective is frequently used in surface characterization methods [163] for determining fundamental aspects about the surface of an adsorbent material, such as surface area available for multilayer adsorption and the existing pore systems [163]. When formulating adsorption isotherms, two different perspectives are considered, namely, kinetic and thermodynamic [164]. A third, the potential theory of adsorption was proposed by M.M. Dubinin in 1959 [165]. The equations proposed in each model are fitted with experimental data to confirm the nature of the adsorption process. Some of the most commonly used isotherms are based on equations developed over time and are listed below. This article will focus on two and three parameter models, respectively, which encompasses most commonly used isotherms. Fig. 24 depicts the common types of isotherms used.

5.2. Adsorption kinetics

Adsorption kinetics defines mass transfer rate during adsorption. It is the measurement of the rate/speed at which adsorbate particles are adsorbed onto the adsorbent active sites. Fast adsorption kinetics is a hallmark of an excellent adsorbent, usually indicated by a steep breakthrough curve. The commonly used models to characterize adsorption kinetics are listed below.

5.2.1. Equilibrium model

This model assumes instantaneous mass transfer between the adsorbent solid phase and gas phase which occurs when there is negligible mass transfer resistance between the phases. Hence, this model is as represented in Eq. (10).

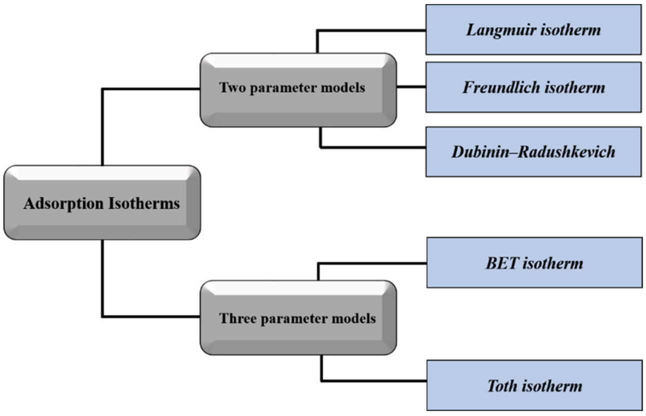


Fig. 24. Different types of VOCs isotherms.

$$\frac{\partial \bar{q}_i}{\partial t} = \frac{\partial \bar{q}_{i,eq}}{\partial t} \tag{10}$$

where q_i is the average adsorbed phase concentration (mmol/g) of species i, $q_{i,eq}$ is the equilibrium adsorbed concentration (mmol/g) between solid and bulk gas phase of species i, and t is time (s).

5.2.2. Lagergreen pseudo-first order model

This is a pseudo-steady state model that has been adopted to describe certain adsorption kinetic data and predates the LDF model [166]. This is given by Eq. (11) and is commonly called the Lagergreen model. While it has been used in many studies, its simplistic model fails to be consistent with the theory proposed [167].

$$\frac{dq_i}{dt} = k_{LA}(q_{ie}^{*} - \bar{q}_i) \tag{11}$$

where q_{ie}^{*} represents the final adsorbed concentration (mmol/g) of species i, q_i represents the average adsorbed phase concentration (mmol/g) of species i, k_{LA} is the kinetic constant (s^{-1}), and t is time (s).

5.2.3. Linear driving force model

Linear driving force model is one of the most commonly used models to characterize the adsorption of gases onto solid adsorbents in packed columns [10,168–170] and was first introduced by Glueckauf and Coates [171]. Eq. (12) describes the classical definition of the LDF model [172].

The mass transfer co-efficient used in the model can also be defined by Eq. (13) [173], but can vary according to the situation considered.

$$\frac{d\bar{C}(t)}{dt} = k_L[\bar{C}^{*}(t) - \bar{C}(t)] \tag{12}$$

$$k_L = \frac{15\bar{D}_{ei}}{r_p^2} \tag{13}$$

where $\bar{C}(t)$ is the adsorbate average concentration (mol/cm^3) in the adsorbent particle at time t, $\bar{C}^{*}(t)$ is the equilibrium adsorbate average concentration (mol/cm^3), k_L is the effective LDF mass transfer coefficient (s^{-1}) at a particular adsorbate loading, $\bar{D}_{ei}$ is diffusivity (cm^2/s), and r_p is the radius (cm) of the particle. This model through a lumped parameter analysis is frequently used to characterize adsorption in column dynamics. The classical definition of this model, however, sometimes does not accurately describe expected kinetics measured in experimental data [174] and several modifications have been made to overcome this issue.

5.3. Reaction kinetics

This is the measurement of the rate/speed at which the reactants react to form products. The form of any chemical reaction kinetics depends on the reaction mechanism/pathway. Reaction mechanism is a sequence of reaction steps (series and/or parallel) that lead to formation of products. Three main mechanisms (ii-iv) have been proposed for total catalytic oxidation of VOCs, namely [76]:

5.3.1. Power law (PL) mechanism

The power law (PL) mechanism is the simplest reaction kinetics model which is commonly used as a first approximation to the reaction kinetics. This model is as shown in Eq. (14).

$$r_R = -r_{VOC} = k p_{VOC}^{m} p_{O_2}^{n} \tag{14}$$

where r_{Rea} and r_{VOC} ($mol/m^3.s$) are the rate of reaction and the rate of conversion of the VOC respectively, p_{VOC} and p_{O_2} (Pas or N/m^2) are the partial pressure of VOC and oxygen respectively, m and n are the reaction order relative to gas phase VOCs and O_2 respectively, and k the reaction rate constant which unit depends on the value m and n and can be calculated using the well-known Arrhenius Eq. (15).

$$k = k_0 e^{-E_a/RT} \tag{15}$$

where k_0 is the pre-exponential factor, E_a is the activation energy (kJ/mol), R is the universal gas constant (J/mol K), and T is the reaction temperature (K). Research study by Özçelik, T.G [175] showed that PL model gives a good agreement between the measured and calculated reaction rates for total oxidation of isopropanol and ethyl acetate on monolith-supported CeO_2 catalyst. Siham Behar et al. [176] used the power law as a first approximation to model catalytic oxidation of toluene.

5.3.2. Eley-Rideal (E–R) Mechanism (Nonthermal Surface Reaction)

Here, reaction occurs between the VOC adsorbed species and the gaseous oxygen molecules. The proposed reaction kinetics for E–R mechanisms is shown in Eq. (16).

$$r_R = -r_{VOC} = \frac{kK_{VOC}p_{VOC}p_{O_2}}{1 + K_{VOC}p_{VOC}} \tag{16}$$

where K_{VOC} is the equilibrium constant (s^{-1}) relative to VOC.

5.3.3. Langmuir-Hinshelwood (L-H) Mechanism

This mechanism proposed that reaction takes place between the VOC adsorbed species and the adsorbed oxygen. Hence it is important that oxygen molecules are adsorbed on the adsorbent.

For single site L-H model, we have Eq. (17).

$$r_{Rea} = -r_{VOC} = \frac{kK_{VOC}p_{VOC}K_{O_2}p_{O_2}}{(1 + K_{VOC}p_{VOC})(1 + K_{O_2}p_{O_2})} \tag{17}$$

For double/duel site L-H model Eq. (18) has been proposed.

$$r_R = -r_{VOC} = \frac{kK_{VOC}p_{VOC}K_{O_2}p_{O_2}}{(1 + K_{VOC}p_{VOC} + K_{O_2}p_{O_2})^2} \tag{18}$$

where K_{O_2} is the equilibrium constant (s^{-1}) relative to O_2.

5.3.4. Mars-Van Krevelen (MVK) Mechanism

In this mechanism, reaction is assumed to occur between VOC adsorbed species and the lattice oxygen of the catalyst instead of the oxygen molecules in the gas phase. The model is as depicted in Eq. (19).

$$r_R = -r_{VOC} = \frac{K_{VOC}p_{VOC}K_{O_2}p_{O_2}}{\gamma K_{VOC}p_{VOC} + K_{O_2}p_{O_2}} \tag{19}$$

where γ represents the number of O_2 molecules required for the oxidation of one aromatic molecule.

The MVK is the most complex of the reaction kinetics. This model has been used by several authors to best describe total/complete oxidation of VOCs [175]. Using nanosized Cu–Mn spinels as catalyst, research work of Siham Behar et al [176]. revealed that MVK model compared to four others is the best mechanism to model total oxidation of toluene. E.Genty et al [177]. also confirmed that MVK is a best fit to describe the mechanism of the total oxidation of toluene on CoAlCe catalyst. J. Niu et al [178]. carried out total oxidation of toluene on $Cu1\text{-}yMn_2CeyOx$/sepiolite and their results affirmed that total oxidation of toluene can be best described by MVK model.

5.4. AdsorptivE–Reactor Dynamics

To accurately model hybrid adsorptive catalytic process or even the adsorptive process, the following phases must be considered in the modelling:

(i) The bed bulk gas phase,
(ii) The pellet pore gas phase,
(iii) The pellet solid phase.

The pellet (macroparticle) solid phase comprises the adsorbent and/or catalyst crystals (microparticles) impregnated on a support. In between those crystals are macropores while micropores are within the crystals as depicted in Fig. 25 [179].

However, due to complexity and cost-intensiveness (caused by longer compilation and execution/run times) involved in models, various means have been employed to simplify the modelling without significant effect on the response/result. Moreover, diverse assumptions are also made to further simplify the modelling.

6. Conclusion and Outlook

The abatement of VOCs is a complex issue with many intricacies to consider. When selecting an appropriate system, both material and process perspectives are considered, and a method is implemented accordingly. Thermal oxidation represents the most mature technology for VOC abatement, and has been widely studied for over twenty-years. While it exhibits many advantages, including high destruction efficiencies (99%), it suffers from extremely high energy penalties that make it widely inefficient for large-scale industrial deployment. Therefore, it has been advantageous to study other VOC destruction methods that can achieve the same removal efficiencies at lower energy costs. The incorporation of catalysts in order to reduce activation energy and temperature requirements can greatly improve the cost efficiencies, and, therefore, many methods have arisen that incorporate catalysts to reduce reaction temperatures. Thermal catalytic oxidation has shown incredible promise for the abatement of a wide variety of VOC types at dilute concentrations ($> 1\%$) in flue gas streams and has been incorporated into many industrial systems. However, catalyst poisoning resulting from flue gas impurities and water humidity reduce the overall effectiveness of this method. Additionally, noble-metal catalysts (such as platinum and rubidium) exhibit the highest conversion efficiencies, but are costly to produce, which adds additional costs for catalytic oxidation, especially when catalyst poisoning is a recognized issue. Therefore, the study of transition metal catalysts and mixed metal oxide catalysts that can achieve comparable conversion efficiencies are a present source of many investigations. Photocatalytic degradation has arisen in recent years as a promising alternative to thermal catalytic oxidation due to high VOC degradation rates in extremely dilute concentrations (ppb range). This makes it a promising method for the abatement of VOCs in indoor air environments, and has been studied for formaldehyde degradation. Additionally, it has shown versatility in the destruction of many different VOC types. However, photocatalytic irradiation has been shown to formulate many harmful byproducts. Additionally, this method has only been studied on lab scales. Further investigations must focus on the study of the cost efficacy if implementation on industrial scales. Non-thermal plasma catalysis has shown promise for high removal efficiencies and for the effective use of MMO catalysts. However, it has also been largely limited to lab scale studies and suffers from similar issues surrounding thermal catalytic oxidation, such as catalyst poisoning. Additionally, the process results in very high temperatures that require considerable attention to process safety. Further investigations are required in order to determine the overall feasibility of this method for industrial integration.

While each system has its own advantages and disadvantages, the synergistic effect of multiple systems can play an important role in minimizing emissions and costs. This has led to a need and investigation into hybrid systems, which incorporate the multiple different advantages of each type of unit operation while simultaneously overcoming their disadvantages.

For example, NTP methods frequently require significant amount of energy to completely destroy the VOC and are frequently associated with many harmful products which are formed due to the ionization of the adsorbate. A catalyst can be employed to reduce activation energies and potentially capture these harmful materials as well. Similarly, one of the drawbacks with catalytic oxidation is that dilute concentrations of the pollutant can greatly affect catalytic performance. This could be

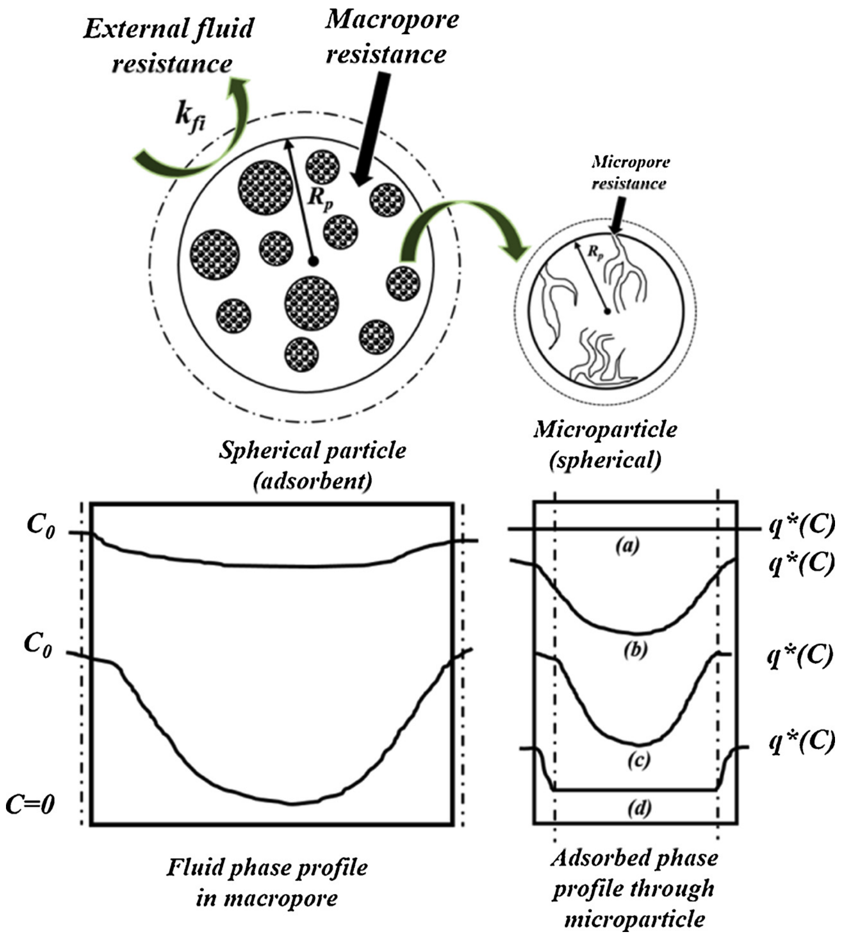


Fig. 25. Schematic diagram of composite adsorbent pellet showing the three principle resistances to mass transfer as well as concentration profiles (Adapted from [179]).

overcome by including a dual-functional material that facilitates both adsorption, which is effective at dilute concentrations, and successive catalysis in different beds. This ultimately increases the catalytic efficiency while also keeping energy costs low by using various regenerative techniques.

Destruction and separation techniques have been greatly explored for VOCs, and so far, the implementation of methods apart from thermal/catalytic oxidation and adsorption in the industry has been scarce. Many novel methods have still been restricted to the lab scale and rigorous economic analyses have yet to be done to determine their efficacy on an industrial scale. One of the biggest hurdles when dealing with VOCs are their carbonaceous and bio toxic nature, which greatly limits the kind of material and process that can be used. For example, coke formation greatly reduces catalytic activity, as does poisoning by by-products such as those evolving from halogenated products. Development of advanced, energy-efficient processes for VOCs abatement requires consideration of various operating parameters such as flow rate, feed concentration, reaction enthalpies, and by-product formation while evaluating the performance of the materials with input from process modeling and optimization. To transition VOCs emission control research from lab-scale to industrial-level, it is imperative to take into account the scale-up criteria alongside performance metrics such as materials cost and availability, capital and operating costs and large-scale viability of the process.

Acknowledgements

The authors thank the National Science Foundation (NSF CBET-1802049) for financially supporting this project.

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