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Advances in the regeneration of spent adsorbents for gas-phase treatment: Thermal analyses and non-conventional approaches

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ABSTRACT

Adsorption is one of the most widely used methods for the treatment of volatile organic compounds from gaseous effluents. When developing an effective adsorbent, it is essential to consider the entire lifecycle: besides achieving high removal efficiency, the potential for regenerating spent adsorbents must also be carefully evaluated. This review examines current technologies for the regeneration of spent adsorbents used in purification of gas streams or to limit emissions, with the goal of extending their functional lifespan. Here, thermal, non-thermal, and emerging technologies for the regeneration of spent adsorbents are presented, with particular emphasis on thermal approaches and their integration in adsorption-desorption cycles. Particular attention is devoted to the influence of key operational parameters such as temperature, purging gas, heating rate, and residence time on the regeneration efficacy. Moreover, thermal characterization analyses are highlighted as key tools for optimizing thermal regeneration strategies to ensure that regenerated materials retain their original adsorption capacity over multiple reuse cycles. The proper use of thermal analyses (thermogravimetry, differential thermal analysis, differential scanning calorimetry) is essential to develop efficient regeneration strategies of spent adsorbent materials. The importance of effective off-gas treatment during regeneration is also addressed, emphasizing its role in sustainable adsorbent management. Finally, the review addresses the lack of studies evaluating the life-cycle environmental impacts of regeneration processes and provides guidance for future research to support the sustainable and circular use of adsorbent materials.

1. Introduction

In recent years, increasing industrialization and consumerism have led to a continuous rise in the release of hazardous pollutants into the environment. As a result, considerable attention has been committed to the development of effective technologies for ensuring both air and water quality. Among the available options, adsorption has emerged as a particularly promising and well-established technique for treating water and gaseous effluents, and for purifying gas streams. It is highly efficient, fast, and cost-effective for the removal of a broad range of contaminants thanks to its versatility in process design and to the wide variety of available adsorbent materials with tailored features and low cost. Adsorbent materials can also be derived from waste, making this approach more sustainable [1–4].

In a circular economy perspective, the regeneration of spent adsorbents is a primary goal. While disposal is the inevitable endpoint, the regeneration of saturated adsorbents can extend their lifetime, representing a more sustainable and cost-effective alternative to current single-cycle usage. In cases where regeneration is technically or economically unfeasible, upcycling offers a complementary strategy. Converting spent adsorbents into value-added materials, such as catalysts, can help mitigate costs and reduce secondary pollution. Indeed, several studies have explored the upcycling of spent adsorbents into functional materials for environmental applications, including NO_x abatement, dye photodegradation, and photocatalytic CO_2 reduction [5–8].

Compared to disposal, regeneration not only allows for multiple reuse cycles, reducing the demand for fresh materials, but also helps to prevent the potential release of harmful contaminants that can occur during or after disposal. Furthermore, disposal operations often incur

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significant costs and may lead to operational slowdowns due to the need for system shutdowns and filter replacement. In contrast, regeneration supports a more continuous and resource-efficient operation, extending the functional lifetime of the adsorbent while reducing environmental and economic impacts [9–13].

Despite these advantages, the regenerability of adsorbents has received comparatively less attention in the scientific literature. Most studies still focus on the performance of fresh materials, with limited investigation into their behaviour and efficiency after repeated use. This review specifically addresses the regeneration of adsorbents used for the remediation of gas-phase contaminants, particularly volatile organic contaminants (VOCs), an area where several commercial technologies are already in place, especially for solvent recovery. However, these technologies often face significant limitations related to the extent of regeneration achievable, which varies depending on the pollutant–adsorbent pair, the number of regeneration cycles the material can tolerate without property degradation, and the often-overlooked issue of off-gas treatment [13–21]. Current systems are generally optimized for single VOCs and non-polar solvents; when complex mixtures or polar contaminants are involved, solvent recovery becomes economically and technically unfeasible.

While liquid-phase regeneration has been extensively explored in the literature, it has seen limited industrial implementation. Several reviews have addressed regeneration in aqueous systems [9–11,22–24], yet comprehensive analyses dedicated to gas-phase adsorbents are still lacking. Therefore, there is a clear need for an updated and critical overview of available regeneration techniques for gas-phase applications, highlighting both commercially implemented technologies and emerging approaches still under development. This review aims to fill the gap by providing an in-depth analysis of regeneration strategies. After first presenting the main adsorbent materials typically used in gas-phase adsorption, the review will then focus on thermal regeneration methods, given their central role in both current practice and ongoing research. The role of thermal analysis in developing efficient thermal regeneration procedures is also highlighted. Non-thermal and innovative regeneration techniques will also be discussed, along with considerations on off-gas treatment solutions. Finally, the review presents preliminary considerations on the environmental impacts and sustainability of the overall adsorption-regeneration process, an aspect still insufficiently explored in the current literature. By addressing these broader implications alongside technical regeneration strategies, the review ultimately aims to support the development of more sustainable and circular pathways, helping industries reduce waste management costs and environmental burdens.

2. Adsorbent materials

Ideal adsorbent materials for gas treatment should exhibit a large specific surface area and pore volume, a high density of adsorption sites, and high adsorption capacity. Additional key features include good chemical and thermal stability—especially important when thermal regeneration is considered—and a fast adsorption rate. The nature of surface functional groups is also critical, as they influence the adsorbent's affinity for specific classes of molecules; their selection should be tailored to the chemical characteristics of the target pollutants, such as polarity or functional moieties, to optimize interaction and adsorption efficiency. The adsorption rate itself is not only a material property but also depends on operational parameters, such as the flow rate of the air stream and the size and configuration of the filter bed, which must be optimized to ensure effective contact time and pollutant capture.

Among the most widely used materials at the industrial level are carbon-based adsorbents such as activated carbon and biochar, molecular sieves like zeolites, mesoporous silica and metal-organic frameworks (MOFs), polymer resins, such as macroporous and hyper-cross-linked polymeric adsorbent (HPA), and modified clays [25]. Fig. 1 shows a schematic overview of the main adsorbent classes, highlighting their characteristic pore architectures and typical ranges of specific surface area (SSA).

Porous carbon materials are particularly attractive due to their low production cost, high thermal resistance, and their inherently hierarchical micro/mesoporous structure, which provides a large surface area and porosity, leading to high adsorption capacity. They suffer competition from water vapor but generally retain good performance in humid environments, making them well-suited for treating industrial flue gases [26]. Activated carbon (AC), both in powdered and beaded form, has been successfully applied for the adsorption of various VOCs, including

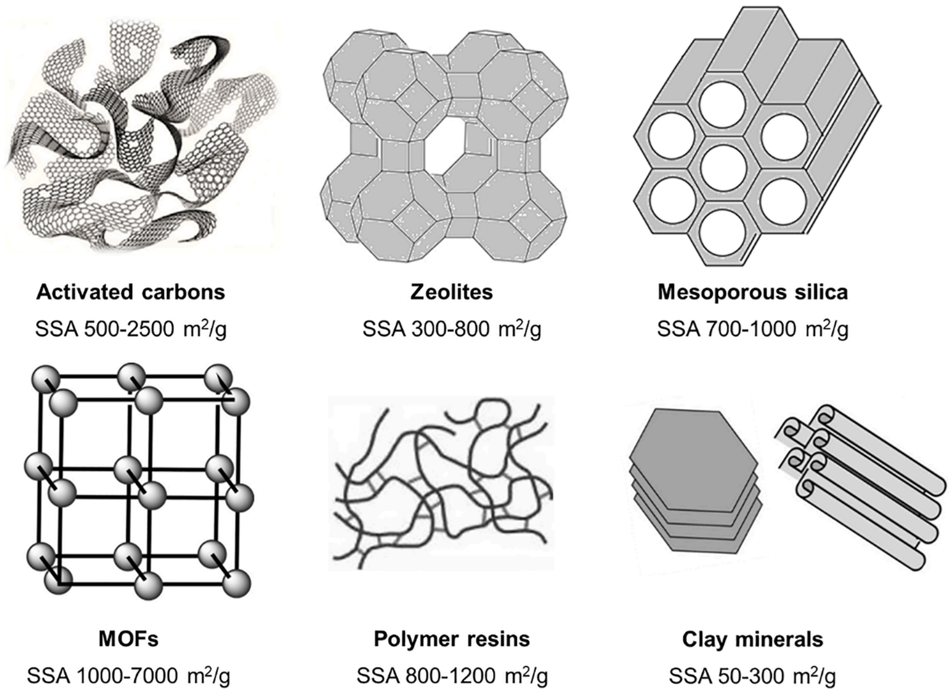

Fig. 1. Representative classes of adsorbent materials used for gas-phase pollutant removal.

n-hexane, cyclohexane, 1-hexene, and ketones such as acetone, butanone, and 2-pentanone, as well as complex mixtures containing alcohols, esters, ketones, alkanes, and aromatic hydrocarbons [27,28]. Indeed, they typically show a limited adsorption selectivity. Even though they are the most used adsorbent, they have some limitations, such as high regeneration costs and potential for spontaneous combustion at high temperatures in certain conditions.

Zeolites, in contrast, offer excellent adsorption selectivity, resistance to combustion and a highly tunable porous structure. Their strictly microporous crystalline framework, composed of well-defined channels and cages, underlies their molecular sieving ability but also contributes to their lower overall susceptibility to contamination (see Section 3.1.2). Moreover, they generally display a lower adsorption capacity and complex synthesis requirements. Zeolite-based composites, including Y/ZSM-5 composites and metal oxide-modified zeolites, have demonstrated effective removal of VOCs such as toluene, isopropanol, cyclohexane, acetone, and butyl acetate under both dry and humid conditions [29,30].

Mesoporous silica materials have also been explored for VOC removal, benefiting from their highly ordered pore structure, large surface area, and chemical tunability. Organic functionalization, such as the incorporation of vinyl groups or other hydrophobic modifiers, can enhance water resistance and increase affinity toward VOCs. These tailored materials have shown effective adsorption of various compounds, including p-xylene, m-xylene, acetone, isopropanol, toluene, styrene, mesitylene, and methanol, with functionalized mesoporous silica often outperforming unmodified counterparts [31–33].

In recent years, increasing attention has shifted toward MOFs, which represent an emerging class of crystalline porous materials with highly tunable structures. MOFs consist of metal nodes coordinated by organic ligands, forming rigid and predominantly microporous frameworks that allow precise control over pore size, topology, and surface chemistry. This structural versatility translates into high selectivity and affinity toward various VOCs [34]. Several MOFs, including MIL-101 [35,36], CuBTC [37,38], FeBTC [37], ZIF-8 [38], and UiO-66 [20,39], have demonstrated significant adsorption capacities for a broad range of VOCs, such as n-pentane, n-hexane, n-heptane, cyclohexane, benzene, toluene, xylene, 2-methylpyridine, 2-methyl-2-butanol, and acetaldehyde. However, despite their excellent performance, MOFs still face important limitations, including moderate thermal stability, relatively high synthesis costs, and the need for reconstruction strategies upon degradation (see Section 3.1), which currently restrict their large-scale use and keep most applications at a research stage.

Among the commercially available adsorbents, polymeric resins, such as aromatic polystyrene and polydivinylbenzene, and aliphatic methacrylic resins, are notable for their tailored surface chemistry and high selectivity, although they are often costly and tend to exhibit lower adsorption capacities compared to conventional adsorbents [25,40–45]. Nevertheless, recent advances in polymer chemistry have led to the development of hypercrosslinked and porous polymeric materials that have shown promoted adsorption capacities toward gaseous toluene, hexane vapors, and other aromatic VOCs, compared to activated carbon, even in humid environments [46–49]. Moreover, their stable and customizable physical/chemical properties have enabled the development of regenerable adsorbents.

Another class of emerging adsorbents for VOC removal from gas-phase effluents is that of modified clays or organoclays. Clays with variable morphology have shown potential for the adsorption of organic contaminants, thanks to their very low cost, high availability, non-toxicity, and durability. As examples, kaolinite and montmorillonite nanosheets are efficient for the removal of benzene [50]. Sepiolite nanofibers are suitable for the adsorption of toluene [51] and formaldehyde [52]. Halloysite clay nanotubes (HNTs) possess relevant adsorption capacity towards some alcohols (ethanol, propanol, and hexanol), chloralkanes (propyl-, butyl-, and pentyl chloride), and carboxylic acids (propionic, butanoic, and pentanoic) in the vapor phase [53]. The surface modification of clay nanotubes represents a successful strategy to improve the removal efficiency toward both aliphatic and aromatic organic contaminants [54]. In this context, hydrophobization of the halloysite cavity with anionic surfactants improves the HNTs adsorption capacity towards n-decane and toluene [55]. Recent literature [56,57] has demonstrated that the incorporation of halloysite within biopolymers, such as alginate and chitosan, leads to porous gel systems with excellent removal actions towards p-coumaric acid, phenol and dodecane. Compared to other adsorbents, such as activated carbon, they suffer from lower adsorption capacity, due to their lower surface area, but their tunable selectivity achieved via surface modification and good regeneration capacity make them highly promising materials.

Overall, the selection of adsorbent material depends on the specific application requirements and trade-offs between cost, efficiency, and operational conditions.

3. Regeneration strategies

Regeneration refers to the recovery and reuse of saturated adsorbents through processes that are both technically feasible and economically sustainable, with the aim of extending the adsorbent's lifecycle and reducing costs associated with raw material consumption. The primary goal of regeneration is to restore the adsorption capacity of the material by removing the previously adsorbed contaminants, thereby enabling its reuse. Depending on the nature of the contaminants, it may be desirable to recover the desorbed compounds, either for reuse as valuable chemical building blocks or for subsequent decomposition in a successive treatment step.

The choice of an appropriate regeneration strategy depends on several factors, including the type of adsorbent, the nature of the adsorbed contaminants, operational parameters and target application, and environmental/economic constraints, such as energy use, secondary waste, scalability [13,58]. Among these, the type of adsorption, whether physisorption or chemisorption, plays a crucial role, as it directly affects the strength of the adsorbate-adsorbent interactions and, consequently, the energy and conditions required for regeneration. Physisorption, characterized by relatively weak interactions, generally allows for desorption under mild conditions such as low-temperature thermal treatment, vacuum, or purge gas stripping. In contrast, chemisorption involves the formation of covalent bonds between adsorbate and adsorbent, often necessitating more intensive regeneration techniques such as high-temperature thermal treatment or chemical regeneration using reactive agents. This fundamental distinction guides the selection of regeneration methods to ensure efficient recovery of adsorption capacity while minimizing damage to the adsorbent material. Consequently, regeneration approaches must be tailored to the specific requirements of the system and the desired fate of the desorbed species.

A wide variety of regeneration methods have been developed to allow the desorption of the adsorbed species, including thermal and vacuum desorption, steam or purge gas stripping, displacement desorption, chemical and oxidative regeneration, solvent extraction, supercritical fluid extraction, microwave irradiation, and ultrasonic treatment. These techniques can be broadly classified into three main categories: thermal, non-thermal and emerging non-conventional approaches (Fig. 2). Each method offers distinct advantages and limitations in terms of energy efficiency, contaminant specificity, adsorbent stability and scalability, which will be discussed in the following sections.

3.1. Thermal regeneration strategies

Thermal regeneration involves heating saturated adsorbents to provide sufficient energy for desorbing the retained adsorbates and restoring the adsorption capacity of the material. Typical regeneration temperatures range from 105 to 800 °C, depending on the thermal stability of the adsorbent, the strength of the adsorption interaction, and

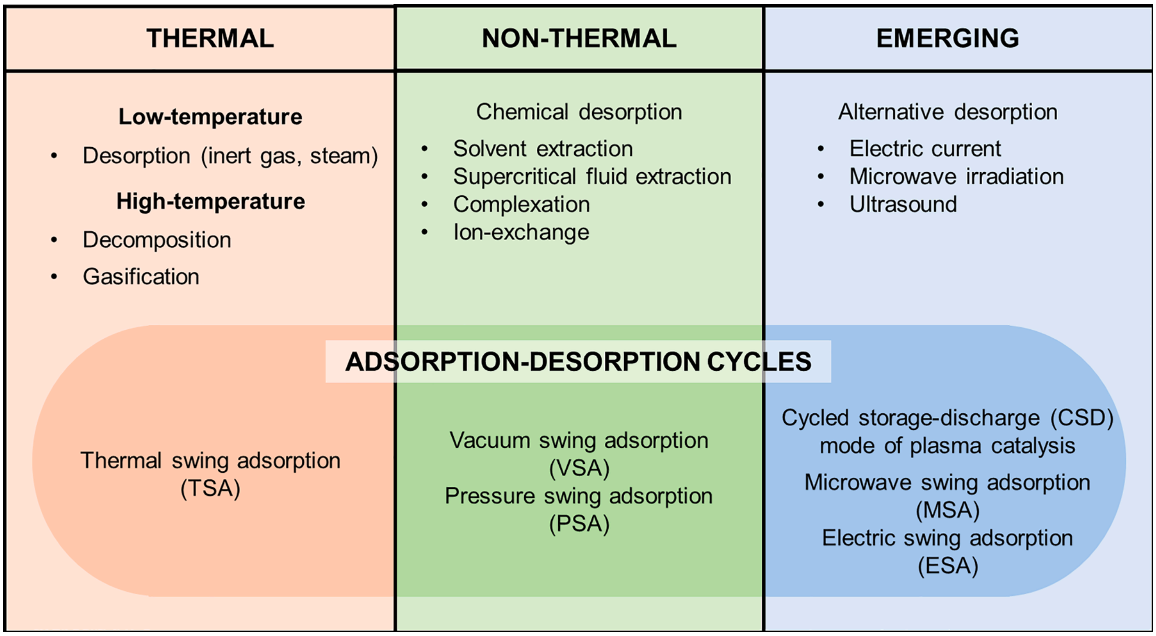

Fig. 2. Classification of adsorbent regeneration methods into thermal, non-thermal and emerging technologies.

the nature of the adsorbed species. Based on the operating temperature, thermal regeneration methods are often categorized into low-temperature (105 – 300 °C) and high-temperature (300 – 800 °C) processes. This classification also determines the fate of the desorbed species, particularly in terms of their thermal stability and reusability [9,15,23,58].

Before examining the specific approaches, it is important to emphasize that the thermal stability of the adsorbent material itself is a fundamental prerequisite for any thermal regeneration process. The adsorbent must endure repeated exposure to elevated temperatures without significant loss of its physicochemical properties, such as porosity, surface area, and structural integrity, in order to retain consistent adsorption performance over multiple cycles. In this context, thermal characterization of the adsorbent is essential. Techniques such as thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and differential thermal analysis (DTA) provide valuable insights into the material's thermal stability, decomposition temperatures, and heat capacity [59–64]. Moreover, an accurate thermal characterization can reveal phase transitions or structural changes that may occur during heating, enabling the selection of regeneration conditions that preserve the structural integrity and adsorption capacity of the material, thereby extending its operational lifetime. For example, Ledesma et al. [65] studied the thermal regeneration of activated carbon saturated with *p*-nitrophenol and examined how this process is affected by the number of regeneration cycles. They monitored the process using TGA/DSC/DTA analyses, which demonstrated that regeneration efficiency is highly dependent on the number of times the carbon adsorbent is reused. As reuse increases, the adsorbent exhibits lower response to the regeneration process, suggesting the increasing persistence of strongly adsorbed compounds on the carbon surface and leading to a significant decline in regeneration efficiency (as extensively discussed in Section 3.1.2). Performance loss after regeneration is a general concern for several classes of adsorbent. The regenerability of metal-organic frameworks (MOFs) is often limited by their thermal and chemical stability. Neshati and Hashisho [37] demonstrated that the regeneration of CuBTC and FeBTC depends strongly on the specific VOC: desorption at 120 °C was effective for n-hexane, 2-methyl-2-butanol, and toluene, but not for 2-methylpyridine. For the latter, the observed poor regenerability at this temperature suggests a stronger interaction with the MOF structure, and complete desorption would therefore require higher temperatures, which could compromise the structural integrity of the material. This observation aligns with Hashemi et al. [66], who showed that repeated regeneration cycles under extreme thermal or moisture conditions can degrade MOF frameworks, leading to partial collapse of the porous structure and reduced adsorption capacity. In such cases, reconstruction strategies, such as solvent-assisted or chemically induced reconstruction, may be necessary to restore adsorption capacity and extend the MOF lifetime during cyclic VOC adsorption.

Additionally, thermal analysis techniques are also powerful tools for optimizing the desorption of retained contaminants. Among them, temperature programmed desorption (TPD) allows to determine the temperatures at which adsorbed species are released from the surface. More importantly, TPD profiles provide insights into the strength and nature of adsorbate-adsorbent interactions, providing valuable guidance for selecting optimal regeneration conditions that ensure efficient contaminant removal from spent adsorbents. Also, TPD combined with other analytical techniques, such as microGC, offers insights into the chemical nature of the desorbed species, shedding light on any degradation of the adsorbed species [67]. As an example, TPD has been employed to investigate the desorption behaviour of aromatic hydrocarbons (toluene, *p*-xylene, mesitylene and naphthalene) from mesoporous silica MCM-41 [68]. The TPD profiles (Fig. 3) exhibited single asymmetric peaks between 110 °C and 170 °C, indicating slow desorption and suggesting first-order desorption kinetics. Both the onset temperature, T_{on}, and the peak maximum temperature, T_m, increased with the molecular weight of the adsorbed hydrocarbons (toluene $<$ *p*-xylene $<$ mesitylene $<$ naphthalene).

Moreover, the TPD data provided insights into specific adsorbate-adsorbent interactions: when analysing the TPD data, the authors assumed readsorption of aromatic hydrocarbon on MCM-41, as the adsorbate molecules can freely diffuse within the material's mesopores. Based on this model, the authors demonstrated that naphthalene is more strongly adsorbed than the other hydrocarbons, due to stronger interactions between its two condensed aromatic rings and the silanol groups of MCM-41. In addition, the variation of T_m with the amount of adsorbed toluene suggested a distribution of adsorption site energies on the MCM-41 surface, likely due to different types of silanol groups. Such insights are crucial for understanding adsorbate-adsorbent interactions and, consequently, for determining appropriate regeneration temperatures to ensure complete desorption of each specific contaminant.

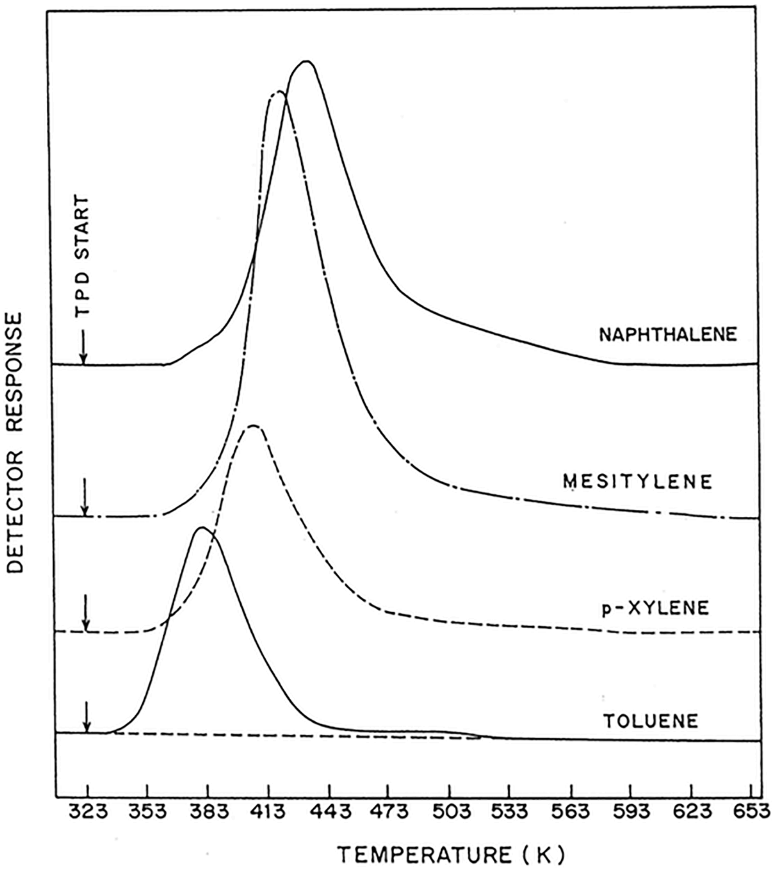

Fig. 3. Temperature programmed desorption profiles of aromatic hydrocarbons (toluene, p-xylene, mesitylene and naphthalene) on mesoporous silica MCM-41. Reproduced with permission from [68].

In another study, *Dohshi* [69] explored the role of adsorbent structure in determining adsorption interactions and, consequently, regeneration performance. The author compared the dynamic adsorption and desorption of toluene on various siliceous materials, including super-microporous silica (SMPS), mesoporous silica MCM-41, commercial microporous silica gel, and HY zeolite ($SiO_2/Al_2O_3 = 5.1$). After saturation of the adsorbents with toluene, thermal desorption was carried out by flowing dry air through the samples at 30 °C. Desorption efficiencies exceeded 90 % for SMPS, MCM-41, and silica gel, whereas HY zeolite exhibited a much lower efficiency of 35 %. This difference was attributed to pore size: the smaller mean pore diameter of HY zeolite ($<$0.7 nm) led to stronger interactions between toluene molecules and the pore walls, in contrast to MCM-41 with a larger mean pore diameter (2.5 nm). These findings were further supported by TPD analyses conducted after a thermal desorption in bland conditions (at 30 °C, with dry air flowing at 50 mL min^{-1}) to determine the residual amount of toluene. The TPD spectra (Fig. 4) revealed that complete desorption of toluene from HY zeolite required temperatures above 300 °C, suggesting strong interactions between the Lewis basic sites of the zeolite framework and the toluene molecules. In comparison, complete desorption from the other silica-based materials was achieved at the relatively low temperature of around 150 °C. These results highlight the importance of thermal characterization of loaded adsorbents to determine optimal regeneration conditions for each specific adsorbate-adsorbent system.

Overall, thermal analysis can provide critical insights into both material thermal behaviour and contaminant interactions, enabling the

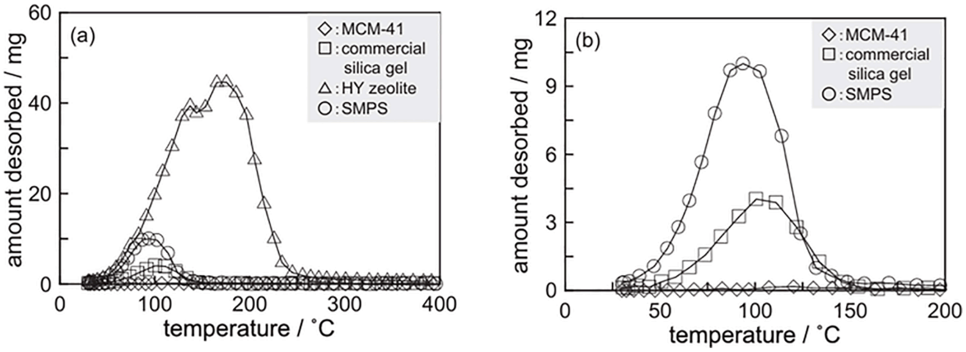

Fig. 4. Temperature programmed desorption profiles for toluene of (a) MCM 41, commercial silica gel, HY zeolite and SMPS and (b) the magnified profiles of MCM-41, commercial silica gel and SMPS. Reproduced with permission from [69].

development of regeneration strategies that maximize desorption efficiency while preserving the structural and functional integrity of the adsorbent.

Several key parameters influence the effectiveness and efficiency of thermal regeneration [13]:

- temperature, which must be optimized based on the volatility of the contaminant and the thermal stability of the adsorbent;
- type of purging gas, which can be inert (e.g., N_2, He, Ar) to enable desorption without chemical modification, or reactive (e.g., O_2, CO_2, steam) to promote decomposition or gasification of the desorbed species;
- heating rate and residence time, which determine both energy consumption and regeneration efficiency.

The choice of purging gas is particularly important when dealing with VOCs, which may form flammable or explosive mixtures in air upon heating. To mitigate this risk, inert gases such as nitrogen or argon, or alternatively steam, are commonly used to ensure safe operating conditions during the desorption process.

Within thermal regeneration, three main approaches can be distinguished [15]:

i) *desorption*, where adsorbates are removed via heating without undergoing chemical transformation;
ii) *desorption and decomposition*, where adsorbates are thermally degraded during or after desorption;
iii) *desorption followed by gasification*, where desorbed species are further oxidized or degraded using reactive gases such as CO_2 or steam.

All three methods have been successfully applied to the treatment of spent adsorbents saturated with VOCs, differing mainly in the stability and final fate of the adsorbates following regeneration. The following sections describe each of these approaches in detail, highlighting their mechanisms, operational conditions, and examples of application.

3.1.1. *Low-temperature desorption*

In the case of thermal desorption, an inert hot carrier gas facilitates the release and potential recovery of organic compounds in their original form. A well-established example is Thermal Swing Adsorption (TSA), a cyclic process of adsorption and desorption widely used for the regeneration of activated carbon. TSA typically requires two reactors operating in parallel, as illustrated in Fig. 5**a**: one for adsorption at low temperatures and another maintained at higher temperatures to promote the desorption of the adsorbed species, which is typically an endothermic process [13,15,70–72].

At temperatures below 300 °C, regeneration primarily involves only physical desorption, without any chemical modification of the adsorbates. For instance, low-temperature thermal regeneration of bead activated carbon used for toluene removal was demonstrated using conductive heating at 150 °C under nitrogen flow by Chen et al. [73]. In this study, nearly 97 % of the adsorbed toluene was successfully desorbed, and the regenerated adsorbent retained 83 % of its initial adsorption capacity after five adsorption-desorption cycles, proving the effectiveness of low-thermal regeneration. Similarly, temperature has a significant impact on regeneration efficiency, as demonstrated by Tan et al. [74] using nitrogen-rich porous carbon adsorbents saturated with ethyl acetate. The authors observed rapid desorption at all tested temperatures, with most desorption occurring within the first 30 min. As the temperature increased from 50 °C to 120 °C, desorption efficiency improved from 47 % to 95 %. At 120 °C, the maximum outlet concentration of ethyl acetate was reached within 10 min, indicating that higher temperatures greatly enhanced regeneration performance. In addition, the long-term performance of the adsorbent was evaluated over multiple adsorption-regeneration cycles. After nine cycles, the adsorbent retained up to 75 % of its initial adsorption capacity, while maintaining a desorption efficiency above 86 %. These results highlight the importance of optimizing operational parameters to ensure effective regeneration and adsorbent reusability.

Table 1 presents a comparative overview of selected studies, where operating conditions (operating temperature, time per cycle, and carrier gas), number of adsorption-desorption cycles, and adsorption capacity retention are compared for different adsorbent types.

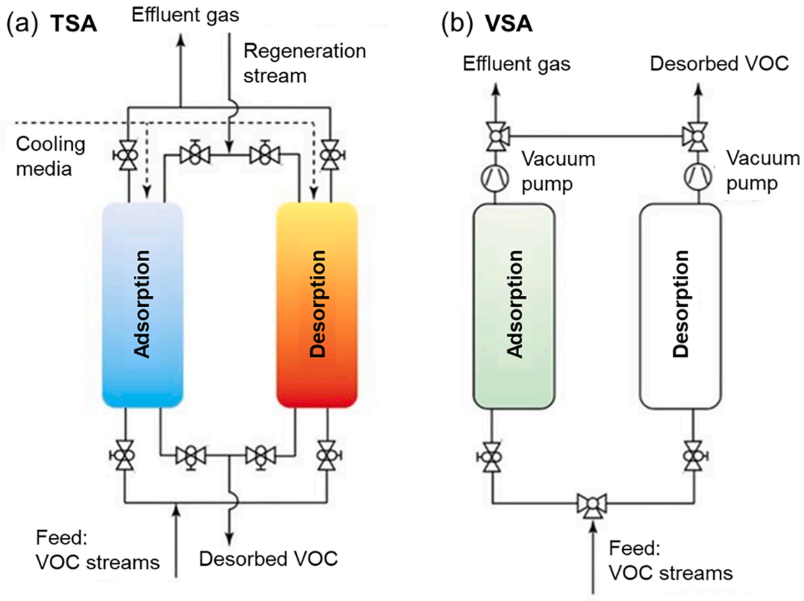

Fig. 5. Dual-reactor setup of (a) Thermal Swing Adsorption and (b) Vacuum Swing Adsorption processes.

Table 1
Selected literature examples of thermal desorption of VOCs with various adsorbents and regeneration conditions.

VOC	Adsorbent	Temperature (°C)	Time per cycle (min)	Carrier gas (mL/min)	Cycles	Adsorption capacity retention (%)	Ref.
Toluene	Bead activated carbon	150	n.a.	Nitrogen (n.a.)	5	83	[73]
Ethyl acetate	Nitrogen-rich porous carbon	50–120	n.a.	Dry flowing air (30)	9	75	[74]
TMB	ACFC10	288	100	Nitrogen (1000)	5	17	[75]
TMB	ACFC10	400	100	Nitrogen (1000)	5	7	[75]
TMB	ACFC15	288	100	Nitrogen (1000)	5	91	[75]
TMB	ACFC15	400	100	Nitrogen (1000)	5	49	[75]
TMB	ACFC20	288	100	Nitrogen (1000)	5	95	[75]
TMB	ACFC20	400	100	Nitrogen (1000)	5	50	[75]
Ethanol	HPA	35	60	Nitrogen with 80 % RH (100)	4	86[a]	[76]
Ethanol	AC	35	60	Nitrogen with 80 % RH (100)	4	82[a]	[76]
n-hexane	HPA	35	60	Nitrogen with 80 % RH (100)	4	86[a]	[76]
n-hexane	AC	35	60	Nitrogen with 80 % RH (100)	4	80[a]	[76]
Ethanol	HPA	110	60	n.a.	4	49[a]	[76]
Ethanol	AC	110	60	n.a.	4	59[a]	[76]
n-hexane	HPA	110	60	n.a.	4	62[a]	[76]
n-hexane	AC	110	60	n.a.	4	73[a]	[76]
n-heptane	HPA	110	60	n.a.	4	38[a]	[76]
n-heptane	AC	110	60	n.a.	4	58[a]	[76]

n.a.: not available.

[a] Values averaged over two initial solvent concentrations.

3.1.2. *Desorption and decomposition*

When the thermal regeneration is carried out at elevated temperatures or in the presence of oxidative gases, the adsorbates are not only desorbed but can also undergo thermal degradation into smaller or less harmful molecules [9,15,17]. However, incomplete desorption or partial decomposition of adsorbed species can lead to the formation of a residual fraction known as *heel*, which remains strongly bound to the adsorbent surface. A schematic representation of the gradual deactivation of activated carbon during adsorption-desorption cycles of VOCs is reported in Fig. 6**a**.

Thermogravimetric analysis and gas chromatography-mass spectrometry (GC–MS) are commonly used to investigate the mechanism of heel formation. For instance, Lashaki et al. [19] studied heel formation during cyclic adsorption-desorption of VOCs from a painting process using a full-scale adsorber-desorber. In particular, they assessed the thermal stability of the heel using TGA. Differential thermogravimetric

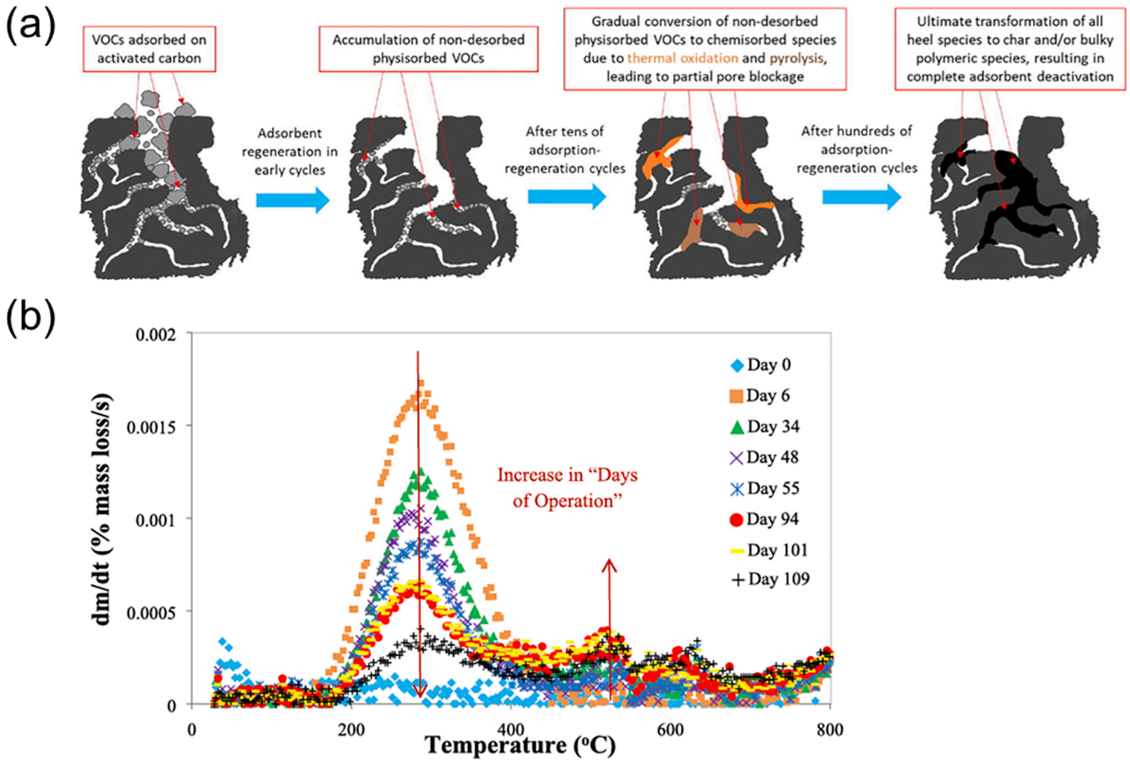

Fig. 6. (a) Proposed mechanism of heel formation and adsorbent deactivation during adsorption-desorption cycles. (b) Differential thermogravimetric curve of bead activated carbon samples as a function of days in operation of a full-scale adsorber-desorber. Reproduced with permission from [19].

(DTG) curve was used to identify distinct weight loss peaks, determine their corresponding temperatures and intensities, and monitor their evolution over time. DTG profiles (Fig. 6**b**) exhibited two main peaks at approximately 290 °C and between 500 – 600 °C. The high-temperature peaks are generally attributed to chemisorbed species, whereas the low-temperature peaks are associated with physisorbed species that were not removed during low-temperature regeneration. A representative example is 1,2,4-trimethylbenzene, commonly present in paint solvents, which is difficult to desorb due to its relatively high boiling point (170 °C). As shown in Fig. 6**b**, the intensity of the low-temperature peak was the highest during the first adsorption-regeneration cycle (day 6) and decreased over subsequent cycles. This trend reflects the progressive accumulation of chemisorbed species formed via thermal oxidation or pyrolysis of physisorbed VOCs, which is shown by the appearance of additional peaks at higher temperatures (500 – 600 °C) in samples subjected to extended adsorption-regeneration cycling.

These findings underscore the critical role of thermal analysis in understanding heel formation, which results from a combination of:

i) physisorbed VOCs not removed during regeneration;
ii) chemisorption of by-products from thermal oxidation or pyrolysis reactions;
iii) formation of ultra-stable char or polymeric species after many adsorption-regeneration cycles.

This issue has been especially observed with activated carbon-based adsorbents [19,75,77–82]. For instance, Niknaddaf et al. [75] studied the thermal desorption of 1,2,4-trimethylbenzene from activated carbon fiber cloth (ACFC) and found that part of the adsorbed species underwent thermal degradation, leading to carbon deposition. The study showed that heel formation increased with regeneration temperature, as higher thermal energy favoured endothermic decomposition processes that produced more carbonaceous residues. To elucidate the mechanism of heel formation, the authors used TGA, which provided critical insights into the thermal stability and decomposition behaviour of the residual species. The authors identified these residues as thermally stable compounds that decomposed at significantly higher temperatures than 1,2,4-trimethylbenzene, confirming the role of thermal degradation in heel formation. This further highlights the importance of thermal analysis in assessing not only material stability but also the chemical transformations of adsorbed species during regeneration.

Importantly, the extent to which heel blocks the porous structure strongly depends on pore size distribution. Several studies have shown that microporous adsorbents convert a significantly larger fraction of adsorbed VOCs into heel, whereas mesopores do not substantially contribute to heel formation and therefore prolong adsorbent lifetime [75,83]. In studies on ACFC samples with progressively increasing pore widths and pore volumes, samples with a higher portion of narrow micropores (ACFC10) lost up to 83 % of its initial adsorption capacity after repeated cycles due to pore blockage by carbonaceous residues. In contrast, adsorbents with larger pores (e.g., ACFC15 and ACFC20) retained their adsorption capacity over multiple cycles (Table 1) despite accumulating similar amounts of heel [75]. These results clearly show that pore architecture plays a central role in determining the functional impact of heel accumulation on adsorbent performance.

Operating conditions, especially regeneration temperature and the composition of the purge gas, also play a decisive role in heel formation [84,85]. Feizbakhshan et al. [85] conducted a comparative study on three activated carbons and a zeolite regenerated at 150, 200, and 250 °C, demonstrating that the presence of oxygen in the purge gas markedly increases oxygen-induced surface reactions at elevated temperatures. Activated carbons, due to their broader pore size distribution, were significantly more susceptible than zeolite. Interestingly, the smallest extent of heel formation occurred at the intermediate temperature (200 °C), while regeneration at 250 °C led to extensive oxidative modification of the surface. TGA profiles of ACs regenerated at 150 and 200 °C exhibited a single low-temperature peak corresponding to the desorption of physisorbed compounds, whereas samples regenerated at 250 °C showed multiple overlapping peaks attributable to the desorption of newly formed heel species. These results indicate a threshold above which oxygen accelerates chemisorption and carbonization reactions, thereby promoting heel accumulation.

These thermally stable carbon residues are difficult to remove under mild thermal conditions and can progressively reduce adsorption capacity by blocking active sites or reducing porosity over repeated cycles. Thus, persistent heel accumulation represents a significant limitation of conventional thermal regeneration approaches. Based on these mechanistic insights, several mitigation strategies can be adopted to minimize thermal degradation of adsorbates during regeneration. Techniques such as microwave heating or resistive heating can be optimized to provide rapid and spatially uniform heating, enabling fast desorption while limiting the extent of adsorbate decomposition and suppressing coke (heel) formation. By reducing the residence time of VOCs at high temperature, these approaches can extend adsorbent lifetime over multiple cycles [86,87].

3.1.3. *Gasification*

To overcome the limitations associated with heel accumulation and incomplete decomposition, more advanced thermal regeneration strategies such as gasification can be applied. Unlike simple thermal desorption, gasification involves the partial oxidation of carbonaceous residues (such as heel or coke deposits) at elevated temperatures in the presence of oxidizing agents like steam or CO_2, facilitating their conversion into gaseous products (e.g., CO and CO_2) [15,17]. According to Salvador et al. [15], the key gasification reactions include:

1. steam gasification:

$$-C-+H_2O \rightarrow CO+H_2 \qquad \Delta H = +31.4 \text{ kcal mol}^{-1} \tag{1}$$

2. CO_2 gasification:

$$-C-+CO_2 \rightarrow 2\ CO \qquad \Delta H = +40.8 \text{ kcal mol}^{-1} \tag{2}$$

Due to their endothermic nature, these reactions are typically carried out at 800–900 °C, depending on the adsorbent and gasifying agent.

While gasification is highly effective for removing coke-like residues and restoring adsorbent performance, it also presents important drawbacks. These include structural degradation of the adsorbent due to high operating temperatures and mass loss from the carbon matrix, which can occur over successive cycles and reduce the mechanical strength and lifetime of the adsorbent [15]. Nevertheless, gasification remains a valuable option, particularly when both adsorbent regeneration and decomposition of hazardous organic compounds are required. Furthermore, the gaseous byproducts (CO, CO_2, H_2) may be valorised for energy recovery or as feedstock for other chemical processes, enhancing the sustainability of the overall system.

Gasification, as well as TSA, is widely used for the treatment of saturated adsorbents such as activated carbons, organoclays and biochars, particularly when targeting VOCs and non-polar organic pollutants. Despite their high effectiveness, high temperature methods still pose challenges, including high energy demands, potential structural degradation of the adsorbent (e.g., loss of porosity or surface area), and the need for off-gas treatment to mitigate emissions of VOCs, CO, CO_2, or other potentially toxic byproducts.

3.1.4. *Steam stripping*

Another alternative, already on the market, is represented by steam stripping, which promotes thermal desorption at relatively low temperatures using steam as an energy source to desorb weakly bound species. Unlike gasification, steam serves solely as a desorption medium, and its high heat capacity enables the use of a smaller volume of carrier gas. In addition, when steam is in contact with a cold adsorbent bed, it partially condenses and may itself be adsorbed. This competitive adsorption of water enhances desorption in two important ways [15,70]:

i) the heat released during the adsorption of water can further raise the temperature of the adsorbent, enhancing desorption;
ii) water molecules can displace previously adsorbed species, promoting their release.

A comparative study by Jia et al. [76] investigated the influence of both adsorbent and VOC properties on the regeneration performance of humid-air stripping at ambient temperature versus thermal regeneration at 110 °C. Ethanol, n-hexane and n-heptane were selected as representative VOCs, while HPA and AC served as the adsorbents. The results demonstrated that humid-air regeneration provided more efficient desorption across successive dynamic cycles, particularly for ethanol and n-hexane (Table 1), while also avoiding the high energy demand typically required for thermal regeneration. The authors attributed these findings to the high solubility of ethanol in water and to the strong affinity of water vapor for HPA, which facilitated VOC displacement. Under these conditions, HPA showed better regeneration performance than AC during humid-air regeneration, whereas AC showed superior performance under thermal regeneration (Table 1). These findings underscore the importance of VOC polarity and water-adsorbate interactions in determining regeneration efficiency.

However, residual moisture remaining after desorption can also hinder the adsorbent ability to remove new contaminants in subsequent cycles, representing a drawback for repeated adsorption-desorption processes. Additionally, the presence of water vapor complicates the recovery of desorbed compounds in their pure form, particularly when the desorbed species form azeotropes with water or are susceptible to hydrolysis. In such cases, an additional separation step is required to isolate the recovered solvents from condensed water. Depending on the physicochemical properties of the desorbed compounds, common techniques such as decantation (for immiscible systems) or distillation (for miscible systems) can be used to achieve efficient separation, although these increase process complexity and cost. For example, VOCs with boiling points significantly different from water (e.g., toluene, benzene) can typically be recovered via distillation. Conversely, compounds that form azeotropes with water (e.g., ethanol, isopropanol, acetone) or that undergo hydrolysis at elevated temperatures (e.g., esters or halogenated solvents) are less suitable for efficient recovery, as separation becomes energetically demanding or chemically unfavourable.

3.2. Non-thermal regeneration strategies

3.2.1. Vacuum swing adsorption (VSA) and pressure swing adsorption (PSA)

Vacuum Swing Adsorption (VSA) and Pressure Swing Adsorption (PSA) are two physical regeneration strategies already on the market that rely on pressure variations rather than temperature changes to induce desorption. While PSA operates by increasing the system pressure during adsorption and reducing it during desorption, VSA typically performs adsorption at atmospheric pressure and desorption under vacuum conditions. Like thermal swing adsorption (TSA), these systems typically operate in dual-reactor setups (Fig. 5**b**) that alternate between adsorption and desorption phases [88–92].

Due to its dependence on vacuum rather than compression, VSA is generally considered more energy-efficient and cost-effective than PSA, particularly in low-pressure applications such as post-combustion CO_2 capture. The milder regeneration conditions help preserve the structural integrity of the adsorbent over multiple cycles, thus extending its functional lifetime. In addition, its operational simplicity and lower maintenance requirements also make it more attractive for industrial applications [88].

These advantages were experimentally demonstrated by Akdag et al. [91], who compared TSA and VSA for post-combustion CO_2 capture using a biomass-derived adsorbent. VSA was found to enable effective regeneration with minimal adsorbent degradation, making it particularly suitable for thermally sensitive materials. However, the authors noted that the estimated energy requirements for VSA may not be precise, since data on the actual power consumption of the vacuum pump were not available. In contrast, TSA offers potential advantages in terms of operating costs because it avoids the need for compression or vacuum and can exploit waste heat for regeneration. The thermal energy needed in TSA cycles decreased as the CO_2 working capacity of the adsorbent increased, with values ranging from 295.4 to 592.7 kWh/kg CO_2 depending on operating conditions and cycle configuration.

By contrast, PSA requires elevated pressures during the adsorption phase, which introduces higher energy demands for gas compression and increases capital investment. A modelling study by Pirngruber and Leinekugel-le-Cocq [90] explored the design and operation of a PSA process for post-combustion CO_2 capture. Their simulations indicated that PSA could achieve competitive CO_2 recovery and purity but highlighted the significant energy burden associated with pressurization. The study also emphasized the importance of cycle configuration and adsorbent selection in the overall performance of the process.

These findings then illustrate that VSA is already supported by experimental evidence as a viable, energy-efficient regeneration method, while PSA remains a promising yet more energy-intensive option whose effective potential should be further investigated.

3.2.2. Chemical desorption techniques

Other non-thermal regeneration methods, including solvent washing and supercritical fluid extraction, are typically classified as chemical desorption techniques. These approaches aim to remove contaminants from spent adsorbents without the use of high temperatures and are particularly used for materials saturated in aqueous phase conditions. These methods often involve organic or inorganic solvents, which are referred to as eluents [9,10,17,23,58,93]. The primary goal of chemical regeneration is to preserve the structural integrity and restore the surface functionalities of the adsorbent, enabling its reuse.

Among these techniques, supercritical fluid extraction (SFE), particularly using supercritical CO_2, has emerged as a promising alternative due to its low operating temperature and minimal solvent residue. Its tunable solvation power enables efficient desorption of various organic pollutants, including non-polar and moderately polar compounds. However, its application is constrained by the need for high-pressure equipment, elevated energy demands associated with pressurization, and limited efficiency for strongly polar adsorbates unless co-solvents are used. Regeneration efficiency in SFE is strongly dependent on operating parameters such as pressure, temperature, and co-solvent composition [94–96].

The selection of a suitable solvent (whether liquid or supercritical) depends on the physicochemical properties of both the adsorbent and the adsorbate. Organic solvents such as acetone, methanol, and isopropanol are commonly used to extract adsorbed organic contaminants from spent adsorbents, due to their ability to solvate hydrophobic or weakly polar compounds. In such cases, the efficiency of regeneration is strongly influenced by the solubility of the adsorbate in the chosen solvent: the lower the solubility, the lower the desorption efficiency [9,23].

For inorganic contaminants, chemical desorption is governed primarily by two mechanisms: pH adjustment and complexation. The former relies on modifying the surface charge of the adsorbent, particularly if it contains ionizable functional groups, by using acids or bases (e.g., HCl, H_2SO_4, HNO_3, NaOH). This facilitates the protonation or deprotonation of surface functional groups, thereby promoting the release of adsorbed ionic species [93,97]. Alternatively, chelating agents such as ethylenediaminetetraacetic acid (EDTA) can form stable metal-ligand complexes, effectively desorbing metal ions via complexation [9,23,93].

These methods are widely used in laboratory-scale applications, especially for functionalized adsorbents or ion exchange resins, owing to their relatively mild operating conditions (typically low temperatures) and their selectivity toward specific contaminants. However, their application in gas-phase systems is limited, hence they fall outside the main scope of this review.

3.3. Emerging non-conventional strategies

Emerging approaches for adsorbent regeneration are increasingly focused on alternative energy inputs to replace or complement conventional thermal energy. Since desorption is an inherently endothermic process, an external energy source is often required to overcome the interactions between the adsorbate and the adsorbent surface. Traditionally, this energy is supplied through conductive heating; however, thermal methods are often associated with high energy consumption, slow heat transfer, and potential degradation of thermally sensitive materials.

To overcome these limitations, alternative energy sources such as electrical energy, microwave irradiation, and ultrasound have been explored. These techniques offer the potential for more selective and efficient energy delivery, reducing thermal damage while maintaining or even enhancing desorption performance. In many cases, energy can be transferred directly to the adsorbent, enabling localized heating and significantly shorter regeneration times [9,14,15,70,98,99].

3.3.1. Electric swing adsorption (ESA)

One notable example is electric swing adsorption (ESA), a variant of TSA, in which heat is generated internally via the Joule effect: when an electric current passes through a conductive material, resistive heating occurs. Compared to conventional TSA, ESA offers faster and more uniform heating with reduced energy dissipation, resulting in shorter regeneration times and improved thermal efficiency. However, ESA may require higher overall energy consumption, which is a critical issue, particularly when thermal energy recovery is feasible and when the electricity used is not derived from renewable sources.

The practical implementation of ESA is strongly constrained by the need for electrically conductive adsorbents and reliable electrical contacts [70,100]. Conductive carbons, such as ACFC or monoliths, remain the most suitable materials, while non-conductive adsorbents can be used only in hybrid, carbon-supported configurations (e.g., zeolite/AC honeycomb monoliths) [98,101,102]. In this context, ACFC has received growing attention due to its intrinsic electrical conductivity, rapid heat and mass transfer properties, and higher adsorption capacity compared to traditional granular activated carbon (GAC), although research in this area is still relatively limited [70,98,103,104].

From an engineering standpoint, scale-up is challenged by the need to ensure uniform current distribution, avoid local overheating, and maintain low-resistance electrical connections, all of which become more demanding in larger beds.

3.3.2. Microwave swing adsorption (MSA)

Microwave irradiation is another promising alternative to traditional thermal desorption, offering selectivity and controlled heating. In typical laboratory and pilot configurations, microwave applicators operate at powers ranging from approximately 200 to 2000 W, depending on reactor configuration and the dielectric properties of the material [15,105]. Unlike conventional heating, which transfers energy from the surface to the bulk of the material, microwave radiation interacts directly with molecules based on their dielectric properties, causing them to vibrate and generate local heat. This kind of heating leads to much faster temperature rises, which can enhance desorption kinetics and reduce regeneration time [14,15,99].

For instance, Gomez-Rueda et al. [106] demonstrated the effective use of microwave heating to regenerate a porous carbon adsorbent saturated with CO_2. First, their results showed that the microporosity of the material remained intact during the microwave swing adsorption (MSA) process, due to the rapid and localized heating rates (ranging from 100 to 400 °C/min) compared to conventional TSA. Additionally, by comparing different microwave powers and irradiation times under equal energy input, they found that higher power applied over shorter periods resulted in more efficient heating with reduced heat loss, thereby accelerating desorption.

Despite these advantages, practical application of microwave systems is still limited by scale-up challenges, and industrial-scale implementation is hindered by high capital costs and operational energy demands. Heating performance depends critically on the dielectric properties of both adsorbent and adsorbate, with selective heating being more effective in materials of low permittivity combined with polar contaminants [105]. At larger scale, non-uniform power distribution, sensitivity to moisture, and the composition of the material matrix complicate reactor design and operational control. Moreover, the engineering complexity of microwave applicators and the need for dedicated pilot-scale validation continue to restrict industrial adoption [9,105].

3.3.3. Cycled storage-discharge (CSD)

Plasma catalytic oxidation is an alternative technology to oxidize a variety of VOCs at low temperature. However, the normal mode of plasma catalysis requires high energy cost and causes secondary pollution (NO_x, CO, CO_2) [107–109]. To overcome these limitations, a cycled storage-discharge (CSD) mode has been proposed. In the storage phase (plasma off), VOCs are adsorbed onto the catalyst or adsorbent surface; during the discharge phase (plasma on), the adsorbed VOCs are rapidly desorbed and simultaneously oxidized to CO_2 and H_2O by reactive plasma species.

In a recent work, Zhou et al. [110] developed an evaluation methodology for investigating reaction kinetics and intermediates during plasma oxidation of adsorbed toluene in the CSD mode. Thermal analyses, such as in situ temperature programmed desorption (TPD), have been used to determine surface species on HZSM-5 after O_2 plasma oxidation, in order to understand the mechanism of intermediates formation. The TPD experiment not only determined the unconverted toluene but also detected the evolution of CO and CO_2, suggesting both the desorption of adsorbed CO_x and decomposition of surface intermediates. Considering that the adsorption of CO_x on the material was negligible, the evolved CO_x in Fig. 7 likely originated from the decomposition of these surface intermediates. Formic acid and oxalic acid have been identified as the major intermediates through a mass spectrometer for online detection.

Despite its potential, the CSD mode remains in the early stages of research and development, with key challenges including the design of stable and selective catalysts, the optimization of catalyst-plasma interactions under realistic process conditions, and a limited mechanistic understanding of surface reactions [107]. All these aspects should be addressed to advance toward scalable and energy-efficient VOCs abatement.

3.4. Off-gas treatment strategies

Until now, attention has primarily been focused on the removal and control of VOCs through adsorption, with the main intent being the discussion of the regeneration of adsorbents saturated with VOCs. The goal has typically been to enable repeated use of the adsorbent, without much consideration for the off-gases generated during the regeneration step. However, in the context of circular economy and sustainability, further treatment of VOC-containing off-gas is essential before its final discharge. Despite this, limited attention has been paid to these aspects when investigating the regeneration of spent adsorbents.

Off-gas treatment technologies can be broadly divided into two

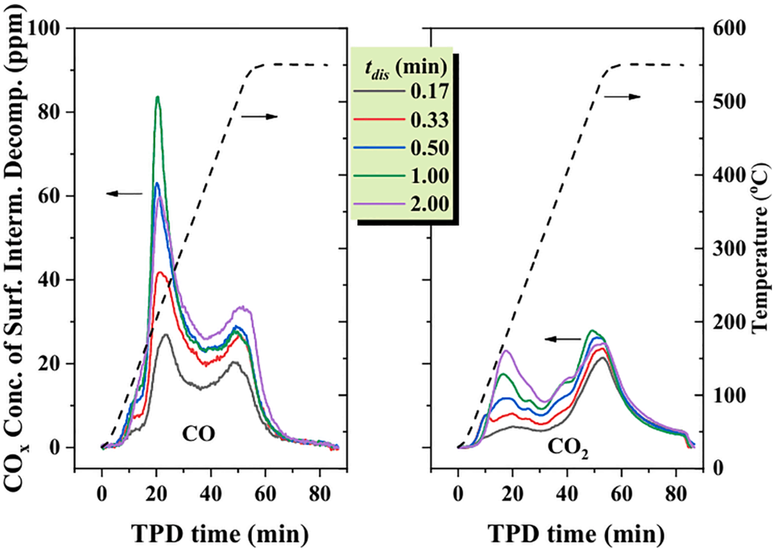

Fig. 7. CO$_x$ evolution of surface intermediates decomposition during TPD analysis for HZSM-5 during the discharge phase of plasma oxidation process in CSD mode. Reproduced with permission from [110].

Table 2
Principles, advantages, limitations, influencing parameters, and applicability ranges of VOC off-gas treatment methods.

Treatment	Operating principles	Advantages	Limitations	Main influencing parameters	Concentration range	Secondary pollution
RECOVERY METHODS						
Condensation	Cooling/compressing of gas stream to condense VOCs for recovery	Simple operation; high recovery purity for single gas mixture	Inefficient for dilute VOCs; possible azeotrope formation; high energy (low temperature/high pressure)	Temperature; pressure; VOC boiling point	High concentration; single or limited VOC mixtures	Liquid waste from condensate separation
Solid adsorption	Physisorption of VOCs on porous solids (activated carbon, zeolites)	High removal efficiency; low energy demand	Adsorbent saturation; sensitivity to humidity; regeneration costs	Humidity; adsorbent surface area and porosity; VOC polarity	Low-high concentration (depending on adsorbent regeneration)	Spent adsorbent or regeneration residues
Liquid absorption	VOC dissolution into a suitable absorbing liquid	Continuous operation; suitable for high flowrates; effective for soluble VOCs	Ineffective for poorly soluble VOCs or complex mixtures; absorbent replacement	VOC solubility; liquid/gas ratio; temperature; absorbent type	Moderate-high concentration (soluble VOCs)	Spent liquid absorbent requiring treatment
Membrane separation	Selective permeation of VOCs through membranes driven by pressure/ concentration gradients	Low energy consumption; no phase change	Membrane fouling; limited membrane lifespan; cost	Membrane selectivity; pressure gradient; VOC diffusivity	Low-moderate concentration; simple VOC mixtures	Minimal (membrane waste)
DESTRUCTIVE METHODS						
Thermal combustion	Oxidation of VOCs to CO_2 and H_2O at high temperature (700–1000 °C)	Very high efficiency; robust technology	Very high energy demand; not suitable for dilute VOCs; NOx formation possible	Temperature; residence time; VOC flammability	High concetration	Formation of NOx or incomplete combustion by-products
Catalytic combustion	Catalytic oxidation of VOCs at reduced temperatures (250–500 °C)	High efficiency; lower energy	Catalyst poisoning/ deactivation	Catalyst type; temperature; VOC flammability	Moderate-high concentration	Catalyst residues; minor by-products
Biodegradation	Microbial oxidation of VOCs into CO_2, H_2O, and biomass	Low operating cost; sustainable	Large reactor volume; slow microbial adaptation; ineffective for hydrophobic VOCs	Temperature; humidity; microbial activity; VOC solubility	Low concentration; biodegradable VOCs	Biomass requiring disposal
Photocatalytic oxidation	Generation of reactive radicals via light-activated photocatalysts to oxidize VOCs	Ambient temperature operation; no added chemicals	Low quantum efficiency; slow kinetics; light penetration limits	Light intensity; catalyst surface area; humidity	Low concentration, very dilute VOCs	Minimal
Low-temperature plasma	Electron-induced oxidation through energetic plasma-generated species	Rapid reactions; ambient temperature; no catalysts required	Equipment cost; formation of undesired by-products; electrical safety	Voltage; gas residence time; humidity	Low concentration	Ozone, NOx, oxygenated by-products

categories: destructive and recovery methods. A comprehensive comparison of these technologies, including their principles, advantages, limitations and applicability ranges, is presented in Table 2.

Recovery off-gas treatment technologies include condensation, solid adsorption, liquid absorption and membrane separation. As already mentioned in Section 3.1, this approach is already commercially applied in the case of steam stripping for solvent recovery. The recovery of valuable solvents can make the overall process economically advantageous. However, condensation and liquid absorption can be costly, particularly because off-gases usually contain complex mixtures of VOCs, making the recovery of single, pure compounds impractical [111]. For instance, in the case of steam regeneration, VOCs may form azeotropes with water vapor, making condensation inefficient and distillation complex. This, in turn, increases energy demands and reduces the feasibility of such separation processes.

Alternatively, destructive off-gas treatment technologies, such as thermal combustion, catalytic combustion, biodegradation, photocatalytic oxidation, and low-temperature plasma methods, aim to convert gaseous contaminants into H_2O, CO_2 and other non-toxic species through chemical or biological reactions. Thermal and catalytic combustion rely on the flammability of VOCs in the off-gas, which are oxidized (with or without a catalyst) into non-toxic compounds [112–114]. These methods are widely used due to their high efficiency and ability to handle high VOC concentrations. In particular, catalytic combustion allows oxidation at lower temperatures compared to thermal combustion, reducing energy consumption and minimizing the formation of secondary pollutants. However, both techniques require significant energy input and are less suitable for treating dilute VOC streams. Additionally, catalysts may suffer from deactivation due to poisoning or fouling by reaction by-products or particulates in the gas stream [112–114].

In contrast, photocatalytic oxidation uses a specific wavelength of light as an energy source and a semiconductor as a catalyst. Upon light irradiation, the catalyst generates electron-hole pairs that react with H_2O and O_2 in the off-gas to produce highly reactive species such as hydroxyl and superoxide radicals. These radicals can then oxidize a range of gaseous contaminants into less toxic compounds like H_2O and CO_2 [115–117]. Photocatalysis offers the potential for ambient temperature operation and the treatment of low-concentration VOCs, making it attractive for indoor air purification and dilute off-gas streams. However, practical implementation is often limited by low quantum efficiency of photocatalysts, slow degradation rates, and the need for effective light penetration and catalyst exposure [115,116, 118]. For example, Li et al. [118] studied the photocatalytic decomposition of formaldehyde and toluene under UV-light irradiation using a SnO_2 photocatalyst. They achieved nearly 60 % of decomposition efficiency after 1 hour of UV-light irradiation. Interestingly, when both compounds were treated as a mixture, a synergistic effect was observed, leading to improved decomposition efficiencies of 80 % for formaldehyde and 83 % for toluene. This highlights the potential of photocatalytic systems for treating complex VOC mixtures, although further development is needed to enhance efficiency under real-world conditions and scalable reactor designs.

4. Environmental impact and sustainability

The environmental sustainability of adsorption-desorption processes for VOC abatement is still poorly explored in the current literature. Most studies focus on materials performance or process efficiency, while the broader environmental implications linked to adsorbent manufacturing, operation, regeneration, and end-of-life management are often overlooked.

In this context, life cycle assessment (LCA), as defined in the ISO 14040 framework, offers a standardized method to quantify environmental impacts across all stages of a product or process, from raw material extraction to disposal. A clear definition of system boundaries, functional units, and impact categories is essential, as these elements shape how trade-offs are interpreted [119]. System boundaries typically range from *cradle-to-gate*, which includes production and use, to *cradle-to-grave*, where recycling and end-of-life are also considered [124]. Functional units must reflect the purpose of the assessment (e.g., removal of 1 kg of VOC during adsorption or desorption of 1 kg of VOC during regeneration), since this choice determines how different materials or processes are compared. Likewise, the selection of impact categories (e.g., global warming potential, cumulative energy demand, resource depletion) depends on the intended application and drives the identification of environmental hotspots [119].

Because LCA studies dedicated to gas-phase VOC adsorption are extremely limited, valuable insights can be drawn from LCA conducted on adsorbents used in water treatment, where methodological principles are directly transferable. Interestingly, LCA studies on composite nanoadsorbents for Cd removal [120] and on activated carbons derived from pine bark [121] consistently show that the major environmental burden is associated with the production phase (e.g., precursor preparation, activation, and other energy-intensive synthesis steps) rather than with the use phase. This observation could be highly relevant for VOC adsorbents as well, especially when high surface area carbons, engineered porous materials, or chemically modified adsorbents require substantial inputs of energy or reagents during manufacturing.

The scarcity of LCA data becomes even more evident when moving from adsorption to regeneration, despite the central role of regeneration in determining the overall environmental and economic viability of adsorption-based VOC abatement. Thermal swing adsorption (TSA) and pressure swing adsorption (PSA) are the most common regeneration strategies, yet systematic environmental assessments for VOC-saturated systems are still lacking. Nonetheless, useful insights can be drawn from LCA of TSA and PSA technologies applied in other contexts [122,123]. These studies consistently show that regeneration energy, electricity use, and system design (e.g., heating configuration, vacuum requirements, and bed geometry) strongly influence the overall environmental profile. For example, analyses of PSA units have shown that electricity consumption during operation is a dominant hotspot [123], while assessment studies of temperature-vacuum swing systems for CO_2 capture highlight how heat source, insulation, and opportunities for heat integration can drastically affect the environmental impact [122]. Although these studies target pollutants other than VOCs, they provide conceptual parallels directly applicable to VOC removal: beyond material choice, the architecture and operating mode of TSA or PSA units can substantially affect the environmental impact of the entire process.

A specific aspect of VOC abatement is the fate of the desorbed VOC stream. Depending on the strategy adopted, whether the VOC is recovered, reused, or thermally destroyed, the environmental impact of regeneration may shift significantly, turning what would be an additional burden into a potential opportunity for resource recovery when valuable VOCs are present. For this reason, defining how desorbed VOCs are managed is a key consideration when establishing system boundaries and functional units in future LCA studies.

In summary, these examples underscore the need for dedicated LCA and techno-economic (TEA) studies on VOC adsorption technologies. Integrating life-cycle considerations into VOC abatement requires a clear definition of the assessment scope, careful selection of relevant impact categories, and transparent reporting of system boundaries. Even though current studies on gas-phase systems remain scarce, existing LCA works on aqueous adsorbents and on PSA/TSA systems in other fields indicate that the main hotspots often lie outside the adsorption step itself; instead, they typically arise from adsorbent production and regeneration energy requirements. These insights provide a valuable basis for developing standardized LCA guidelines for VOC-oriented adsorption technologies and for supporting the design of systems that are not only effective but also environmentally and economically sustainable.

5. Conclusions and perspectives

The regeneration of VOC-saturated adsorbents remains a critical aspect for the sustainable use of adsorption technologies, as it directly influences both operational efficiency and environmental impact. Based on the analyses presented in this review, several key considerations emerge and are summarized below:

- The regeneration techniques and characterization methods discussed throughout this review, while primarily applied to VOC-saturated adsorbents, offer valuable insights for broader applications, including gas-phase adsorbents targeting other pollutants and liquid-phase systems.
- The high variability of adsorbent materials and VOCs makes direct comparisons between regeneration methods challenging, highlighting the importance of case-specific strategies. In this context, thermal analyses (TGA, TPD, DSC) are essential tools to determine optimal regeneration conditions, minimize heel formation, and preserve adsorbent performance over multiple cycles. Notably, TGA can provide insights into the mechanisms of heel formation, helping to identify the fraction of strongly adsorbed or thermally resistant species that may accumulate during repeated regeneration cycles.
- Thermal desorption is generally preferred for thermally stable adsorbents and VOCs with low boiling points. In such cases, selecting appropriate operational parameters (e.g., heating time and temperature, or the nature of the carrier gas) is crucial, as insufficient or overly severe conditions can promote heel accumulation and ultimately reduce adsorption capacity during successive cycles.
- Steam stripping is particularly suitable for VOCs that are poorly soluble in water and can be separated from the aqueous phase by decantation. This method enables effective recovery of solvents while minimizing thermal stress on the adsorbent, making it an attractive option when solvent recovery is a priority.
- Gasification is justified when it is necessary to eliminate carbonaceous residues (coke or heel) and simultaneously decompose hazardous organic compounds. This approach requires very high temperatures (typically 800–900 °C) and is therefore limited to thermally stable adsorbents.
- At present, commercial-scale regeneration is often implemented only when recovery of the adsorbed species is economically viable. In many other cases, adsorbents are still discarded after saturation, generating off-gases that require proper treatment. Systematically integrating regeneration with off-gas management is therefore critical to reduce environmental impacts and promote more sustainable practices.
- Finally, the lack of comparative life cycle assessment (LCA) studies for different regeneration techniques and gas-phase adsorbents represents a significant research gap. Future work should adopt cradle-to-grave system boundaries, explicitly considering the fate of the recovered solvent, whether it is reused, recycled, or disposed of, in order to provide a complete picture of environmental impacts. In addition, economic analyses comparing the energy consumption, operational costs, and overall feasibility of different regeneration strategies for VOC adsorbents are still insufficiently explored, highlighting the need for dedicated future studies. Addressing these gaps is essential to support the development of a circular and responsible use of adsorbents, ensuring that regeneration strategies are effective, economically feasible, and environmentally sound.

CRediT authorship contribution statement

Tiziana Avola: Writing – original draft, Visualization, Investigation. **Giuseppe Cavallaro:** Writing – review & editing, Validation, Funding acquisition. **Maria Vittoria Diamanti:** Writing – review & editing, Validation, Funding acquisition, Conceptualization. **Daniela Meroni:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

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

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Data availability

No data was used for the research described in the article.

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