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REVIEW PAPER

Pressure Swing Adsorption Based Air Filtration/Purification Systems for NBC Collective Protection

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ABSTRACT

The respiratory protection against chemical warfare agents (CWA) has become a worldwide security concern in light of the many recent international threats utilising CWA. Till date the carbon filtration was adequate to protect the soldiers from the threats of CWA. With the advent of further advancements in the CWA a new threat is looming large that is known as the carbon breakers. pressure swing adsorption (PSA) is a well-established gas separation technique in air separation, gas drying, and hydrogen purification separation. Recently, PSA technology has been applied in the area of chem-bio defence by virtue of its unique advantages. This article reviews recent advances and developments in the field of PSA based purification, separation, and its use in defense sector. This emerging and advanced PSA technology can provide regenerative nuclear, biological and chemical (NBC) collective protection for ground vehicles, aircraft, ships and shelters. This PSA technology challenges threat scenario developed which includes nerve, blood and blister agents, as well as a "carbon breaker" agent, and proved that this technology will be a viable concept for future NBC collective protection systems. New technological breakthroughs and greater sophistication of PSA technologies will transform the collective protection based PSA technology in real field sense, addressing the escalating threat of CWA. We conclude this review with future prospects and challenges associated with PSA technology.

Keywords*:* Adsorption, environmental protection, PSA, chemical warfare agent, activated carbon

1. INTRODUCTION

Air is an irreplaceable source of oxygen needed for respiration by a human being and the requirement of breathable air is very critical in war field condition in order to combat terrorism and is one of the most challenging requirements for security monitoring[1-3]. The continuous threat of chemical warfare agent (CWA) accidently or intentionally by enemy nation or terrorist group has led to a urgent gush of research in the area of protection to combat terrorism and as to provide a proper medical protection[1-3]. Time and again history witnessed the contamination of the air with the toxic gases either intentionally or accidently. CWA have been abused as weapon of mass destruction (WMD) since WWI, and its deliberate use continues till date[1-3]. In CWA scenario, the early detection and protection will be highly beneficial to combat terrorism. To counteract the adverse effect of CWA proper protective measures such as NBC individual protective equipment IPE should be taken. In general, the area of protection is very vast and can be technically classified in to 3 categories namely individual protection, collective protection and medical protection. The individual protection deals with the protection of individual by using over garment, mask, hood, over boots, protective gloves, individual decontamination kits, and antidotes with the instrument such as detectors. The protection of large number of personnel, food, water, and other supplies are dealt in collective protection. In collective protection, each shelter is fitted with filters to provide uncontaminated air for the occupants, while in medical protection, antidotes and medicines are required for treatment of casualties.

The activated carbon met with outstanding success in purification of contaminated atmosphere and it removes the toxic gases from the contaminated air and water streams, by physisorption and chemisorption. Therefore, it has become the primary defense against the threat of a chemical warfare attack[4-9]. Different impregnants mainly in form of metal salts have been added to the activated carbon to increase its sorption capacity and at the same time for *in-situ* degradation of CWA[4-9]. However, the service life of these filtration systems is limited due to the limited quantity of impregnated carbon and moisture sensitivity[10-11]. Quantity of impregnated carbon in filtration systems as well as quantity of impregnant in carbons is limited due to place constraints in filters and carbon as area available is limited[10]. In contrast, the filter needs to be replaced frequently even without exposing to the CWA, which leads to an unnecessary logistic and economic burden as filter replacement significantly increases the operational cost of the system. Furthermore, the disposal of exhausted filters further poses an environmental risk which needs to be addressed more elegantly. Moreover, the adsorption and catalytic capacity of the impregnated carbons decreases during storage and use, therefore they should be replaced at certain time intervals[10,12],

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which restricts its applicability for a longer duration. Hence, there are urgent needs to develop a re-generable system for chem-bio threats to address the limitations and drawbacks of presently available filtration system.

The advantages of the self-regenerating filter equipment are that it can be used for a long time because of the regeneration which significantly reduces the required logistics capacity[13-15]. The other major advantage is that this filter provides protection also against toxic industrial chemicals[13-15]. Self-regenerating equipment uses physical adsorption and operates on the principle of pressure swing adsorption (PSA)[13-15]. In last few decades, there has been a considerable increase in the applications of adsorptive gas separation technologies, based on PSA[13-15]. PSA is a versatile technology for separation and purification of gas mixtures[13-16], in this, the total pressure of the system 'swings' between high pressure in feed and low pressure in regeneration[17-19]. The advent of commercial PSA operations started with the early patents but its first application was offered later[20]. Since then, PSA has become the state-of-the-art separation technology for large variety of applications like air fractionation and hydrogen production[21-24]. The PSA processes are much more efficient in separation and are also associated to low energy consumption when compared to other technologies because only stepped changes in pressure are required[25]. Due to its outstanding capability and versatility, this PSA technology has been extended for the use in NBC filtration system for increased and extending protection against CWA. Self-regenerative filtration systems can provide the continuos protection to the user for an indefinite period of time, without changing filter. PSA system makes use of cyclic adsorption-desorption process which can be used in regenerative filtration systems to increase service life of system against CWA.

This article reviews documented current and developing PSA technologies, its types and their application in defence and highlights the opportunities and challenges of this important field. Particular attention has been given to PSA technology for defence sector. The PSA systems was described which possess a universality of physical adsorption of NBC agents and yet have full regeneration capability. The aim of this review is to educate the defence community about the opportunities and the potential use of PSA technologies for various applications in defence, security and industry sector. Due to its greater flexibility in term of compactness, reliability and energy efficiency, PSA systems can be routinely operated on a continuous basis for full NBC protection of military facilities and vehicles.

2. HISTORY OF PSA PROCESS

The introduction of PSA processes is introduced in 1957-1958 by the pioneer work of Skarstrom[26-28]. After the Skarstrom cycle in 1960, PSA technology has gained the rapid pace and entered into some major technology such as air drying, hydrogen purification, n-paraffin removal, and air fractionation[26]. After the landmark achievements of PSA technology other technology such as, temperature swing adsorption (TSA), and simulated moving bed (SMB) processes have made rapid progress during the 1980s, which are now widely available and are routinely used in the development and optimisation of adsorption processes[29-30]. The 1990s have seen documented for the adsorptive removal of contaminants such as volatile organic compounds (VOCs) from air and for desiccant cooling systems using PSA technology[31-35]. To miniaturise an adsorption process of PSA, one has to reduce the adsorption cycle time, by using this PSA processes can be established for few seconds adsorption cycle times. PSA has undergone rapid changes as the technology of separation processes advanced with the passage of time. Some other key date in chronological development of PSA technologies are summarised in Table 1. Nowadays, PSA processes are widely used on a very large scale for a variety of gas separations. In particular, environmental and defense applications of PSA technology proves major potential for growth.

Table 1. Chronological order for the historical development of PSA processes

Date	Milestone Achieved
1930-1933	First PSA patents issued to Finlayson and Sharp
1953-1954	First research article on principle of PSA and its applications for removal of CO_2, hydrocarbon and water vapor
1957-1958	Vacuum swing PSA cycle and low purge step is introduced
1959-1970	Development and commercialization of PSA
1970-1973	O_2 PSA processes
1976	N_2 PSA processes
1982	Large scale vacuum swing process for air separation
1988	Second generation zeolite adsorbents for air separation
1990	Removal of trace levels of contaminants such as VOCs from air and for desiccant cooling systems
2000-2013	Improvement in term of PSA capacity; the first (twin) 2x14-bed PSA system

3. THE PROCESS OF PSA

PSA is a very versatile technology for separation and purification of gas mixtures. A pressure swing may be defined as the change in pressure associated with an adsorption cycle[37]. For example, many PSA systems have a pressure swing from some positive pressure (above atmospheric pressure) to a lower pressure, for example, atmospheric pressure. The force acting between the gas molecules and the adsorbent molecule depends on many parameters such as gas component, type of adsorbent material, partial pressure of the gas component and operating temperature. Based on the adsorbed species characteristics and affinity with an adsorbent material the PSA process used to separate the desired gas species from a mixture of gases under applied pressure. Generally at a fixed time, PSA processes usually include at least two columns of adsorbent, one column is being regenerated, and other is in the adsorption phase (Fig.1). Thus, by swinging the pressure, product gas is delivered constantly[38].

Thus PSA process has a pressure swing from positive pressure to lower pressure or vice versa. At positive pressure (above atmospheric pressure), gas adsorb more while at

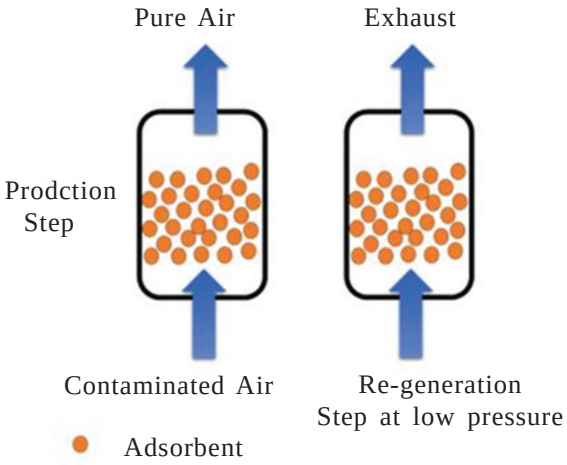

Figure 1. Schematic of the PSA technology: Air purification process.

lower pressure gas desorbed. Due to this pressure swing, PSA processes used to separate gaseous mixture different gases as the attractive forces for each gases toward the solid surfaces are different.

To understand design and operation of PSA process, some important terminology such as adsorption, desorption, and a multitude of complementary steps need to be understood, which are designed to control the product gas purity and recovery and to optimize the overall separation performance. The overall performance of a PSA depends on both equilibrium and kinetic factors, however, the importance of these interdependent parameters varies significantly for different system[39]. The majority of PSA processes are 'equilibrium driven' and some are the kinetic driven. In case of equilibrium driven process the selectivity depends on the differences in the equilibrium affinities. While in kinetic driven process the separation depends on differences in adsorption rate rather than on differences in equilibrium affinity.

3.1 Basic Scheme of PSA Process

Conventional PSA system utilize multiple vessels, connected well through a piping and valves to switch the gas flow one to other while environmental PSA processes utilize a twin bed system with a Skarstrom-type cycle[13]. A typical PSA system consist of four basic steps in a cyclic manner starting from: production, depressurising, purging and finally repressurising. The first step involve a feeding of gas mixture into a adsorbent containing vessel under high pressure. When one bed undergoes adsorption the other bed is purged, and while one bed undergoes repressurisation the other bed is depressurised[37]. In this way, the beds operate 180 degree out of phase with each other. Impurities of feed gaseous mixture PSA system provide a purified product gas through the vessel and it can be withdrawn at under pressure from the top of the vessel. During the blow down step, the pressure in the adsorption vessel is then reduced by withdrawing gas through the feed end of the bed and product gas remaining in the void spaces of the vessel is removed (as shown in Fig. 2). While regenerating the adsorbent bed, the adsorbed unwanted impurities are goes back into the gas phase. During the purge step, the vessel

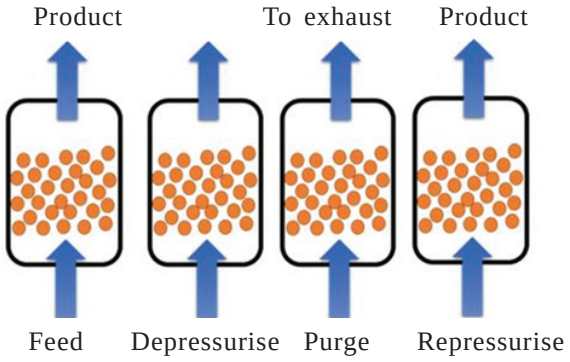

Figure 2. Schematic of the PSA technology showing the cyclic repetition of four basic steps.

is purged with a small amount of purified product gas, to complete regeneration of the adsorbent bed. Impurities exit the PSA process in a low-pressure exhaust stream. Finally, the vessel is repressurised with a mixture of product gas from the depressurisation step, feed gas and high-purity product gas (as shown in Fig. 2). Once the bed reaches the high pressure, feeding commences to begin a new adsorption step and thus it completes its cycle.

3.2 The Process of Adsorption, Absorption and Adsorbents

Adsorption is the surface phenomena which occur on the surface of a material. In this process, a gas molecule near a solid surface interacts with the molecule or atom in the solid which leads to reduction in potential energy and leads to the concentration of gas molecule in the vicinity of solid surface in the form of adsorbate film[40]. The strength of the surface forces depends on the nature of both the solid and the sorbate. Depending on the force involved between adsorbate and adsorbent the adsorption process again classified as physisorption and chemisorption. In physisorption, the bonding forces are relatively weak involving vander Wall interaction or electrostactic interaction. While in chemisorption, the interaction forces are strong involving a significant degree of electron transfer. Chemisorption is limited to a monolayer, whereas, in physical adsorption, it is multilayer. Mostly PSA process involves physical adsorption.

3.3 Adsorbents for PSA

In PSA system, porous material having a high surface are widely used. Mainly activated carbon, silica gel, molecular sieve carbon, molecular sieve zeolite, alumina and polymeric adsorbents are used as adsorbents[13]. Each adsorbent material has its own characteristics and advantages such as porosity, pore structure and nature of its adsorbing surfaces[13]. In PSA system, usually very porous materials are chosen as adsorbent because of their large surface area. Typical adsorbents are activated carbon, alumina, silica gel, and zeolite. Silica gel and zeolites are typically hydrophilic and polar adsorbent. Carbon based adsorbent such as activated carbon and graphits is hydrophobic and non-polar. While polymer based adsorbents are polar and non-polar depending on functional group present on matrix. In case of activated carbon, the effect of moisture is

less as it is hydrophobic and without requiring prior stringent moisture removal, PSA process can be used for separation and purification purposes. However, of alumina, silica gel and zeolite are hydrophilic in nature, so before performing PSA process, moisture should be removed for efficient separation and purification. By heating silica get at around 150 ºC regeneration can be achieved and it can be used further. While for zeolite regeneration temperature goes to 350 °C. Table 2 provides a perspective of the adsorbent used and the major gas separations performed in industry.

Table 2. List of various adsorbent materials used in gas separation

Adsorbent	Major uses
Activated carbon	Air purification in PSA, removal of nonpolar gases and organic vapors. Extensively used in NBC protection to make canister, filter and suit.
Zeolite: Synthetic and Natural	Air purification, drying, H_2 purification, air separation, gas chromatography
Silica gel	Gas chromatography, drying, refrigerants, dew point control of natural gas.
Activated alumina	Gas chromatography, drying

4. CLASSIFICATION OF PTSA TECHNOLOGY

PSA process can be categorised according to the nature of adsorption (equilibrium or kinetics) and types of interaction of adsorbed species. PSA adsorption technique involves the physical interaction of gas molecule with the adsorbent and it depends on the partial pressure of a gas and the operating temperature. Based on the principle of adsorption and its regeneration principle, adsorption separation processes are designed to operate in a cyclic manner. Usually following two types of separation processes are used for separating components from gaseous mixture[13].

4.1 Temperature Swing Adsorption

In this technique separation of a mixed gas is achieved by repeating adsorption at a lower temperature and desorption at a higher temperature[36,37]. In this process, an increase in temperature at fixed partial pressure leads to desorb the adsorbate from the adsorbent packed bed. A relatively modest increase in temperature can affect a relatively large decrease in loading. This adsorption process take a longer time than the PSA process because of a low heat transfer due to poor thermal conduction in the adsorbent packed bed.

4.2 Pressure Swing Adsorption

In this process, separation of a mixed gas is achieved by swinging the pressure from positive to lower pressure or vice versa. In this case, the time for desorption and adsorption is of the same order of magnitude. Due to this, PSA process has shorter cycle time with more productivity compared to TSA. In case of PSA, the pressure can be changed more rapidly than the temperature as in case of TSA, which is one of the major advantage of this technique. The majority of PSA processes are 'equilibrium driven' in the sense that the selectivity depends on differences in the equilibrium affinities.

Apart from PSA and TSA technologies, another technology namely concentration swing adsorption (CSA) is widely utilised when the free fluid phase is a liquid. Such aforementioned processes (PSA, TSA and CSA) are collectively called as periodic adsorption processes.

5. PERFORMANCE INDICATORS PARAMETERS OF PSA PROCESS

The performance of PSA process is measured by three parameters (1) product purity (2) product recovery and (3) adsorbent productivity[13, 37]. All three performance indicators are related to the separation efficiency of the PSA. The effluent concentration and flow rate of PSA process vary with time; hence the product purity is a volume averaged quantity. While product recovery is the ratio of the amount of component in the product stream and in feed mixture. Adsorbent productivity is the amount of product per unit amount of sorbent per time. Product recovery and productivity have an integral term that is mainly due to variations in flow rate in the exit streams. For a particular separation, the product purity is predetermined, as recovery is proportional to the energy requirement and sorbent productivity is inversely proportional to the amount of sorbent bed. Most works on PSA processes have shown that normally the purity and recovery present a trade-off for the design. In the case of recovering the less adsorbed gas, if more purges is used, more of the contaminants can be desorbed from the column and purity increases, but since more light gas is exiting from the 'bottom end', light-gas recovery is smaller.

5.1 Air Liquefaction and Separation

Air is a mixture of various gases. Atmospheric air mainly contains 78 per cent nitrogen, 21 per cent oxygen, and rest of other gases by volume. The cryogenic separation of air involves liquefaction followed by distillation. In order to separate single component from the air, different methods are available apart from cryogenic method, such as membrane separation, PSA and vacuum pressure swing adsorption. For small scale production of purified gas such as oxygen production, membrane separation technologies are more commonly used while for large scale production of oxygen cryogenic plants are required. When compared to other method, a lower pressure or vacuum is used to desorb the adsorbent bed and PSA cycle can be operating close to isothermal condition, for these reason PSA cycle is attractive to bulk separation operations. A low temperature and a high pressure are required for liquefaction. One advantage of this process is to use gas compression as the main source of energy. The PSA processes are normally associated to low energy and cost effective when compared to other technologies for which gas are separated easily. The principal disadvantage of the PSA cycle is high gas loss resulting from the pressure release during desorption.

6. APPLICATIONS OF PSA TECHNOLOGY IN DEFENCE INDUSTRY

Considering the urgency of the situation the CWA may cause, combatant, therefore, needs adequate protective measures for easiness of operation and ability to protect themselves

against these agents in real war field conditions. In light of NBC threat, especially for respiratory protection, activated carbon based system was widely used in canister, filters, ships and tanks for providing respiratory protection against these CWA. In case of respiratory protection, particularly canister contains two components one is particulate filter and another is gas filter and its performance mainly depends on the particulate and gas filters. A commonly used particulate filter is the high efficiency particulate aerosol filter media. For collective protection same formulation has been used in many filters, however, they show serious limitations. In general, the filters used in tank and ships are nonregenerable, the impregnated carbon must be replaced at regular intervals of time which represents a significant logistics support problem. Moreover, the impregnated carbon beds are easily contaminated and can be rendered non-effective even under non-combat conditions. Moisture and heat can adversely affect the carbon impregnants, and normal atmospheric contaminants such as hydrocarbon vapours and exhaust fumes can poison the sorbent beds prior to a chemical warfare attack. Due to the above mentioned shortcomings and technological advancement in the properties of CWA, there is urgent requirement of respiratory protection system which can provide breathable air for a longer duration and it is easily regenerable to promote timely medical treatment and effective CWA decontamination to reduce the mortality rate. PSA is a very versatile technology for separation and purification of gas mixtures. The PSA technology was widely used in large variety of application such as hydrogen purification[41-43], CO_2 capture[44-45], methane[46], toxic gas H_2S removal[47-48], noble gas purification[49], etc.

Due to its outstanding capabilities, PSA technologies have been found to be more effective against CWA in terms of time duration, regenerability, and avoid the unnecessary logistic and economic burden for the filter operation. Verrnando[10], *et al.* developed a PSA system for NBC collective protection using 13X molecular sieve. In that work, two system has been used; one system is for supplying purified air to a shelter and another system to fed the purified air to a pressure-swing oxygen concentration using type 5A molecular sieve[10]. On the other hand H_2S removal was achieved using selective metal organic frame work PSA[50]. The advantage of using a PSA system in NBC scenario is that it provides an adsorption system that can be routinely operated on a continuous basis for full NBC protection of critical military command posts, medical facilities, pilot ready rooms, operating shelters, and military vehicles, thereby reducing the impact of surprise attacks and sabotage with a reasonably compact, energy-efficient, and highly reliable manner. Briefly, an NBC collective protective system includes a PSA system based on an activated or impregnated carbon filter which adsorbs a wide range of NBC agents and is capable of complete regeneration over a prolonged service life. Furthermore, when PSA system is integrated with environmental control system, it provides the air which is not only free of chemical contaminants, but is also temperature controlled. The collective protection technology-based research should be directed in such a way that it must give protection against current threats and also it should add protection against future threats. At the same it should reduce logistical burdens by developing advance material based filtration system with longer useable lifetimes. Collective protection efforts should focus on following points:

(a) Improvements or modification in current adsorptive materials,
(b) Advanced non-reactive filtration processes,
(c) Advanced reactive filtration system,
(d) Regenerable filtration system for NBC protection of military vehicles, aircraft, ships, shelters, and buildings, and
(e) Reduced logistics burden along with longer usable lifetimes.

PSA systems are particularly well suited for installations requiring prolonged, high quality protection such as in continuous-use shelters and provides protection over a long period of time. In CWA scenario, particularly in protection field the aim is to counter the threat of chemical and biological weapons, and to ensure the safety of soldiers in a contaminated environment. Two types of regenerative filtration systems, TSA and TSA-based regenerative filtration system have been extensively studied for CWA applications and it have been evaluated at the prototype level. Since PSA and TSA filtration system works on different principle, hence the design requirements of the system is greatly different. However, both the system rely on adsorption and regeneration steps. In order to design and develop the system as per user requirement, the design should be tailor made to integrate regenerative air purification system. Some time, the optimum design of regenerative filtration system is contrary to expectation. For example, by increasing the amount of adsorbent, increased adsorption capacity cannot be achieved as equal attentiveness must be given to select adsorbent material and type of gas which need to be separate for achieving rapid/efficient regeneration.

7. OUTLOOK, PROSPECTS, AND CHALLENGES

This review article has reviewed the application of PSA system for respiratory protection against CWA threats in the shelters, tanks, ships, etc. This review has attempted to summarise the literature on the recent progress made in the development of PSA based filtration system for protection against WMD and has discussed key requirements and challenges in this important area are like natural gas up-gradation and its separation (CH_4-CO_2 separation). A considerable research efforts are required to make a highly efficient collective protection system in order to have compliance with the standards of respiratory protection and still, we need to develop PSA system capable of providing continuous breathable air in shelters and can be routinely operated on a continuous basis for full NBC protection of military facilities and vehicles. Although the great flexibility of PSA processes still constitutes its main advantage and is one of the reason for its diversity. However, process complexity is still one of the major issues to introduce this technology in defence sector. PSA technology can be considered a mature technology in air separation, drying, and hydrogen purification, but there is plenty of work to be done to establish this technique in NBC field. The PSA technology is still at the infancy stage as this lab based technology is not translated to the product for the CWA protection, though more research have been done in

this field along with many research paper. Several aspect of PSA technology need to be addressed before translating the lab based PSA technology to real field NBC shelters. Nowadays PSA units are well controlled by microprocessor which gives more flexibility of operation and precise control over the functions. Moreover, future endeavors must be concerned with the development of light weight, in-situ decontaminable PSA based system which can provide protection against all type of CWA including carbon breakers. This would enable the first responder to provide adequate comfort zone to take rapid decision for the remediation, decontamination and proper medical treatment. Despite the large number of papers published in this field of PSA system, and its widespread use in industry for many years, the commercialisation of PSA in defence technology, particularly in India is still at infancy stage, considerable research efforts are still required to enhance the regenerative PSA technique capabilities so that we can translate this unprecedented technology from bench to the real field conditions.

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