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Review Article

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A comprehensive review on removal of VOCs from air using fly ash as an adsorbent

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ABSTRACT

Volatile Organic Compounds (VOCs) play a critical role in the atmosphere and are produced from biogenic and anthropogenic sources. These chemicals have serious health consequences for humans. Among many types of industrial waste available, Coal Fly Ash (CFA) are mostly produced by coal-fired power plants with the ability to capture VOCs from the air. The use of an inexpensive, high-performance electrospun nanofiber membrane to filter out airborne impurities. Adsorption is thought to be the best approach out of all of them due to its convenience, ease of usage, and easy-to-understand design. This review article covers the procedure, and environmental effects of employing fly ash for the adsorption of VOCs. The main concerns with fly ash disposal are the need for massive land areas for landfills and the harmful effects and groundwater pollution caused by the accumulation of heavy metals. Additionally, the methods for overcoming the benefits of using fly ash are also examined.

Introduction

Air pollution poses a massive threat to humans as well as the environment. Heavy metals like phosphorus, fluoride, boron, phenolic chemicals, and dyes, as well as pollutants like Nitrogen Oxides (NOx), Volatile Organic Compounds (VOCs), and Sulfur dioxide (SO_2), are some commonly identified pollutants found in both outdoor as well as the indoor environment. The key source of concern for scientists in this century is how successfully pollution can be controlled and reduced [1]. Air pollutants are major contributors to human diseases and have particularly negative effects on the respiratory system. Ozone can also have an impact on the respiratory and cardiovascular systems [2].

Fly Ash (FA) is a type of industrial waste that can

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be emitted into the atmosphere and be able to harm the ecosystem in numerous ways. However, FA can also be employed as an inexpensive, highly effective adsorbent for treating environmental pollutants due to its large porosity, wide specific area of the surface, and other distinctive properties [1]. Fly ash exhibits a significant capacity to adsorb air and water contaminants, including toxic organic dyes, heavy metals, SOx, NOx, and VOCs. In 2014, Bhattacharyya et al. established that FA can be employed as an adsorbent in conjunction with a plasma reactor to mitigate NOx emissions from biodiesel engines [3]. Hower et al. have shown that FA carbon is highly efficient in capturing mercury [4]. According to studies by other researchers, with very simple modifications, FA is an effective adsorbent of Sulphur dioxide (SO_2) [5] and VOCs [6].

Organic substances with high vapors pressure and a low boiling point are known as VOCs. They are one of the most common air pollutants, mostly produced by petroleum refineries, fossil fuel combustion, chemical industries, motor vehicles, paint, and building materials areas [7]. It is possible to identify certain naturally occurring VOCs sources originate from biogenic sources of land and ocean environment in addition to anthropogenic sources [8]. Benzene, xylene and toluene are some examples of VOCs that are damaging to both the health of humans and the environment. Aldehydes (RCHO), aromatic chemicals, and Polycyclic Aromatic Hydrocarbons (PAHs) are common yet very hazardous and cancer-causing VOCs [9, 10]. They may increase the number of respiratory conditions and raise the risk of cell cancer [11]. In the troposphere, some VOCs interact photochemically with SO_2 and Oxides of Nitrogen (NOx) to produce Ozone (O_3) and photochemical pollution, which contributes to the thinning of the stratospheric ozone layer and the development of the Antarctic Ozone Hole (AOH) [12, 13]. VOCs must, therefore be under control and reduced in the air. One of the most efficient strategies for mitigating VOCs in this industry is to reduce the use of fuels in transportation for the improvement of vehicles generated by electric-powered or cars that use other alternate fuels [14, 15]. Numerous studies have shown that the amount of VOCs produced by the combustion of biodiesel fuel combined with gasoline is significantly lower than that produced by the combustion of clean diesel fuel [16, 17]. Other methods, such as burning, membrane separation, absorption, catalytic oxidation, adsorption, biodegradation, and other post-processing management techniques have been used to reduce VOCs in addition to using less conventional fuel or switching to alternate fuels [8]. The adsorption approach is the most practical and cost-efficient way to lower and regulate VOC emissions into the air [18, 19]. Coal-fired power facilities produce Coal Fly Ash (CFA), which is a waste product. Without proper handling of direct discharge, CFA, which is an environmental hazard, will result in significant air and water pollution [20]. Electrospinning has generated a lot of interest as an efficient and affordable approach for reuse CFA to fabricate several functional fibrous film from CFA [21]. CFA effectively transforms industrial waste into a multipurpose and high-value material, it is an environmentally responsible method of manufacturing. Electrospun fibrous film may be used in a diversity of filter applications to remove air contaminant and show great probable for use in controlling contaminant. This article proceeds with a short summary of the different properties of coal-based fly ash including bituminous, sub-bituminous, and lignite coals. This study's objective is to outline some recent developments in processing techniques used to retrieve usable components from coal-based fly ash and to investigate their prospective uses.

VOCs' roles in the atmosphere

VOCs, which are major troposphere constituents, are released by both biogenic and anthropogenic sources [22]. VOCs include alkanes, carbonyl, alkenes, esters, organic acids, aromatic hydrocarbons, and alcohols. VOCs are important contributors to photochemical smog, and some of their gas-phase products, such as isoprene, terpenes, and aromatics, can subsidize to the formation of Secondary Organic Aerosol (SOA) [23-25]. VOCs have the potential to undergo photolysis or engage in reactions with atmospheric Oxidants, including Hydroxyl (OH), Nitrate (NO_3), and O_3 molecules. Following the given below reactions (Eq. 1 to Eq. 8) involving O_2 and nitrogen oxides can result in the formation of new oxidants, such as HO_2, RO_2, RO radicals, peroxides, and new VOCs [26].

$$VOCs \xrightarrow{OH/NO_3/O_3/hv} R^{\bullet}[H^{\bullet}] \tag{1}$$

$$R^{\bullet}[H^{\bullet}] \xrightarrow{O_2} RO_2^{\bullet}(HO_2^{\bullet}) \tag{2}$$

$$RO_2^{\bullet}(HO_2^{\bullet}) \xrightarrow{HO_2^{\bullet}} ROOH\ (H_2O_2) \tag{3}$$

$$RO_2^{\bullet}(HO_2^{\bullet}) \underset{}{\overset{NO_2}{\rightleftarrows}} ROONO_2 \tag{4}$$

$$RO_2^{\bullet}(HO_2^{\bullet}) \xrightarrow{NO_2 \;\; h\nu\; O_3 \;\; NO} RO^{\bullet}(HO^{\bullet}) \tag{5}$$

$$RO_2^{\bullet} \xrightarrow{RO_2} R'O + ROH \tag{6}$$

$$RO^{\bullet}(HO^{\bullet}) \xrightarrow{NO_2} HNO_3 \tag{7}$$

$$RCHO/O_3 \xrightarrow{hv} RO^{\bullet}(HO^{\bullet}) \tag{8}$$

VOCs control techniques

There are numerous ways available for reducing VOC emissions. These approaches are broadly divided into two categories: (1) process and equipment change; (2) add-on-control approaches. Control of VOC emissions is achieved in the first group by modify procedure tools and raw materials or changing the procedure but in the second group another control mechanism is required to manage emissions [27].

Process and equipment changes

Process and equipment changes are typically favored option for decrease emissions. Modifications contain raw material replacement to minimize VOC input to the method, modifications in operating situation for reducing VOC generation or volatilization, and equipment modification to decrease possibility for VOC get away into the surroundings. Modification tools can take various forms, but the aim is always to stop VOCs from escaping. VOCs are able to produce from open vessel tops or leaks at flange or they might be caused by method condition. Monitor and renovate approach can be establish to frequently prevent discharge caused by pumps, leaks from valves and procedure pipe connector. In addition, process enclosures can be developed to reduce emissions. A useful mechanism for collect emission can be given by enclosing the source. However, simply enhancing an enclosure is insufficient to reduce emissions. Pollutants will eventually escape into the environment if emissions are collected in enclosures but no other safeguards are implemented. End-of-pipe solutions are typically used to manage this scenario [28-30].

Add-on-control approaches

Add-on control approaches are generally classified into two types: destruction and recovery, with more information provided in the following sections [27].

VOC destruction techniques

Thermal oxidation

Technology of thermal oxidation be capable of achieve 95-99% elimination efficiency of VOCs and it has the potential for energy recovery. The concentration range that is appropriate 100 to 2000 mg/L. The average residence duration is between 0.5 and 1.0 s. The operating temperatures vary from 1300 to 1800 degrees Fahrenheit. The combustion products, mainly those containing halogenated VOCs, need further treatment [27].

Catalytic oxidation

Similar to thermal oxidizers, catalytic oxidation systems directly burn volatile organic compounds. Catalytic oxidation systems perform at lower temperatures, usually between 700 and 900 degrees Fahrenheit. This process can be able to achieve 90–98% efficiency, with the potential for up to 70% energy recovery; on the other hand, certain combustion products can reduce catalytic activity [31].

Bio-filtration

For the removal of VOCs from polluted gases, biofiltration is a type of biological treatment. Biofiltration has an efficiency range of 60-95%. Control efficiency from 90 to 99% have been documented for compounds produced during the palletized polymer manufacturing process. In industrial settings, biofilters have been successfully tested and commercially set up to eliminate solvent VOCs such as ethanol and toluene [32-34].

VOC recovery techniques

VOC recovery methods, including condensation, absorption, adsorption, and membrane separation.

Condensation

Condensation is most capable for VOCs with a boiling point of more than 100°F and concentrations greater than 5000 ppm. Efficiencies ranging up to 70-85% are possible [25].

Absorption

VOCs are removed from gas streams through absorption, which involves coming into contact with polluted air and a liquid solvent. Soluble VOC will move into the liquid phase. VOC concentrations range from 500 to 5,000 parts per million (ppm), and an absorption system can be built to accommodate capacities of 2000 to 100,000 cubic feet per minute. Achieving 90 to 98% VOC elimination efficiency is possible using an absorber [35].

Adsorption

Based on the interaction between the adsorbent and adsorbate, the adsorption process is divided into two categories: chemisorption and physical adsorption. The process of physical adsorption take place when organic molecules attract to the adsorbent's surface and pores by the weak Van der Waals force of attraction. It is often characterized by a low heat of adsorption and a reversible, quickly established adsorption equilibrium [36]. One popular technique for reducing VOC emissions is activated carbon-based adsorption. Physical adsorption onto the carbon surface removes VOCs from the intake air [37, 38].

Membrane separation

Membrane separation is useful for recovering VOCs from a range of industrial processes, including as bulk pharmaceutical dryers, commercial sterilizers, and surface coating operations. Through membrane separation, contaminants such as acetone (CH_3COCH_3), benzene (C_6H_6), toluene ($C_6H_5CH_3$), xylenes (C_8H_{10}) , and acetaldehyde (CH_3CHO) can be recovered [39].

VOCs in indoor environments

For benzene, toluene, ethylbenzene, xylene

(BTEX) and other ambient VOCs, the United States Environmental Protection Agency (USEPA) has not suggested any guidelines. However, the Occupational Safety and Health Administration (OSHA, 2004) set 1 ppm (3.19 mg/m^3) and 200 ppm (753.6 mg/m^3) as the highest acceptable levels. For benzene, toluene, ethyl benzene, and xylene, the weighted average regulation limits are 100 ppm (434 mg/m^3) for an 8-hour workday or a 40-h workweek, respectively [40]. VOCs have an immediate impact on several human body organs and can trigger various allergies. To reduce health hazards in both indoor and outdoor environments, it is preferable to get rid of VOCs that are released from various sources, which are shown in Table 1.

Table 1. Possible origin of VOCs

Serial Number	Origin	VOCs	References
1.	Carpet	Dodecanol, acetaldehyde, vinyl acetate styrene, 4-phenylcyclohexene, and vinyl acetate	[41]
2.	House Paint [exterior and interior]	Toluene, Benzene, m-xylene, p- xylene, o-xylene, ethybenzene, styrene	[41, 42]
3.	Households spray products	Benzene, ketones, iso-valeraldehyde, toluene, p-xylene, o-xylene, m-xylene, propane, acetaldehyde, butyraldehyde, ethyl alcohol.	[43]
4.	Cleaning Products	Ethanol, phenol, toluene, limonene, decane, 1-propanol, o-xylene, butoxyethanol, 1,4-dichlorobenzene, and chlorobenzene	[44]
5.	Kitchen activities	Ethnal, butyraldehyde , propanal, Isoprenol, styrene,Isobutanol and propanoic acid	[45, 46]
6.	Furniture	Methanal, cyclohexanone, ethyl benzene, dichlorobenzene, hexanal, butylacetate, styrene and benzene	[47-49]
7.	Personal care Products	3-Carene, camphene, p-xylene, , n-decane, pinene and styrene	[50, 51]

Fly ash: Some facts

China, being densely populated, exhibits significant per capita electricity demand. Consequently, coal plays a pivotal role as a primary energy source in China, contributing approximately seventy percentage of the overall consumption of energy during 1978 and 2009. China holds the title of being the largest coal mining and consuming nation globally. In 2008, it overtook Japan to become the leading coal importer worldwide [52]. In 2010, China combusted about 3 billion metric tonnes of coal [53]. China's dependence on coal-based energy is evident. However, burning coal releases FA into the atmosphere, which increases environmental issues such as acid rain, smog, and fog, as well as heavy metal pollution [54-56]. Resolving the issue of coal-burning FA pollution would have a significant positive impact on both human and environmental health. Approximately 580 million tonnes of FA were generated by the end of 2015, making up almost 77% of the FA production worldwide [57]. Based on statistical data, the average global rate of FA utilization is approximately 25% [58]. According to reports from other researchers, roughly 67% of FA is used [59]. The specific uses of FA in China encompass the production of construction materials such as FA blocks, FA bricks, ceramics, cement, concrete, and mortar. Additionally, FA is utilized in the construction of roads, embankments, and pavements, as well as in the filling of mines and places affected by coal mining subsidence.

India's energy consumption is rising annually as a result of the country's expanding economy and growing population. According to a United state Energy Information Administration Department analysis, India's consumption of energy growth is expected to will exceed that of China, the US, and Russia through the ending of 2035 [60]. As a result, India's annual FA production is also rising quickly. FA production reached over 130 million tonnes in 2010 and 2011, almost 85.7% more than in 1996 and 1997. Additionally, over a 15-year period, the FA application rate expanded by 466%, from 9.63% in 1996–1997 to 54.53% in 2010–2011 [61]. In India, FA is used for the following purposes: roads and embankments (6.51%), cement (44.76%), reclamation (16.72%), mine infill (9.1%), and ash dyke rising (6.89%), concrete (0.74%),bricks and tiles (6.86%) and 7.38% for other uses, [57].

A tiny amount of FA is produced by coal-fired power in other nations. Australia produces 10 million tonnes, the UK produces fifteen million tonnes, and Germany produces 40 million tonnes annually. Neither Canada nor France, Denmark, Italy, nor the Netherlands produce 10 million tonnes of FA annually. Compared to China and India, these nations produce very little FA annually, but they use a lot of it. Germany, the UK, China, Australia, France, and Canada have usual utilization rates of 76%. Italy, Denmark, and the Netherlands have averages that reach 100%. These nations use FA in the same manner as China, India, and the United States [62-64].

Before we review the literature about various uses of fly ash, for the sake of conciseness, only a brief mention will be made of its composition and characteristics.

Fly ash composition and characteristics

Fly ash is mainly made up of iron oxides (Fe_2O_3), silica (SiO_2), and alumina (Al_2O_3) are the main constituents, with trace amounts of carbon, calcium, magnesium, and sulfur. Based on the prevalence of several critical constituents, the following (Eq. 9) has been presented as a fly ash empirical formula [65].

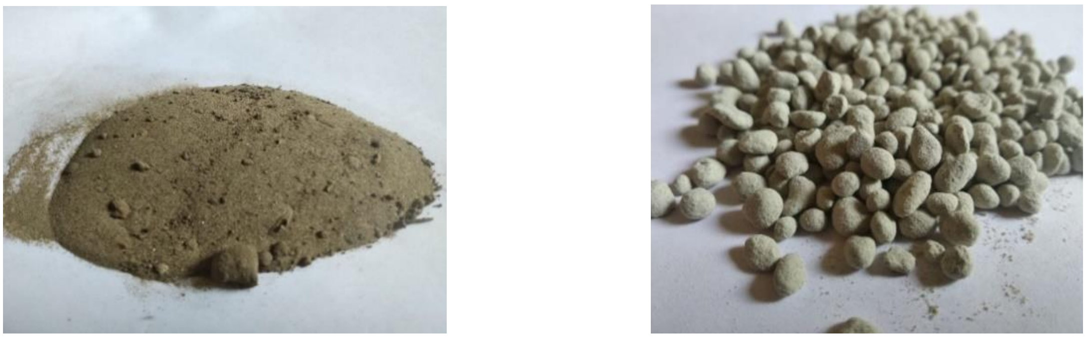
$$Si_{1.0}Al_{0.45}Ca_{0.51}\,Na_{0.047}Fe_{0.039}Mg_{0.020}K_{0.013}Ti_{0.011} \tag{9}$$

Coal combustion comes in two different forms: Having less than 7% calcium oxide and manufactured from bituminous, anthracite, or sub-bituminous coals, called Class F and other is Class C, which are made from lignite coals and include greater CaO (5–30 wt. percent). It is thought to possess a porous structure and a hydrophilic surface in general. Analysis of the surface chemistry, mineralogy, and reactivity of FA is critical for the development of various FA applications [66].

Physical properties

Fly ash is made of hollow, spherical, and typically amorphous powder particles. It is made up of bituminous coal having particle size dispersion (less than 0.075 mm or No. 200 sieve) that resembles a slit. It can have a specific surface area of 170 to 1000 m^2/kg and a specific gravity of 2.0 to 3.0 [67-69].

It can be grey or black in appearance, depending on how much unburned carbon is present. Fig. 1a and b shows the two forms of FA, whereas Table 2 summarizes the fly ash's physical characteristic.



a b

Fig. 1. a) Fly ash as Powder form; b) Fly ash as Pellets form

Table 2. Physical characteristics [70]

Sr. No.	Parameter	Range	Methodology
1.	Density	1.96-2.90 g/cm^3	Bulk chemical analysis
2.	Size of Particle	10^{-2} nmx10^5nm	Gradation test and hydrometer test
3.	Relative density	~3.0	Pycnometer measurements
4.	Porosity	30-65%	Hg-imposition porosimetry
5.	Water-retention capability	40-60%	Column- separation method
6.	Surface area	170-1000 m^2 /kg	N-BET method
7.	Permeability	10^{-4}-10^{-6} cm/s	Permeability analysis
8.	Optimal content of moisture	18-38%	Aashto T99 test

Chemical properties

Coal has been classified into four groups: sub-bituminous, lignite, anthracite, and bituminous. For the purpose of generating electricity, lignite coal is used. It is woody in texture, has a brown to black tint, and contains a lot of moisture, and it is considered the coal of the lowest quality. Sub-bituminous coal is nothing but lignite coal that has darkened in color and gotten tougher in texture over time. Bituminous coal has a larger percentage of carbonaceous matter than other types of coal. Anthracite is a black, flammable substance that produces smoke and flame when burned [71-73]. In Table 3, the chemical compositions of all three types of FA are contrasted in their normal parameters. It also contains a number of trace elements, some of which are shown in Table 4.

Toxicity of fly ash

Fly ash powder has an impact on the environment, but it also directly affects people's bodies in many ways. The outcome of FA powder on the atmosphere and human health are outlined in Fig. 2 [76]. The picture demonstrates that precipitation in landfills and powdery residue results in the leaching of many poisonous metals including cadmium, mercury, arsenic, lead and others. This process leads to the contamination of groundwater, rivers, and ponds. Fine fly ash powders are inhaled as a result of the atmosphere's winds, which is harmful to human health. The image also shows that, as a result of bioaccumulation, we ingest contaminated groundwater, diverse marine plants, and animals as food supplements, which adversely affects human health.

Table 3. Comparison of chemical content of different fly ashes [74]

Constituents (wt%)	Bituminous coal fly ash	Sub-Bituminous coal fly ash	Lignite coal fly ash
Siliconedi-oxide	20.0-60.0	35.0-60.0	20.0-45.0
Aluminum oxide	4.0-30.0	21.0-30.0	15.0-25.0
Ferric oxide	11.0-40.0	5.0-10.0	5.0-15.0
Calcium oxide	1.5-12.0	5.0-35.0	20.0-40.0
Magnesium Oxide	1.0-5.0	1.0-5.0	4.0-10.0
Sulphur tri-oxide	1.0-4.0	1.0-2.0	1.5-10.0
Sodium oxide	1.0-4.0	1.0-2.0	1.0-5.0
Potassium oxide	1.0-3.5	1.0-4.0	1.0-5.0
Loss on ignition	1.0-15.0	1.0-3.0	1.0-5.0

Table 4. Trace elemental composition of fly ash [75]

Trace Elements	Part per million (ppm)
Manganese	55.0-3000.0
Zinc	10.0-3000.0
Copper	15.0-2500.0
Boron	10.0-620.0
Arsenic	2.5-6400.0
Cadmium	0.5-120.0
Chromium	5.0-1000.0
Mercury	0.03-1.0
Molebednum	5.0-150.0
Nickle	6.5-4400.0
Lead	3.3-5000.0
Selenium	0.1-135.0

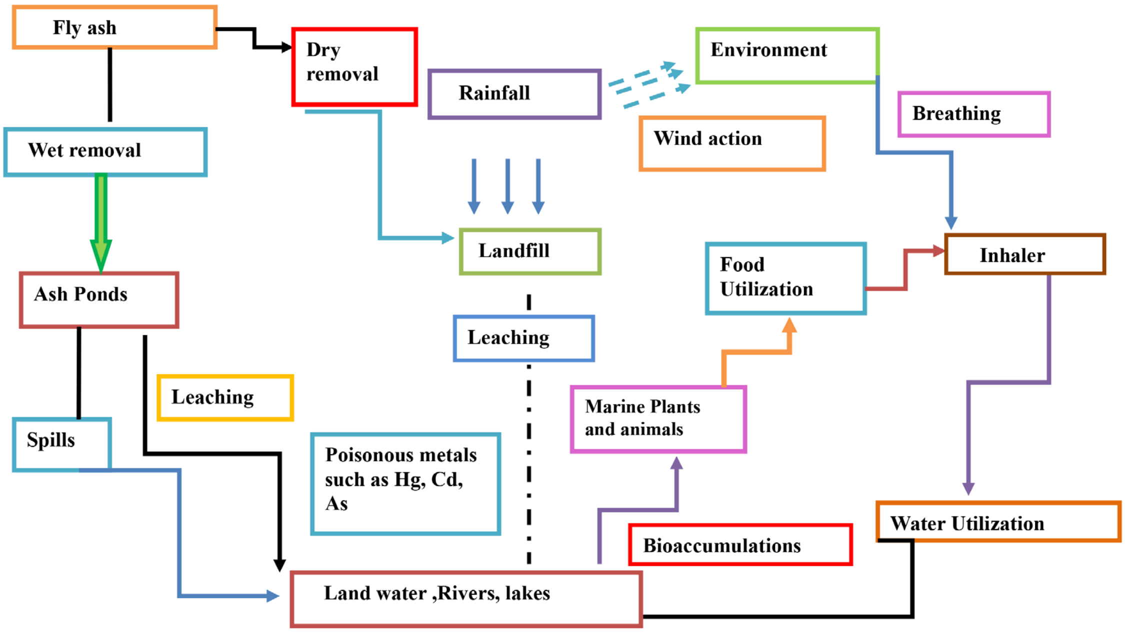


Fig. 2. Exposure pathways for fly ash

FA includes hazardous heavy metals including mercury (Hg), nickel (Ni),arsenic (As), chromium (Cr), lead (Pb), and selenium (Se). Excessive amounts of hazardous heavy metals can have severe health implications for both humans and animals. Exposure to high levels of chromium (VI) in concentrated fly ash can lead to carcinogenic effects and impairment to the circulatory system in organisms [77].

Importance of VOCs abatement

VOCs are a type of air pollution created mostly by fossil fuel burning [78, 79], painting [80], refining [81], construction, and other industries [82, 83]. The fast rise of industry in recent decades has resulted in a considerable increase in man-made VOCs, comprising approximately three hundred chemical compounds including alkanes, aromatics, esters, and aldehydes [84, 85]. Many VOCs, such as benzene and formaldehyde, which are probable carcinogens, are dangerous to humans in even small concentrations [86]. The paint industry is the primary source of xylene and aliphatic hydrocarbons, both of which are hazardous to the environment and humans [87, 88]. O_3, H_2O_2, nitro-CHO, and smog chemicals are harmful to people's health because they cause secondary pollution, which harms the respiratory systems and eyes. It is caused by the photochemical interactions between VOCs and NOx in the presence of sunlight [89-93]. Fig. 3 and Table 5 depict the most significant harmful effects on human health, emphasizing the health issues linked to specific Volatile Organic Compounds (VOCs) such as BTEX (Benzene, Toluene, Ethylbenzene, and Xylenes) [94].

Prolonged exposure to elevated amounts of benzene can have detrimental effects on the human central nervous system, resulting in symptoms such as migraines, nausea, and vertigo. Long-term benzene exposure can also result in chromosome abnormalities, haematotoxicity, genotoxicity, reproductive weakness, and mortality [95].

High amounts of toluene can produce short-term headaches and dizziness and but continuous exposure to toluene can cause permanent hearing and vision loss [96].

Three to five minutes exposed to 200 ppm of xylenes have been linked to symptoms such as throat/nose irritation, chest pain, dryness and shortness of breath, and skin cracking. Regular exposure to high xylene concentrations can harm the kidneys and liver [97].

Vertigo, dizziness, and irritation of the eyes and/or throat can result from short exposure to ethylbenzene. Prolonged exposure to ethylbenzene can cause more serious issues, such as kidney and ear damage [98]. As a result, VOC reduction and control are major research areas for air purification.

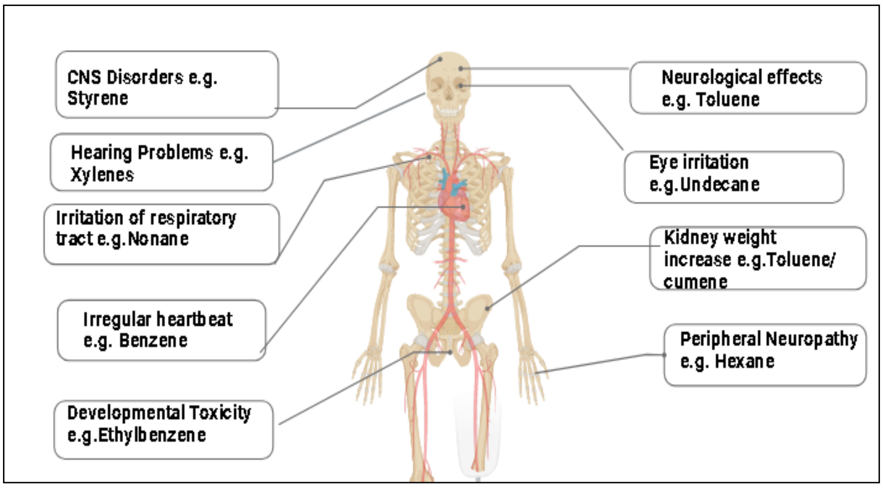


Fig. 3. Representative diagram showing health effects of VOCs

Table 5. VOCs sources and their health effects on humans [8, 99, 100]

Volatile organic compounds (VOCs)	Unsafe Conc. (ppm)	Sources of VOCs	Health Effects on Humans
Benzene	500	Incomplete combustion of liquid fuel and Petroleum products	Carcinogen
Ethylbenzene	800		
Carbon tetrachloride	200	Paints, Polymer synthesis	Acute toxicity
Acetone	2500	Lacquers, Paint thinners, home care products.	Irritation of eyes, nose, headache, and nausea
Ethyl butyl ketone	1000	Adhesives	Depression, headache, and nausea
Formaldehyde	20	Fabrics, and bio-waste decomposition	Irritation of throat, skin, and eyes, Nasal tumors
Acetaldehyde	2000	VOCs degradation, bio-waste decomposition	Eye, nose, and throat irritation ozone predecessor
CH_3OH	6000	Sterilizers, Antibacterial, and Personal and home care products	Shortness of breath, Central nervous system disorder.
CH_2CH_3OH	3300		
Isopropyl alcohol	2000		

Traditional approach for VOCs risk calculation

Inhalation risk calculation

The following (Eq. 10) calculation is used to calculate the chronic daily intake of each analyzed VOC through inhalation:

$$CDI_{inhal} = \frac{CA*IR*ET*EF*ED}{BW*AT} \quad (10)$$

Where, CDI_{inhal} = Chronic daily intake of contaminate through inhalation (mg/ kg/day)

CA = Concentration of the contaminant (mg/ m^3) in air

IR = Inhalation rate (m^3/h)

ET = Exposure time (h /day), frequency of exposure (h /day, 2 h)

EF = Exposure frequency (days/year),(260 working days in a year)

ED =Exposure duration (years)

BW = Body Weight (70 kg on average)

AT = For the risk assessment of cancer disorders, AT is multiplied by 365 days (equal to 8,016 days) and is expected to be around 30 years (industrial and urban areas).

Cancer risk assessment of VOCs

Even a small amount of the desired pollutant can increase the risk of cancer in humans, as determined by cancer risk assessments. The formula (Eq. 11) is used to calculate the cancer risk rate following the determination of chronic daily intake (CDI) through inhalation. The cancer slope factor (CSF) for VOCs was estimated in Table 6 [101].

$$\text{Cancer Risk} = CDI *CSF \quad (11)$$

Table 6. CSF of toxic VOCs

Toxic VOCs	CSF
Benzene	5.5×10^{-2}
Toluene	NA
Ethylbenzene	NA
Xylene	NA
Styrene	1.3×10^{-2}

Table 7. RFC Values for VOCs [103]

Toxic VOCs	RFC
Benzene	1×10^{1}
Toluene	5×10^{1}
Ethylbenzene	1×10^{3}
Xylene	2.2×10^{2}
Styrene	9×10^{2}

Non-cancer risk assessment of VOCs

The non-cancer risk rate was calculated using the inhalation Reference Dose (RFDi) factor. HQ (Hazard quotient) factors (Eq. 12) show non-cancer risk [102]. In the non-cancer risk, contaminants may be tolerable if the HQ value is less than 1. Table 7 shows inhalation reference dose values for a VOC.

$$HQ_{\text{inhalation}} = CDI_{\text{inhalation}} / RfC_{\text{inhalat}} \qquad (12)$$

The review will proceed in the direction of VOCs abatement utilizing the solid industrial waste fly ash as an electrospun nanofibrous sheet.

Recent advances and progress electrospun nano fiber membrane for air purification

91% of the world's population, according to the WHO, resides in areas with air pollution levels that are over recommended standards [104]. Furthermore, the World Health Organization approximates that an annual death toll of seven million individuals occurs due to the presence of both indoor and outdoor air pollution. Therefore, there is a pressing need for innovative methods that can effectively and affordably reduce both indoor and outdoor pollution. Polymer materials with a high affinity to absorb harmful chemicals and gases can be used in the electrospinning process to fabricate air filter membranes at a low cost. In order to remove PM_{10}, VOCs, $PM_{2.5}$,germs, and viruses, researchers have looked into the possibility of using electrospun nano-fibrous membranes [105].

Currently, nanofiber mats can be employed independently or in combination with other filtration media in a wide range of air filtration applications. Throughout the world, a lot of people use high-efficiency particle air filters, or HEPAs, in order to protect themselves from harmful gases and diseases that can be transmitted by aerosols. Extremely thin diameter of electrospun nanofibers have numerous higher properties over conventional mask filter media, including a large ratio of area-to-volume ,structure of thin pores, and high energy of surface , and relatively large strength. These properties indicate higher filtration efficiency without losing permeability during the filtration process because the lip flow surrounding the nanofibers could significantly increase the diffusion, interception, and inertial impaction efficiency. The nanofibrous filter should have an ultralow pressure drop in addition to great filtering effectiveness; in other words, these face masks should be highly breathable [106].

A capable option for indoor air purification is electrospun nanofiber membranes, which can filter out harmful germs, virus and other contaminants from the air movement system and give people in these environments a purified air quality. This is especially important for hospitals, where they have strict requirements for indoor air quality and an absolutely aseptic and dust-free environment [107].

By using an optimized "green" solvent and electrospinning,consistent gelatin nanofiber membranes were effectively created. Moreover, the gelatin nanofibers not only successfully remove a wide range of PM particles that are similar to HEAP, but they also attain outstanding toxic chemical absorption effectiveness such as 80% for formaldehyde, 76% for carbon monoxide [108].

The purifying soy flour/PEO nanofiber filter has high bacterial filtering capacity was studied by Lubasova and coworkers. These innovative nanofiber filters made of protein have the potential to effectively retain and remove E. Coli bacteria during air filtration. As a result, they can be used to reduce bacterial infections in settings like hospitals and residential areas that demand an extremely high level of air quality [109].

Jeong et al., was demonstrated that a novel transparent, reused, and effective $PM_{2.5}$ air filter produced from a silver nanowire percolating network. It has several excellent qualities, including high level efficacy (greater than 99.99%), antibacterial properties, and low consumption of energy [110].

In summary, electrospun nanofibrous films are currently become an effective replacement for traditional filter media, offering excellent filtering effectiveness and resistance of low air to reduce air pollution. Nanofibrous films generated through electrospinning, particularly those derived from green electrospinning, are vital for protecting human health and purifying indoor air. They are particularly useful in prevent the breathing of particulate matter and germs from the atmosphere.

Techniques to generate electrospun nano fiber

Nanofibers can be created using a variety of techniques, including vapour growth [111], arc discharge [112], laser ablation, and chemical vapour deposition [113]. However, because of the limited product yield and the expensive equipment required, these are very expensive procedures. A polymer solution can be spun into fibers with sizes ranging from 10 nanometers to 10 micrometers [114, 115] using the electrospinning technique, which was developed in 1934.

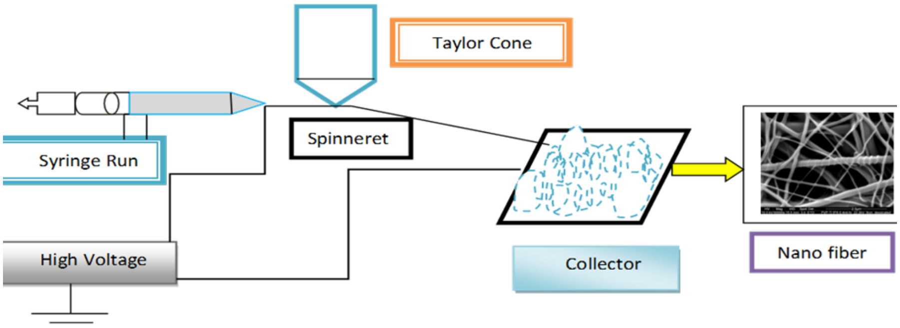


Fig. 4. Electrospinning system

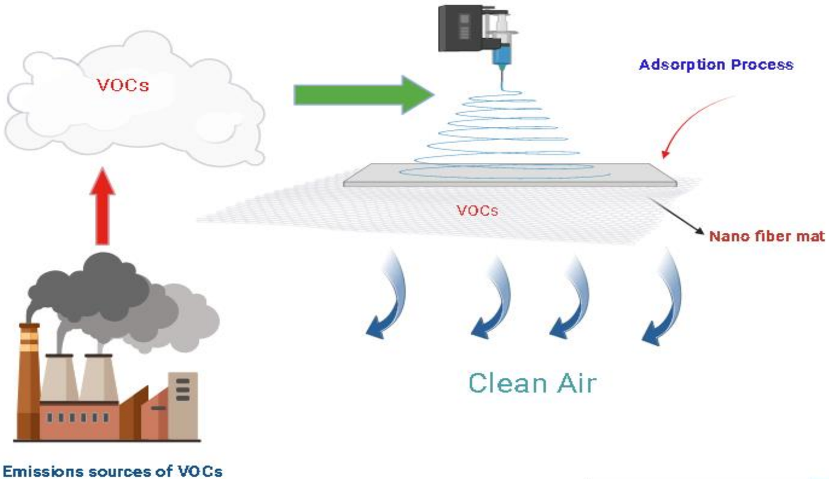


Fig. 5. Adsorption Process of VOCs

In addition to length of jet, viscosity of solution, ambient gas, flow rate, and collector assembly design,electric field that is applied and conductivity of solution are important factors that determine fibre diameter during spinning [116, 117]. The electrospinning procedure is shown in Fig. 4; prior papers [118-121] provide more information.

Electrospun nanofiber membranes for capturing VOCs from air using fly ash

Using FA innovative study that uses a nano fiber membrane to capture VOCs from the atmosphere shows a novel method for utilizing of FA fiber membrane to clean air pollutants Fig. 5. Fibrous membranes made of FA, a highly significant substance, have the potential to be converted into various types of air filters, making substantial advancements in the field of contaminant management [122, 123].

Solvents such as butanone and N, N dimethylformamide is mixed in a specific proportion with the functional substance used for spinning namely coal fly ash along with polymer viz. polylactic acid, polyacrylonitrile and polyurethane is then processed using ultrasonication and magnetic mixer. It should be noted that the viscidity, velocity of spinning fluid, conductivity, the distance between collector and outlet, and other factors affect the size and arrangement of electrospun fibers [123, 124].

In 2009, a study conducted by Seo et al., the adsorption capability of several building materials was examined inside a confined experimental setting. They discovered that materials included, gypsum, activated carbon, porous ceramic material, and silicate calcium. when compared to other construction materials activated carbon has the greatest ability for VOC adsorption [125].

In 2002, Chmielewski et al investigated the use of electron beam treatment to reduce VOCs from coal combustion and discovered that the VOCs concentration was considerably decreased from 40% to 98% [126].

In 2013, Kim et al [123] concluded that polyurethane fibers made up of fly ash with different concentrations were successfully produced, and their capacity to bind chemicals like $CHCl_3$, C_6H_6, C_7H_8, C_8H_{10}, and C_8H_8 have been tested. It was reported that the highest VOCs adsorption capability of all the investigated fibrous membranes was achieved by polyurethane fibers containing 30-weight percent fly ash, which had the lowest fiber thickness along with the largest total surface area. In comparison to other fibrous membranes, it exhibits the most superior potential for adsorbing volatile organic compounds (VOCs). Furthermore, VOC adsorption by fibrous membranes occurred in the following order: $C_8H_8 > C_8H_{10} > C_7H_8 > C_6H_6 > CHCl_3$. The adsorption of volatile organic compounds (VOCs) is influenced by various factors, including surface area, fibre length, dipole moment, boiling point, temperature, humidity, chemical functional groups, pore size, porosity, molecular mass, adsorption kinetics, molecular polarity, steric and electronic effects, molecular structure, π-complexes, and ionisation potential. [8, 127, 128]. FA/PAN membranes have excellent adsorption capacity may make them more advantageous to utilize as adsorption materials with potential and growing applications in air filtration [129]. Electrospun nanofibrous PAN membranes that had been subjected to a steam activation process (carbonization at temperatures above 700 °C) were used to create activated carbon nanofibers (ACNFs). For benzene and ethanol, the ACNFs showed maximum adsorption capacities of 104 and 135 cm^3g^{-1}, respectively. Additionally, it was discovered that as the carbonization temperature rises, the increase in porosity enhances the VOCs adsorption capacity [130]. Similar to this, FA/PAN based electrospun nanofiber membranes embedded in them be created and used to collect BTX (benzene, toluene, and xylene) aromatic hydrocarbon vapours. For benzene, xylene, and toluene, respectively, the resultant membranes showed high adsorption capacities of 24.05,75.26, and 34.46 µg/g [129].

Generalized physicochemical interactions for the adsorption processes include electrostatic attraction and nonpolar attraction. Fig. 6 depicts a potential adsorption method for FA/PAN nanofibrous membranes to trap BTX. BTX's capacity for trapping is connected to the Ionization Potential (IP). The formation of charge transfer complexes is encouraged by BTX with low ionization potential, which makes it easy to be adsorbed [123]. According to adsorption performance, the values for ionization potential of benzene, toluene, and xylene are 9.24 eV, 8.82 eV, and 8.56 eV respectively. Additionally, the higher weakest intermolecular attractive forces and lower IP would upsurge the molecular overpopulation of BTX, which would then increase the surface contact with the membrane and result in stronger interactions [132]. Other Stronger π-π interaction between the surface of the PAN/FA nano fibre film and the BTX, on the other hand, resulting in a larger BTX trapping capacity (π-complex increases with increased $-CH_3$ group). Other studies have also been reported similar results Furthermore, due to the stronger intermolecular forces, molecular mass, and high temperature of evaporation of BTX are easily captured by nano fibrous membrane and strongly interacting attached functional groups [123, 133].

Surface chemical functional groups, pore structure, and specific surface area (BET) of fibrous membranes play a crucial role in determining their ability to adsorb BTX. These factors directly influence the performance of the membranes in trapping BTX, hence defining their BTX trapping capacity [8].

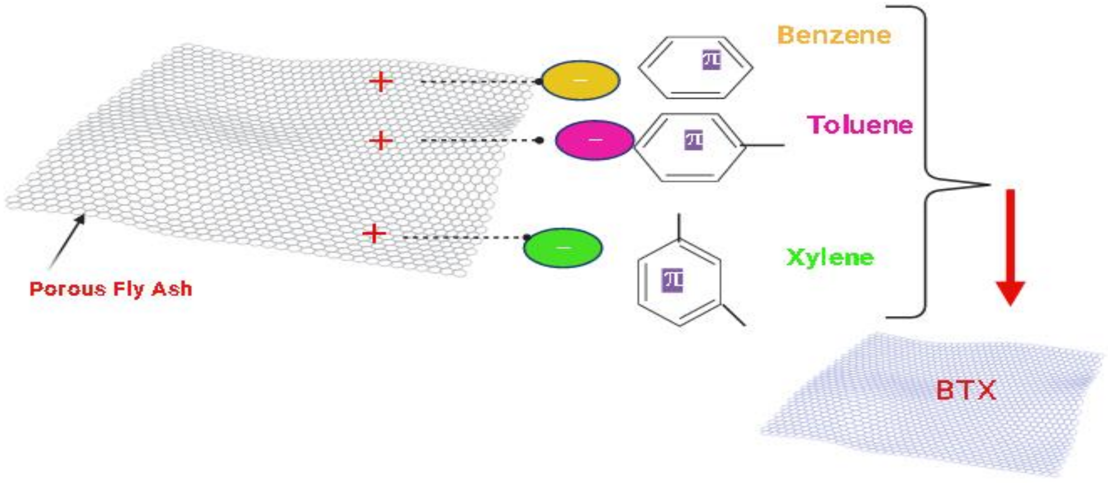


Fig. 6. Postulated mechanism of capture BTX

Factors influencing the effectiveness of fly ash adsorption

The effect of interaction time and initial pollutant concentration are significant factors influencing adsorption performance. The starting levels of pollutants have a major impact on the ability of various industrial waste products to be adsorbed. The adsorption ability frequently exhibited an upward trend as the starting concentration of the pollutant increases. The initial concentration serves as a significant driving factor in surmount any resistance to mass transfer of contaminants among the solid and aqueous phases. The elimination of contaminants to achieve equilibrium varies by interaction time. Furthermore, the effect of particle size is crucial in adsorption ability. An internal diffusion investigation reveals that the particle size of the waste materials used has a significant influence on the adsorption rate. A reduction in particle size would lead to an augmentation in surface area, hence enhancing the adsorption potential at the external surface of the waste materials. The adsorption capacity of waste materials is significantly influenced by surface activity, which refers to the specific surface area that is accessible to solute-surface interaction. It is anticipated that the adsorption capacity will be enhanced as the surface area is raised. To clarify, a reduction in particle size leads to an increase in adsorption capacity. Ionic strength is a significant determinant that impacts the equilibrium of the aqueous phase. The observed phenomenon may be recognized to fluctuations in activity of pollutant or the characteristics of the electrical double layer. According to surface chemistry theory, when two phases, such as waste particles and variety of pollutants in an aqueous solution, interact, inevitably be enclosed by an electrical double layer as a result of electrostatic interaction. Therefore, since the phenomenon of adsorption is influenced by the strength of electrostatic attraction, it can be inferred that adsorption is inversely proportional to the rise in ionic strength [134].

Challenges with employing fly ash as an adsorbent and difficulties

Since FA is produced in significant amounts as waste material during combustion processes worldwide, it is drawing attention as a byproduct of thermal power plants. 500 Mt (million tonnes) of fly ash is thought to be created yearly globally [135]. The production of fly ash from coal-based thermal power plants in India is currently 131 Mt/year, but by 2016–2017, it is estimated to reach 300–400 million tonnes per year [136]. Based on probable estimates, it is anticipated that the production of FA will increase to roughly 1000 Mt by the year 2032 [137]. FA be able to used in a variety of ways, but the efficiency of those uses depends on the property. FA's eventual outcome is mostly related to its disposal in landfills, although this raise worries for the environment and the economy. Therefore, it becomes vital to look for an efficient method that addresses these issues. The dispersal of this substance occurs through airborne transmission originating from an ash pond, particularly prevalent during periods of low precipitation. This phenomenon poses a significant threat to the respiratory health of the neighboring populace. The issue of effectively utilizing fly ash waste has become a significant problem for authorities of power plant owing to the requirement for a substantial earth area for its removal [138]. Furthermore, it persists in making significant contributions to various environmental, economic, and social concerns [139, 140]. Despite the growing utilization of fly ash in various industries, its production still exceeds its usage by a wide margin. Consequently, endeavors are being focused on environmentally advantageous applications that maximize the utilization of this abundant substance.

Conclusion

In conclusion, fly ash is a typical example of waste-to-treatment waste since it may be used to remediate pollution. Air pollutants indoors are mixtures of various gases including NOx SO_2, VOCs, etc. along with coarse, fine, and superfine particulate matter. These pollutants have been repeatedly reported to cause various health-related disorder such as chronic obstructive pulmonary disease and asthma, skin dermatitis, epilepsy, liver and endocrine dysfunction, etc. Despite such harmful effects of the above pollutants, the mitigation technologies available in the market have major scientific and applied drawbacks which make them somehow inefficient in low- and middle-income countries like India. These technologies are highly expensive and non-degradable; hence, prove to be an inappropriate option for developing and under-developed countries. The current review discusses an eco-friendly and economical substitute of the techniques available for the abatement of air pollutants. Utilizing solid industrial waste can be a cost-effective and sustainable way to mitigate noxious air pollutants such as VOCs, often found in very high concentrations in households. Out of many, fly ash may be employed as an adsorbent such as an electrospun nano fiber sheet to remediate pollutants may it be air or water, attributed to its elevated porosity, total surface area, a high proportion of quick lime/calcium oxide. It may be made into a range of complex constituents, include fiber membranes. An outline of fly ash's current and future applications has been given in this study. Within certain application areas, additional research and development are needed. This paper's secondary goal is to describe the most recent developments in processing methods that would make it possible to use fly ash for several components.

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Competing interests

The authors have no conflict of interest.

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Ethical considerations

Ethical issues (Including plagiarism, Informed Consent, misconduct, data fabrication and/or falsification, double publication and/or submission, redundancy, etc) have been completely ob-served by the authors.

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