



Adsorbing Prospects of Fly Ash - A Review

¹KSVL Meenakshi, ²A Bhargav, ³K Yasaswi, ⁴V Veda Rishi, ⁵T Bala Narsaiah

^{1,2,3,4}IV B.Tech, Department of Chemical Engineering JNTUHUCEH, Kukatpally, Hyderabad

⁵Professor & Head, Department of Chemical Engineering JNTUHUCEH, Kukatpally, Hyderabad

Abstract : Fly Ash is a residue generated during the combustion of coal in coal-based power plants, it is coined as an Environmental pollutant since it was released directly into the atmosphere. Fly ash is used in many applications worldwide to reduce the disposal into the environment. Because of its versatile chemical composition, fly ash is primarily used in the construction sector, soil amendments, and the synthesis of zeolites. In the present paper, we discuss the usage of fly ash as a low cost adsorbent and various applications in different fields of waste water treatment. It also reviews the implementation of the Electrospinning technique which is employed to incorporate the fly ash particles into zinc oxide's nanofibrous membranes, increasing its photocatalytic efficiency and adsorptive capabilities of the nano-composite fibers exponentially. Since, Adsorption and catalytic activity go hand in hand, we can further expand the scope of fly ash in the field of catalysis, where in different applications of fly ash as a catalyst have been discussed. Activated fly ash is proven to be more efficient than the highly effective micro porous cation exchanger in regards to the elimination of lead from waste water.

Keywords: Fly Ash, Zeolites, Adsorption, Electrospinning, Photocatalysis, Waste water.

1.0 Introduction

Electricity is the cornerstone to furnish the needs of the modern world and serves as an economic dependence for technology. India consumes 966,288,693 tonnes of Coal per year as of the year 2016[1], most of the coal consumed is directed to thermal power plants for the generation of electricity which is bound to increase with time. Once the pulverized coal is placed in the coal-fired boiler, it is used to produce an enormous amount of heat along with the mineral residue. This mineral residue hardens to form ash after cooling which comprises of bottom ash and fine particulate matter with flue gas and these fine particles are removed by a means of electrostatic precipitators or mechanical collection devices such as cyclones.

Numerous byproducts of coal-fired power plants comprise of gypsum, CO₂, NO₂, SO₂, volatile organic compounds like benzene, toluene, aldehydes, methylene chloride, etc, coal ash, and a range of heavy metals. Coal ash, for example, has been regarded as a hazardous waste until 2000, wherein the ministry acknowledged the importance of coal ash in various sectors of the economy, declaring it as non-hazardous waste. Luckily some of these byproducts like gypsum and coal ash have commercial applications and can be sold. Coal ash is the culmination of two components namely Fly Ash and Bottom Ash. The coal ash that rises with the exhaust gases is called Fly Ash and is the topic of interest in this paper.

Fly ash derived from coal-based thermal power plants is home to various contaminants like Arsenic, Barium, Cadmium, Nickel, Lead etc, thus being potentially rich in poisonous constituents, these tend to cause cancer, lungs, heart, and neurological disorders and sometimes loss of life if left unattended. Hence fly ash particles are considered to be highly virulent. However, rather than disposing fly ash in landfills, lagoons, and storage ponds which pose a potential threat to the environment, we can use it economically in various sectors. Thus, the assembly-line producers of electricity are awaiting to make capital out of fly ash. With many proven applications of fly ash and policy-making in India, fly ash utilization is predicted to surge in the course of time.

Fly ash comprises of powdery dust generally spherical in shape, with size ranges between 10-100 microns with high bulk density, water holding capacity, porosity, large surface area, and “pozzolanic properties” which equips it for varied applications. Fly ash is predominantly grey in colour due to the presence of a certain amount of unburnt carbon. Depending on the type of coal used, the chemical configuration of the fly ash varies significantly. Major contents of fly ash include SiO_2 , CaO , Al_2O_3 . [2] Fly ash also includes elements such as arsenic (As), boron (B), cadmium (Cd), chromium (Cr), lead (Pb), and mercury (Hg) among other heavy metals as minor constituents.

An empirical formula is proposed for fly ash based on the presence of certain key [3] elements:-

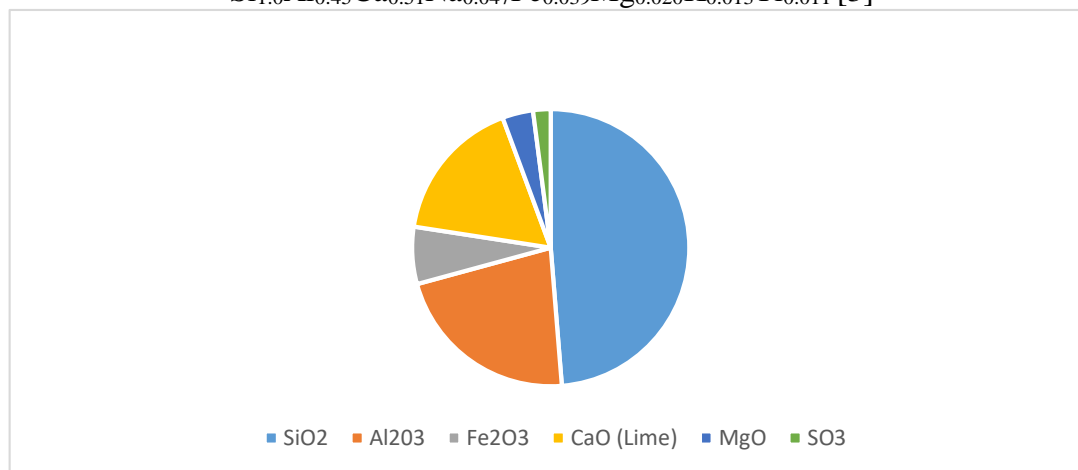


Fig.1. Composition of Fly Ash

Corresponding to these properties, fly ash is widely used in sectors like agriculture such as soil remediation, constructions as in manufacturing bricks, cement, and structural fills or infiltration barrier, as well as many proven applications in wastewater treatment. Being an economical adsorbent, an interesting field of employment of fly ash is the purification of air and water. [4]

Due to the incorporation of dyes and heavy metals in wastewater like precipitation, reverse osmosis, coagulation, traditional techniques of wastewater treatment turned out to be exorbitant. When dealing with bulk quantities of water, convenience, practicality and mainly the diverse options in adsorbents like fly ash make adsorption favourable over other techniques. [5]

In due course, we will be reviewing the study of adsorption capacities of fly ash as follows: Module 2 briefs on the classification and morphology of fly ash; Module 3 overviews factors affecting adsorption capabilities using FA and emphasizes adsorption kinetics, some utmost mechanisms, and thermodynamics for FA-based adsorbent; Module 4 interprets the use of electrospinning and photocatalysis; Module 5 discusses about the synthesis of zeolites and HM removal and its role as a heterogeneous catalyst; Module 6 wraps the outlook of this review paper.

2.0 Classification of fly ash

According to ASTM standards, based on the composition differences, fly ash is classified into the following categories containing the sum of major oxides SiO_2 , Al_2O_3 , Fe_2O_3 over 70% by weight into class F and class C [4], which is proven to possess good adsorbent capabilities. F type fly ash can be further combined with a new substrate in order to obtain good affinity towards adsorbing heavy metals from multi cation wastewater treatment. Anthracite and Bituminous coal are used to derive F type Fly ash by combustion. [6]

Fly ash with composition of SiO_2 , Al_2O_3 , Fe_2O_3 between 50-70% is known as class C fly ash, this type of fly ash is produced from the combustion of sub-bituminous and lignite coals. Class C fly ash often has more amount of CaO , compared to class F. Due to the presence dominant presence of calcium oxide, class C fly ash has self-cementing and pozzolanic properties. LOI (Loss on Ignition) test is a conventional process to gauge the quantity of unburnt carbon in Fly Ash. According to ASTM C311 [7], a higher amount of unburnt carbon in fly ash, results in better adsorption capacity. [8] The mineral matter present has little to no absorption capacity rather it is a result of the unburnt carbon present in fly ash.

2.1 Morphology

Under the eyes of a Scanning Electron Microscope[9] fly ash is found to consist of cerospheres, plenospheres and agglomerates. Cerospheres are inert, lightweight, and hollow spherical structures made of alumina and silica. Plenosphere is a sphere bounding a collection of microspheres, at times, plenospheres may further breakdown and give rise to further micro-sized particles, gases and volatile components as a result of combustion. These micro-sized particles, often find themselves attached to large particles or form an agglomerate of small particles, which results in the subduing of the particle size distribution. Due to this subduing, the particle size, shape, surface area, and charge of the particles is affected which affects the adsorbing capabilities of fly ash. The SEM (Fig. 2) image below shows the particles are fine powders and sphere like.[10]

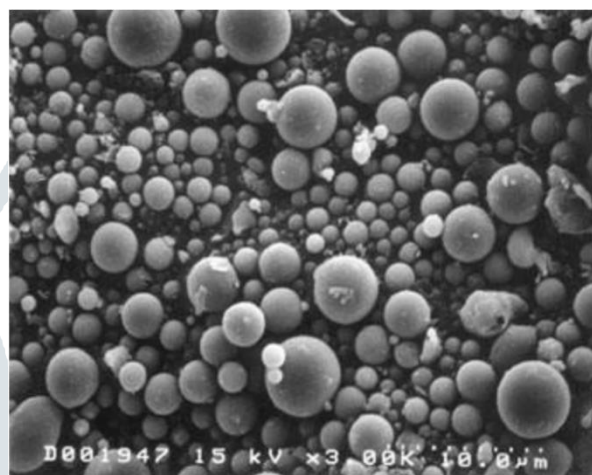


Fig.2. SEM image of fly ash particles [10]

1. Adsorbing Capabilities:

Sustainable development in technologies has persuaded the utilization of by-products of coal, for instance, fly ash as an industrial resource. As discussed earlier, applications fly ash are not only confined to the construction or agricultural sector but to wide-ranging techniques of air and water purification as a good adsorbent. When the current trend is demanding for adsorption techniques, many associated research have been conducted to give an account of the employment of fly ash in purification technology. A detailed narrative of these applications is analyzed in this paper below.

We contemplate fly ash as a cost-effective adsorbent for exhaust gas cleaning, eliminating heavy metals from waste water and organic matter, and catalytic activity to satisfy commercial needs. Large surface area and pore volume emanate in higher adsorption of heavy metals and volatile compounds. Its unique spherical shape, charge and particle size distribution, and morphology play a major role in enhancing the adsorbing capabilities of fly ash. Owing to its composition of SiO_2 , Al_2O_3 , CaO , and marginal amounts of Fe_2O_3 , fly ash is an ideal forerunner in the synthesis of zeolites or geopolymers which is best suitable for the removal of pollutants from waste water.

3.1 Adsorption Kinetics:

For a heterogeneous catalyst solid-liquid mass transfer model, the solute transfer is depicted by the following steps :

- The solute particles should navigate through the liquid film to the exterior fly ash (adsorbent) surface, from the bulk.
- Penetration and diffusion of solute particles from the exterior of the fly ash surface to the pores of the adsorbent except for adsorption on external surface to a small extent.
- Adsorption of solute on internal surface of pores and capillary of adsorbent.

Since the third step is rapid and has little to no say on the kinetics of adsorption, the overall kinetics of adsorption is governed by either the diffusion through film or diffusion through pores of the adsorbent or both, depending on rates of individual steps. Adsorption is always accompanied by desorption due to which, the third step is an equilibrium process.

Different kinetic models have been proposed to understand the kinetics of adsorption,

1. Pseudo-first order kinetics:

$$\log(q_e - q_t) = \frac{k_1}{2.303} t$$

2. Pseudo-second order kinetics:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

3. External Diffusion Model:

$$\frac{dC_t}{dt} = -k_s S (C_t - C_s)$$

4. Intra particle diffusion model:

$$q_t = k_i (t)^{\frac{1}{2}}$$

From many studies it is evident that pore diffusion is the rate controlling step and the adsorption follows first order kinetics.

where,

k_1 = pseudo 1st order rate constant. [s^{-1}]

k_2 = pseudo 2nd order rate constant. [$L \text{ mole}^{-1} s^{-1}$]

k_s = coefficient of mass transfer.

k_i = rate parameter of intra particle diffusion control stage.

q_e = amount of solute adsorbed at equilibrium. [mg/g]

q_t = amount of solute on the surface of adsorbent at time t . [mg/g]

S = specific surface area. [m^2]

C_s = surface concentration.

C_t = solution concentration.

3.2 Adsorption Isotherms

Attempts have been made to explain the adsorption of heavy metals onto fly ash, many concentration and amount of metal adsorbed correlations have been made. In general, Freundlich, Langmuir, DKR, and Redlich Peterson have been used.

Langmuir isotherm is applicable for adsorption onto homogenous surfaces with no or negligible interaction between adsorbed molecules, the Langmuir isotherm for a single solute is given by

$$\frac{x}{m} = \frac{v_m k C_e}{1 + k C_e}$$

V_m is the monolayer capacity, K is an equilibrium constant that is linked to the heat of adsorption by equation, C_e is the equilibrium concentration of the solution, x/m is the amount adsorbed per unit mass of the adsorbent, and m is the mass of the adsorbent.

$$k = k_0 e^{\frac{q}{RT}}$$

q depicts the heat of adsorption, most heavy metals adsorption onto fly ash can be best described using Langmuir isotherm. The values of V_m and k will increase with increase in temperature. This implies that the

adsorption capacity and adsorption intensity amplifies at higher temperature. A linear plot can be drawn from the linearized form of the above equation from which the values of V_m and k can be obtained using the least square method.

Freundlich's isotherm:

An empirical relation was formulated to study the adsorbing capabilities of fly ash in regard to heavy metals. The isotherm is depicted using the mathematical relation given below. Freundlich isotherm is applicable for multi-layer adsorption at heterogenous sites on the adsorbate surface. Where k_f is adsorption capacity, $1/n$ is the measure of adsorption intensity.

$$\frac{x}{m} = k_f C_e^{\frac{1}{n}}$$

Redlich Peterson model:

Elements from both Langmuir and Freundlich isotherms are incorporated into Redlich-Peterson isotherm in which, their inaccuracies are amended. Redlich-Peterson Isotherm is an empirical model consisting of 3 parameters (A , B , and β), the mechanism of adsorption is unique and does not follow idiosyncrasies of mono layer adsorption.

$$\frac{C_e}{x/m} = \frac{B}{A} + \frac{1}{A} C_e^\beta$$

The Redlich-Peterson isotherm describes adsorption on heterogenous surfaces with heterogeneity factor β which ranges between 0 and 1. The equation reduces to Langmuir isotherm when β approaches 1.

DKR isotherm:

DKR model is used to explain the physical and chemical properties of the adsorption processes in accordance with the mean Adsorption energy (E), wherein when $E < 8 \text{ kJ mol}^{-1}$, it indicates that the dominant type is physisorption, for $8 \text{ kJ mol}^{-1} < E < 16 \text{ kJ mol}^{-1}$, chemical ion-exchange is the predominant type. The equation for DKR adsorption can be written as below, A straight line is inevitable when $\ln Q_e$ is plotted against \mathcal{E}^2 .

$$\begin{aligned} \ln Q_e &= \ln Q_m - \beta \mathcal{E}^2 \\ \mathcal{E} &= RT \ln \left(\frac{1}{C} \right) \\ E &= \frac{1}{-2\beta^{0.5}} \end{aligned}$$

Where,

Q_e = Amount of metal adsorbed.

Q_m = DKR mono layer capacity.

β = constant related to adsorption energy.

\mathcal{E} = Polanyi Potential.

T = Temperature

C = Equilibrium concentration of adsorbate in solution.

Temkin isotherm:

The heat of adsorption of all molecules decreases which is linearly correlated with an increase in adsorbent coverage using the Temkin isotherm. It also shows that the adsorption is represented by uniform binding energy distribution.

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$$

where K_T is the equilibrium binding constant ($L \text{ mol}^{-1}$) corresponding to the maximum binding energy, b is related to the heat of adsorption, R is the universal gas constant and T is the temperature (K).

3.3 Adsorption Thermodynamics:

Using the Thermodynamic equilibrium constants at various temperatures and pressures, Adsorption Thermodynamics can be calculated to verify various adsorption mechanisms. The adsorption of a material can be characterized by using thermodynamic parameters like the Gibbs free energy change (ΔG). The following equation can be used to calculate the Gibbs free energy change.

$$\Delta G = -RT \ln K_D$$

Where the thermodynamic equilibrium constant K_D can be found by a plot of $\frac{q_e}{C_e}$ vs q_e .

van t Hoff factor can be used to describe thermochemical parameters such as ΔH (adsorption enthalpy) and ΔS (adsorption entropy), Gibbs free energy can be correlated to adsorption enthalpy and entropy by the following equation,

$$\Delta G = \Delta H - T\Delta S$$

further the relation between K_D and the thermo chemical parameters can be formulated as

$$\ln K_D = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

where R is the universal gas constant and T is the temperature. A linear plot is obtained when $\ln K_D$ is plotted against $1/T$ for the adsorption of heavy metals onto fly ash. The spontaneous and feasibility of adsorption can be seen from the plot by the negative value of the Gibbs free energy. An exothermic process is indicated by a negative enthalpy value, and a negative entropy value indicates that the process's randomness decreases at the solid-liquid interface.

4. Removal of Flue Gases

4.1. Adsorption of VOC's :

Volatile organic compounds (VOC's) such as benzene, styrene, xylene, methylene chloride etc., are released from human made contaminants that evaporate into the atmosphere and are transported along with the other gases in air, thus contributing to the formation of ground-level ozone. These organic compounds may be aldehydes, aromatics, ketones, esters, etc. Ozone molecules are developed when VOC's bond with NO_x along with the formation of some peroxides as well as nitro-aldehydes. Ground-level ozone can provoke a variety of health problems like chest pain, respiratory diseases, congestion, cancer etc., and is the chief contaminant that ends in smog. VOC's are produced in many industries such as painting, refining, fossil fuel combustion, etc. Therefore, we must find ways to reduce the amount of VOC's present in the air.

The adsorption capacity of VOC's displayed by activated carbon was found to be very high. Although activated carbon is a low-cost and highly available adsorbent, it is not a good adsorbent of macro molecules and hydrophilic VOC's. This is because of its polar nature and micro porous structure. A technique known as Electrospinning can be employed to fabricate nanofibers of polymers, composites and metals of size varying from nanometers to micrometers, hence the above-mentioned nanofibers made from electrospinning have varied usage in the field of adsorption, mainly when fly ash is our material of concern. Various fibers such as natural and synthetic polymers, pure and composite fibers, ZnO fibers, organic, inorganic fibers, fibers of mixed metal oxides etc can be produced using electrospinning technique[13]. Electrospinning uses electric force to draw charged threads of fiber from polymer solutions. These membranes act as a barrier for both man made and natural adulterants. Therefore, an apparent method to remove VOC's from air is to adsorb them on a material having higher surface area and large porosity. Scholten et al revealed that VOC's from the atmosphere can be

efficiently adsorbed from polyurethane (PUR/PU) microfilaments [11]. It has been affirmed that PU fibers have equal mass as that of activated carbon even though the latter has greater adsorption power and surface area, nevertheless, embodiment of adsorption particles onto PU fibers has been proved to promote efficiency.

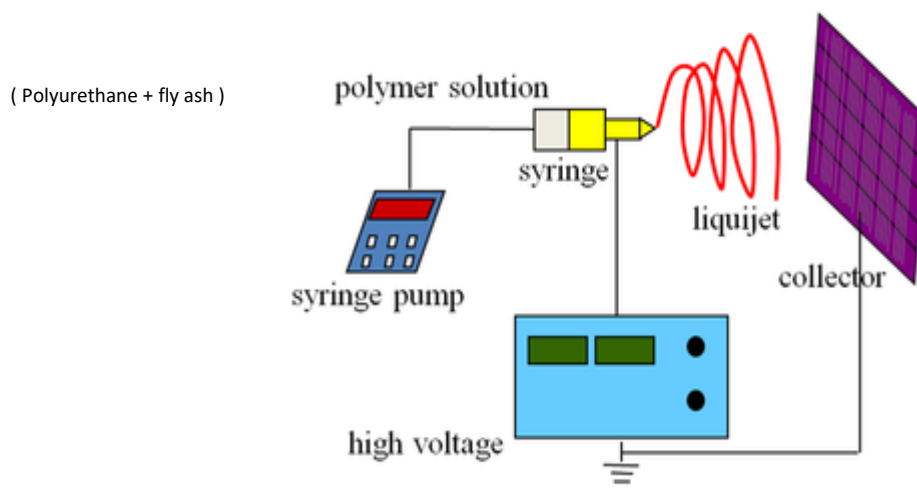


Fig.3. Schematic representation of electrospinning [12]

A solvent such as methyl ethyl ketone or m-dimethyl formaldehyde, is combined with a polymer (PAN, PU/PUR) and fly ash (spinnable material) in some desired ratio. On magnetic stirring and ultra sonification, the above mixture will give rise to a homogenous spinning solution. From the works of Choi et al, the process of collecting the above fibers on a roller under the influence of an electrostatic field is called as electrospinning. It is useful in the production of fibers of large and complex molecules as electrospinning does not require high temperatures or coagulation chemistry. Other researchers reported that inorganic compounds are added to the polymer solution.

An experiment run by H.J. Kim et al demonstrated that PU/FAP composite mat containing 60 wt% FAP can decrease CO₂ level by 32 % in half an hour compared to the pristine PU. [13] The absorption of CO₂ was accounted for the presence of FAP into PU/PUR microfiber. Consequently, the use of this discarded solid waste via electrospun fibrous membranes to adsorb volatile organic materials from the atmosphere is proven to be worthwhile.

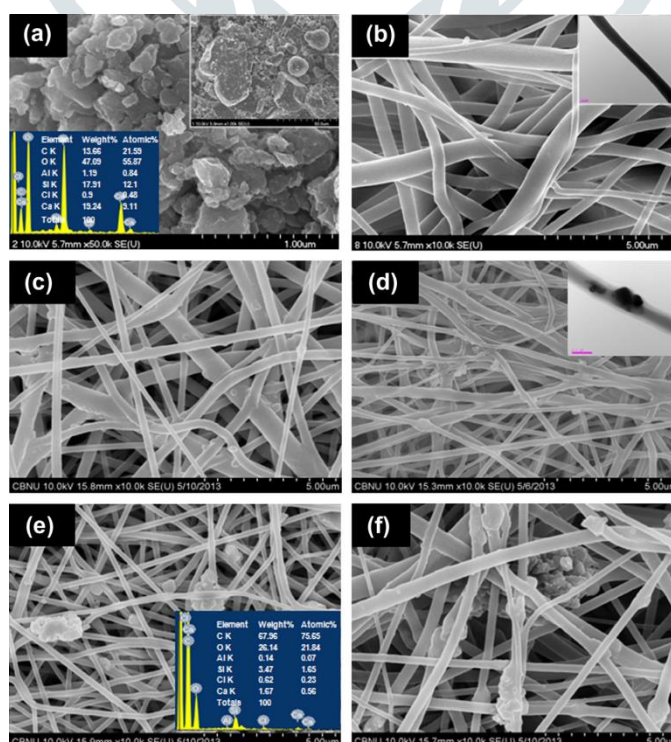


Fig.4. FE-SEM images of (a) grinded FAPs and (b),(c),(d),(e), and (f) are PU electrospun fibers containing 0, 10, 30, 50 and 70 wt% FAPs respectively.[13] (with permission from Elsevier)

Aromatic compounds like benzene, toluene, and xylene with low ionization potentials are generally easily adsorbed by electrospun fly ash fibrous membranes as these compounds are unstable. Using fly ash fibrous membranes is an inventive idea that creates a means of utilizing waste fly ash to produce fibrous membranes that can be used to filter air pollutants. Distinct absorption kinetics on the surface of the composite nanofibers is due to the chemical framework and structural effects of these aromatic hydrocarbons. [14]

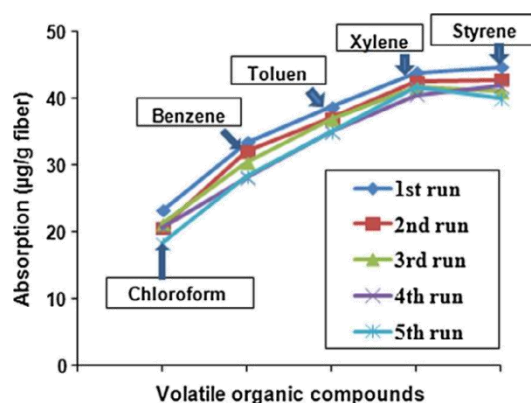


Fig.4. Cyclic adsorption behaviour of VOCs on polyurethane composite mat acquired from 30 wt% fly ash particles containing polyurethane solution. [13] (with permission from Elsevier)

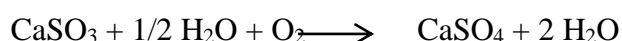
These electrospun nanofibrous membranes of high surface-volume ratio are drawn from a rotating collector which act like a mat placed over a foil or sheet entrapping the VOC's. Subsequently, these adsorbed pollutants are analyzed through a VOC analyzer. Considering that they can efficiently collect various air contaminants, electrospun nanofibers have significant promise in the sustainable energy, environmental quarters, health, clothing and textiles. [15]

4.2 Removal of SO_x

During the combustion of coal, sulphur present on coal is responsible for the emission of SO₂, a colourless poisonous gas which when reacts with atmospheric moisture causes acid rain phenomenon. Flue gas desulfurization (FGD) systems or Spray-tower scrubbers are widely used for the removal of SO₂ with higher efficiency up to 95%. However, these systems are susceptible to major concerns like liquid re-entrainment, corrosion, and the need for treatment of spent liquid. For instance, to eliminate SO₂ from exhaust gases, dry FGD mechanism is employed using adsorbents like limestone (CaCO₃) and slaked lime (Ca(OH)₂).

FGD outline :

Gas to adsorbent reaction :



Flue gas containing SO₂ is made to react with the limestone slurry, thereby producing calcium sulfite which is then turned into gypsum (CaSO₄) under forced oxidation. Many researchers are now trying to synthesize calcium-based adsorbents from coal ash, since the latter is an inexpensive solid waste. Adsorbents fabricated from fly ash differ in their ability to capture SO₂ depending on their porosity and surface area. Coal ash being versatile in structure with large surface area, therefore, acts as good adsorbent with Ca(OH)₂. Desulfurization experiments were performed using a fixed bed test rig, by K.T. Lee et al [16] using CaO, fly ash, and CaSO₄ as raw materials. Fly ash combined with slaked lime [CaO] or quick lime [Ca(OH)₂] in the presence of water is established as an economical adsorbent in desulfurization process. An adsorbent composed of fly ash, CaO, and Ca(OH)₂ is successfully produced. This FA/CaO/Ca(OH)₂ adsorbent showed greater SO₂ adsorption capacity than pure fly ash, slaked lime or quick lime. This is because the adsorbent had a larger specific surface area. The capacity of fly ash to absorb SO₂ mainly depends on the surface area, Ca ion content and pore structures. Activated carbon derived from fly ash can also be used to adsorb SO₂ apart from NO_x. In another study, zeolites were synthesized using coal fly ash which was used to adsorb SO₂ from the air. These zeolites were found to be very effective in removing almost all the SO₂ in the flue gas. A brief review of synthesis of zeolitic fly ash is studied further in this paper.

To elucidate the portrayal of SO_2 in desulfurization, many studies have run to validate that desulfurization largely depends on the adsorbents and their surface area of contact and is expected to increase exponentially with the increase in surface area.

4.3 Removal of CO_2

The primary source of emission of CO_2 into the atmosphere is fossil fuels, such as coal. This gaseous pollutant is a chief cause of the greenhouse effect, causing the temperature of the atmosphere to increase by about 0.2 degrees Celsius every year according to IPCC reports. Nevertheless, there were many applications that have been endorsed to reduce the emission of CO_2 and its capture in a very effective way. The most popular CO_2 capture process is through absorption using chilled ammonia as a solvent [17]. However, despite its high efficiency, it is an expensive process due to high regeneration costs of absorbent, oxidative degradation of solvent, solvent losses by volatilization, and corrosion.

Due to the following issues, an alternative process must be used to capture CO_2 . Adsorption and desorption take place simultaneously and the former being a physisorption. Adsorption or desorption seeks for an adsorbent with greater surface area support and porosity, hence micro porous materials, such as zeolites, are used due to their high adsorption capacity [18]. Zeolites of the type NaX and NaA are used as they exhibit greater selectivity for CO_2 compared to other gases.

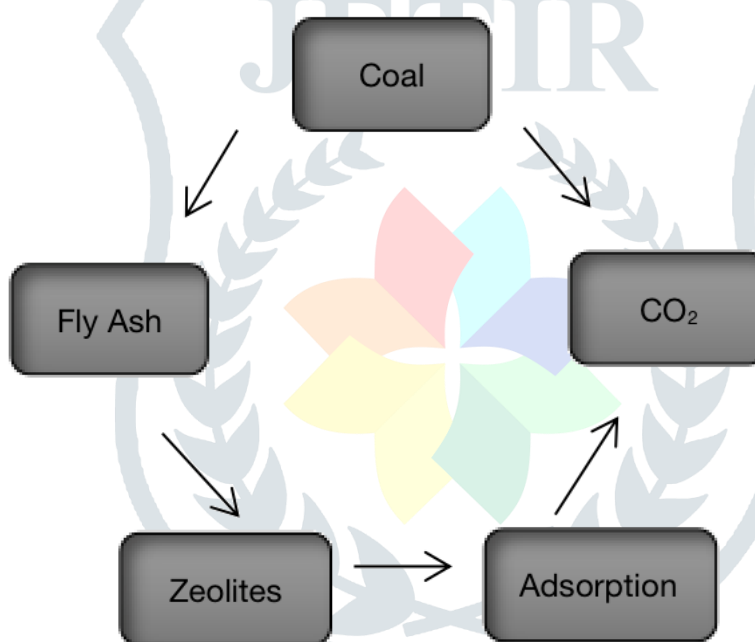


Fig .5. A cycle of CO_2 adsorption by fly ash zeolites .

Now the synthesis of zeolites is carried out in a two-step process, first is the prior fusion of fly ash with NaOH followed by a hydrothermal reaction. It was found that the zeolites synthesized from fly ash showed high CO_2 adsorption capacities and zeolite X showed adsorption capacities similar to that of commercial zeolites. Zeolite X (NaX) showed higher adsorption capacity when compared to Zeolite A (NaA). Also, the CO_2 adsorption capacity of the zeolite was found to be heavily dependent on temperature and is inversely proportional to it. In an experiment run by T Gunawan et al, it was seen that for a temperature of 30°C , 40°C , and 50°C , the adsorption capacity and the desorption were 9.51 wt%, 5.60 wt%, and 3.47 wt%, and 59.83%, 69.70%, 77.501% respectively.[19]

4.4 Removal of NO_x

NO_x emissions include nitrogen oxides that are major environmental pollutants such as nitrogen dioxide (NO_2), nitric oxide (NO), etc. most of them being colorless. These pollutants result in the formation of ground-level ozone that poses a threat to human life causing respiratory diseases, eye irritation, and chronic lung infection. Under ambient conditions, NO_x reacts to form nitrate particles and also reacts with sulfur to form acidic

aerosols. Both nitrate particles get in contact with atmospheric moisture and contribute to the formation of acid rains. [20]

Unburned carbon in fly ash promotes the adsorption of NO_x pollutants from the air largely because of the surface area. Therefore, this carbon can be excited to further enhance the adsorption capacity of fly ash. Fly ash also contains Mn and Fe oxides (such as MnO_2 , and FeO) which show great catalytic activity in NO removal. A work conducted by Kai Qi et al 2018 revealed that the impregnation technique was implemented to fabricate various MnO_x based FA catalysts.[21] This is one of the most popular methods for catalyst preparation. Fly ash is immersed in a precursor solution (Mn or Fe oxides). The slurry obtained, is first dried and then calcined at an appropriate temperature in the presence of catalysts. Later BET tests were carried out to calculate the adsorption capacity.

5.0 Fly ash applications in water treatment :

Zeolites can be used extensively in water treatment for removal of turbidity, heavy Metals, Organic Matter, Inorganic Matter and odors. They also have innumerable applications as a catalyst and adsorbents due to their consistent pore size and massive surface area.[22] Thus converting fly ash into Zeolites can deal with ever plaguing problem of fly ash disposal and hence we can make the best of what's left behind in regard to fly ash utilization.

Fly ash conversion into zeolites does not imply that the issue of fly ash disposal has been taken care of. The performance of zeolite thus formed will determine the feasibility of the conversion. Zeolitic formation from fly ash is complicated due to the composition of chemical entities in fly ash which varies with a number of factors as discussed earlier. Zeolites formed from fly ash such as Zeolite A and faujasite have better ion exchange properties compared to naturally occurring and other synthetically formed zeolites. These Zeolites have been shown to have a good affinity towards Cs^+ and Co^+ found generally in nuclear wastes and NH_4^+ generally found in wastewater samples.

5.1 Synthesis of Zeolites

Fly ash before being utilized for the preparation of zeolites has to be screened for the removal of large particles, it has to be calcinated at 800°C in order to remove unburnt carbon and other volatile components. Dealumination of fly ash is done by acid treatment to a certain extent which helps in improving the activity, thermal stability, and better catalytic activity.

Sodium hydroxide and the treated fly ash were milled and fused in a predetermined weight ratio. The temperature at which the process took place for about an hour was in the range of $500\text{--}650^\circ\text{C}$, the resultant mixture was further ground and added to water after being cooled to room temperature. Formed slurry is agitated repeatedly and is left to settle at around 90°C for about 6 hours. The resultant precipitate is washed filtered and dried in order to remove excess sodium hydroxide. This process of formation of zeolites from fly ash is called as hydrothermal treatment.[20]

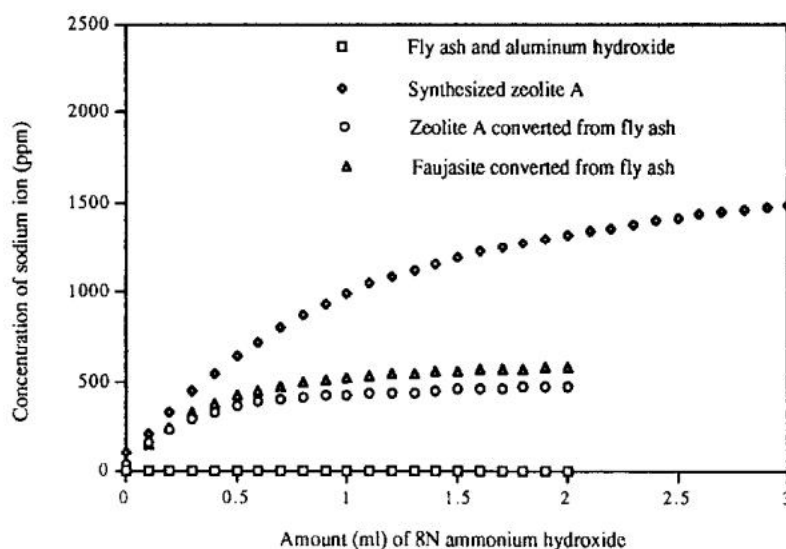


Fig.6. Concentration of sodium ions on 80ml solution of 1.8 g of zeolite or fly ash as a function of the amount of 8N ammonium hydroxide added.[21] (with permission from Elsevier)

The growth of formed zeolite crystals can be attributed to nucleation which is a function of the alkalinity of the resultant mixture. The ratio of NaOH/fly ash content influences the growth of crystals directly up to a point wherein it increases with increase in the amount of NaOH to a point after which it shows a downsizing trend. Fusion temperature in the vicinity of 823K was found to bring out the maximum crystallinity among the zeolites, above this point the crystallinity was found to decrease. The aging time increases the crystallinity of the zeolite up to a time of 24h beyond which it attains a point of saturation, however the maximum amount of silica alumina ratio was found to be at 18h which was valued at 1.72 hence for an aging time of 18h is optimal for high crystallinity and silica alumina ratio.[22] Hydrothermal treatment time increases the surface area of the prepared zeolite up to a time of 6h and then decreases. It was also conclusive that there was no appreciable crystal growth beyond this time, this was in accordance with the results published by TatiÖ and DrÖaj (1985).

Synthesized zeolites contain certain components along with silica and alumina, these components will act as poison during the catalytic utilization of zeolites. These undesirable components can be removed by acid treatment which will increase the amount of silica in the mixture to an extent. The thermal stability of the synthesized zeolite is found to be far less than that of the commercially available ones. The synthesized zeolite would lose its crystallinity above 973K and the structure of zeolite was found to disintegrate beyond 1073K.[23]

5.2 Adsorption of various substances from waste water using fly ash

Coagulation, flocculation integrated with flotation and filtration, precipitation, electroflotation, electrokinetic coagulation, etc are the orthodox techniques used for the removal of organic matter from wastewater. These methods may give rise to other contamination anomalies due to the use of excessive chemicals, Also the disposal of accumulated sludge thus formed is a hassle to contend with. These methods are commercially demanding and not so soothing electrically. Other methods such as micro-filtration, nanofiltration, and membrane separation are not so efficient in dealing with large volumes of effluent also they need periodic replacement of membranes with is quite often, the problem of membrane deterioration is pronounced in this regard. Hence the fly ash application in effluent treatment is quite viable as it acts as an low cost adsorbent producing high quality effluent post treatment especially since the former is vastly economic and feasible.[24] Due to the fact that the properties of fly ash depend on where it comes from, numerous studies have been conducted on the use of fly ash from various sources to remove organic matter from effluent water.

The lack of toxic heavy metals in fly ash obtained from sugar industry makes it capable of the adsorption of aromatic alcohols. Even though the adsorption capacity of activated carbon is about 3.6 times that of fly ash, the latter's economic attributes are dominant enough to overshadow the adsorption capacity. The various experiments conducted reveal that the temperature and pH of the solution influence the adsorption of phenols onto fly ash. Various researches were performed in order to know the dependency of contact time, carbon content, and various other parameters of fly ash during the absorption of various phenols. For example, for the adsorption of 2,4-dinitrophenol(DNP), fly ash with high content of carbon is prioritized. The adsorption

decreases with an increase in pH irrespective of the carbon content of the fly ash. The electrostatic interaction between the positively charged carbon present on the fly ash surface and the ionized DNP molecules characterizes the adsorption. Studies have also proven that the phenol adsorption onto the fly ash is controlled by intraparticle diffusion thus the presence of an abundance of carbon, lime, and silica makes fly ash an impressive adsorbent for the removal of phenol from waste water.[24]

Coal ash can be used to remove planar organic contaminants from waste water, such as poly-cyclic aromatic hydrocarbons (PAHs) and some poly-chlorinated biphenyls (PCBs), due to the planar structure of the residual carbon, which has a strong affinity for organic contaminants. The percentage of aromatic compounds that are eliminated is significantly higher when compared to functional groups like alcohols, aldehydes, and ketones. When the characteristics of the fly ash and the adsorption data are compared, it becomes evidently clear that the residual amount of carbon in the fly ash is the most important factor in determining the adsorption rate.

The commodity of pesticides takes precedence in water pollution compared to other organic contaminants. Bagasse fly ash which is a byproduct of the sugar industry is used to eliminate pesticides such as DDD and DDE [25] from waste water. The percentage removal is found to be around 93%, increasing the adsorbent dosage and decreasing the dimensions of the particles facilitated the removal of pesticides. Using column experiments, at optimal conditions the percentage removal was enhanced to around 97-98%. At low concentrations, film diffusion depicts the adsorption whereas at higher concentrations particle diffusion mechanism controls the adsorption. Promising results were obtained when fly ash was impregnated with the oxides of Al, Cd, Ni, etc was used for the removal of organic acids from wastewater. The percentage removal was higher than that of pristine fly ash.

Apart from organic substances, fly ash can be employed to eliminate certain inorganic matter like phosphate, boron and sulphate. The presence of Al, Fe, Ca and silica make it viable for the removal of phosphate ions. Fly ash with different composition of calcium was used for removal of phosphate from wastewater and it was concluded that the precipitation of phosphate ions with Ca^{+2} ions facilitated its removal. Using fly ash with higher calcium content at alkaline conditions, higher removal of phosphate was achieved. The same was mirrored while using all pH values for different calcium concentration in fly ash.

The presence of fluorine in water causes serious **discrepancies** in human life wherein long exposure will result in conditions such as skeletal fluorosis, arthritis, and many more abnormalities. High fluoride containing effluents are generally a result of coal-based power plants or semiconductor industries, in which the fluoride content may mount up to 2% hence the need for defluoridation is imminent.[4] Fluorine from wastewater can be removed either by adding a chemical to the water and precipitating it or by the addition of a suitable substrate for adsorption or ion exchange. Coal ash proved to be an effective alternative for processing fluorine, since 100% removal of fluorine was evidenced even though the process was time consuming.

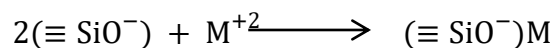
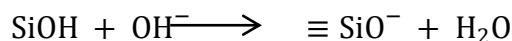
Boron is found naturally as boric acid and borate ions in large water bodies, not much light has been shed on fly ash for facilitating the removal of boron. Batch and column reactors were used by Ozturk and Kavak[26] to investigate the adsorption of boron from aqueous solutions using FA. But from the few experiments carried out, it is evident that the adsorption of boron is done through a ligand exchange mechanism. The adsorption of boron increases with an increase in pH of the solution when considering minute concentrations.[27]

5.3 Adsorption of Heavy Metals from waste water :

Heavy metals are among the common contaminants present in effluents, them being a persistent pollutant has the ability to climb up the food chain right from marine ecosystems to human bodies. Heavy metals, even at low concentrations are harmful to the human body its presence poses many health complications which should be avoided at all costs. Conventional methods of removing heavy metals from wastewater include physiochemical techniques such as precipitation, flotation, ion- exchange, reverse osmosis, membrane filtration, and electrodialysis among others. These aforementioned methods are highly expensive and demand a lot of maintenance and service in the long run. In such cases, using fly ash as a viable adsorbent is a no brainer subjected to the adsorbing capabilities of fly ash for different metals. The efficient adsorption of metals from effluent water can be accomplished using modified fly ash. Many studies have been carried out and many experiments have been recorded in this regard, the results of which have been reviewed down the lane. [28]

5.4 Adsorption Mechanism:

Fly ash is a material of versatile composition, its surface predominantly consists of SiO_2 and Al_2O_3 with whom the metal ions have a good rapport. Oxygen atoms attached to the silicon have low basicity and are free to react with water since the affinity of the central atom towards electrons is high, this causes the surface of silica to act as a mild acid. Oxygen on reacting with water results in the formation of SiOH with the prospect of pH depicting the charge on silica surface. For low pH values, the resulting surface is positively charged and vice versa. Similar properties are shown by Aluminum and Iron.[29]



Copper:

Copper adsorption using fly ash as the adsorbent was studied by Pandey et al, the experiments conducted have paved a way for understanding the ideal conditions for the eradication of copper. The effect of concentration was studied, and it was evident that it plays an important role in removal of copper from the solution. The capability of adsorption for fly ash increases with increase in temperature. The process was deemed to be endothermic. The heightened rate of intraparticle diffusion, variation in pore size, desolvation of adsorbing species may attribute to the fact. The firm affinity between the adsorbate and adsorbent is obvious from the change in enthalpy during the process. The adsorption was found out to be feasible at higher temperatures due to the negative and seemingly decreasing values of free energy change. Varying the solubility of alumina with pH shows the maximum solubility to be near the neutral pH neighborhood, which indicates a small number of sites available for the Cu^{+2} ions adsorption. The blueprint for maximal Cu^{+2} ions adsorption maybe confronted as,



A whopping 100% removal of copper was adsorbed at an elementary concentration value of 10^{-4} M, at a temperature of 30°C . [30]

Arsenic:

The employment of pristine coal based fly ash for the elimination of arsenic turned out to be a disappointment since after adding the pristine fly ash, it is found that the concentration of arsenic in the solution increased. Hence the modification of fly ash was carried out by coating it with ferrous sulphate, which increased the affinity of fly ash in adsorption of arsenic.

From the experiments carried out by C R Ramakrishnaiah and Deepika B Naikar, the optimal parameters for the removal of arsenic were presented as follows, the ideal dosage of ferrous sulphate laced fly ash is 0.5 gm, at a pH level in the range of 8-10 produced best results in favor of the experiment. with a contact time of 15 minutes and starting with the initial As concentration of $140\mu\text{g/l}$ and agitating the solution at 150RPM, the removal efficiency was found to be maximum at 80-100%. [31]

Chromium :

Adopting traditional fly ash for the removal of heavy metals from water is not mandated, however, bagasse fly ash which originates from the sugar refinery has been utilized to fulfill this task. The treatment of the ash with hydrogen peroxide was carried out in order to remove lingering organic matter. It was then reduced to an appropriate size and stored in an optimal manner to for use down the lane.

From the experiments conducted by V.K. Gupta and Imran Ali, Various parameters have been experimented with substantially in order to find the ideal values at which maximum efficiency is viable.[25] For a contact time of 40-60 minutes, at an initial concentration of 20ppm, pH in the close vicinity of 5.0, amount of fly ash used is around 10g/l , the whole process if being executed at a temperature of 30°C will yield in a adsorption efficiency of 95-96%.

Lead :

Lead being a heavy metal, is a harmful entity in wastewater since excess quantities of lead will lead to many diseases and symptoms in the human body. Removal of lead can be facilitated by using fly ash which was evident from the experiments conducted by Anca et al. For broad concentrations and low contact times, adsorption of lead is highly favorable using FA-Z, a modified form of activated fly ash.[32] The effectiveness of FA-Z for the removal of lead is found to be better than that of the highly effective micro porous cation exchanger, therefore ion exchange abilities are enhanced by fly ash zeolitization. [33] Selectivity for the adsorption of heavy metals under various conditions is found to be dependent on the ionic radii of the metals such as $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$. Upon investigation it has been found that affinity for the adsorption of lead is high under ambitious adsorptive conditions.

5.5 Zinc Oxide Nanofibers and fly ash:

Modification of fly ash using Zinc oxide nanofibers proved to be instrumental in increasing the activity of fly ash since, zinc oxide being an n-type semi conductor has ingenious applications in photocatalysis and water treatment. The zinc oxide nanofibers made using electrospinning technique, provides new ways of utilization by doping, coupling, increasing sensitivity etc. However the drawbacks of using the ZnO nanofibers is their poor adsorption capability which can be increased by the use of fly ash. Pairing of oxides in fly ash with ZnO resulted in formation of a composite at the interface. This fine material is proven to have increased photocatalytic properties compared to that of pristine compounds.

Method of Fabrication of FA/ZnO nanofibers:

Fly ash nanofibers can be prepared by dispersing the ball milled fly ash powder in water, the solution is stirred for about 6 hours after it is exposed to ultrasonication for 3 hours, the suspension was allowed to sediment during which the heavier particles took residence at the base of the tank.[33] Prior to electrospinning, centrifugation was used to separate the fly ash nanoparticles and drying was incorporated for 6 hours at 120°C. Electrospinning is followed by a calcination procedure for the formation of the FA/ZnO composite.

Dyes are one of the most frequently used substances that are used in various industries such as wood, cotton, silk among others. One such dye methylene blue is used to gauge the performance of the synthesized nanofibers. MB is self degrading when exposed to sunlight but the experiments have shown an inconsequential effect on self degradation of MB. The incorporation of FA/ZnO nanocomposites increases the rate of degradation of MB since the metal oxides in fly ash such as iron oxide and titanium oxide facilitate in improving the light adsorption capacity which results in elevated photocatalytic activity.

The ability of FA to adsorb the dye nurtures its ability to incorporate the photocatalytic activity using ZnO which is evident using the Zinc Oxide NF and FA as one. From the adsorption data it is evident that the removal of the dye was about 4% using pristine ZnO NF's whereas, from the use of the synthesized nanofibers, the removal is found to be around 40% over a span of 45 minutes. The higher adsorption capacity while using ZnO/FA NF's can be attributed to the alkaline condition of the solution, homogenous distribution of fly ash on ZnO nanofibers reinforces the surface area which in turn has the intended effect. The electrical conductivity of the nanocomposite is influenced by the photocatalytic process since it includes oxidation and reduction as essential processes. [33]

5.6 Fly Ash based catalyst

Heterogeneous catalysts are of greater importance due to their recyclability, robustness and low operational cost and hence can be easily recovered from the reactants. Using fly ash as a base, a variety of catalytic active sites can be created within the geopolymer through an ion-exchange method. Adding on, geopolymers made from a variety of class F fly ashes have also been shown to work as heterogeneous catalysts[34]. A study held by Al-zeer *et al* presents the synthesis of sustainable bifunctional heterogeneous catalysts made from fly ash-based geopolymer, particularly those with a high Ca content (C-class) fly ash [35]. Many studies have taken place to fabricate FA based catalyst using different preparation methods posing various applications, for example 5FeSCA prepared by treating it with phosphoric acid and then followed by loading of iron for VOC oxidation of

n-butanol[36]. $\text{CuCl}_2\text{-MF}$ catalyst was prepared by impregnation of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and thermal treatment for mercury oxidation and removal of flue gas. [37]

Table 1. list of Abbreviations

ASTM	American Standard of Testing Materials.
BET	Brunauer-Emmett-Teller
CFA	Coal Fly Ash
DDD	Dichlorodiphenyldichloroethane.
DDE	Dichlorodiphenyldichloroethylene
DNP	dinitrophenol.
FA	Fly Ash
FAP	Fly Ash Particles.
FGD	Flue Gas Desulphurization.
HM	Heavy Metals.
IPCC	Intergovernmental Panel on Climate Change.
MB	Methylene Blue.
PAC	Polycyclic Aromatic Hydrocarbons.
PCB	Polychlorinated biphenyls.
POC	Planar Organic Contaminants
PU/PUR	Polyurethane.
SEM	Scanning Electron Microscope.
VOC	Volatile Organic Compounds

6.0 Conclusions

- Fly ash can be utilized in many ways instead of disposing off as landfill. Fly ash has applications in the fields of building, agriculture, and various sectors are just scraping the surface.
- Composed mainly of unburnt carbon and alumino silicates, the prospects of fly ash are of notable worth in the field of treatment and purification of water and air.
- Being a sustainable adsorbent for the adsorption of metals like Arsenic, Barium, Lead, Chromium, and various organic and inorganic compounds makes it a good resource while effectively enhancing the economics of the process.
- Modification using compatible materials is proven to be viable and increases the adsorption capacity of fly ash as in the case of formation of fly ash-zeolites.
- Hydrothermal treatment has been instrumental in converting fly ash into an effective absorbent for various purposes.
- Utilization of fly ash as a heterogeneous catalyst is picking up pace since the size and shape of the particles makes it a suitable compound to be electrospun and increase the catalytic activity of ZnO nanofibers and other such compounds as discussed.
- This paper also threw light on heterogeneous catalytic activity of fly ash and different catalysts produced from it. Owing to their recyclability, low preparation costs, and eco-friendly, coal fly ash catalysts are proven to be effective in all the fields discussed in this article.

References

- [1] <https://www.worldometers.info/coal/india-coal>.
- [2] Roy E. Bickelhaupt (1975) Surface Resistivity and the Chemical Composition of Fly Ash, Journal of the Air Pollution Control Association.
- [3] R.S. Iyer, J.A. Scott, Power station fly ash—a review of value-added utilization outside of the construction industry, Resour. Conserv. Recy. 31 (2001) 217–228.
- [4] A review on the utilization of fly ash M. Ahmaruzzaman* Department of Chemistry, National Institute of Technology Silchar, Silchar-788010, Assam, India.
- [5] www.elsevier.com/locate/jmrt

- [6] ASTM standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete (C618-05). In: Annual book of ASTM standards, concrete and aggregates, vol. 04.02. American Society for Testing Materials; 2005.
- [7] ASTM C311/C311M-22 Standard Test Methods for Sampling and Testing FlyAsh or Natural Pozzolans for Use in Portland-Cement Concrete.
- [8] Environmental-benign utilisation of fly ash as low-cost adsorbents Shaobin Wang*, Hongwei Wu . Department of Chemical Engineering, Curtin University of Technology, GPO Box U1987, Perth, WA 6845, Australia.
- [9] Morphology, Mineralogy and Chemistry of Fly Ash from the Ptolemais Power Stations, Northern Greece, and its potential as partial Portland cement substitute , Cristina Apostolidou , Andreas Georgakopoulos , Aristotle University of Thessaloniki.
- [10] Article Feedback Pilot, Coal, Coal-fired power stations, y 7 más.
- [11] Elke Scholten, Lev Bromberg, Gregory C. Rutledge, T. Alan Hatton Electrospun polyurethane fibers for absorption of volatile organic compounds from air, ACS Appl. Mater. Interfaces 3 (10) (2011) 3902–3909 .
- [12] Comparison of Adsorption/Adsorption of Volatile Organic Compounds (VOCs) on Electrospun Nanofibers with Tenax TA for Potential Application in Sampling Lanling Chu, Siwei Deng, Renshan Zhao, Jianjun Deng, Xuejun Kang .
- [13] Composite electrospun fly ash/polyurethane fibers for absorption of volatile organic compounds from air, Han Joo Kim, Hem Raj Pant, Nag Jung Choi, Cheol Sang Kim, Chemical Engineering Journal ,Volume 230, 2013.
- [14] Ge, J.C.; Choi, N.J. Fabrication of functional polyurethane/rare earth nanocomposite membranes by electrospinning and its VOCs absorption capacity from air. Nanomaterials 2017, 7, 60. [CrossRef].
- [15] Filatov V, Budyka A and Kirichenk V. Electrospinning of micro and nanofibres. fundamentals and applications in seperation and filtration processes. USA: Begell house, 2007, p.488.
- [16] K.T. Lee, A.R. Mohamed, S. Bhatia, K.H. Chu, Removal of sulfur dioxide by flyash/CaO/CaSO₄ sorbents, Chemical Engineering Journal, Volume 114, Issues 1–3, 2005.
- [17] Victor Darde, Kaj Thomsen, Willy J.M. van Well, Erling H. Stenby, Chilled ammonia process for CO₂ capture, Energy Procedia, Volume 1, Issue 1, 2009 .
- [18] Hedin et al., 2013; Melendez-Ortiz et al., 2014; Zelen ak et al , 2008.
- [19] Teuku Daniel Gunawan, Mariana, Edi Munawar, Syawaliah Muchtar, Preparation and characterization of chemically activated adsorbent from the combination of coconut shell and fly ash, Materials Today: Proceedings, Volume 63, Supplement 1, 2022.
- [20] Health effects of acid aerosols formed by atmospheric mixtures. MT Kleinman, R F Phalen, W J Mautz, R C Mannix, T R McClure, and T T Crocker.
- [21] Conversion of fly ash into zeolites for ion-exchange applications Wei-Heng Shih, Hsiao-Lan Chang. Department of Materials Engineering, Drexel University, Philadelphia, PA 19104, USA .
- [22] Kai Qi, Junlin Xie, Di MEI, Feng He, De Fang. "The utilization of flyash-MnOx/FA catalysts for NO_x removal", Materials Research Express, 2018
- [23] Wei-Heng Shih, Hsiao-Lan Chang, Conversion of fly ash into zeolites for ion-exchange applications, Materials Letters, Volume 28, Issues 4–6, 1996.
- [24] N. Nirmala, V. Shriniti, K. Aasresha, J. Arun et al. "Removal of toxic metals from wastewater environment by graphene-based composites: A review on isotherm and kinetic models, recent trends, challenges and future.
- [25] X Querol, J.C Umaña, F Plana, A Alastuey, A Lopez-Soler, A Medinaceli, A Valero, M.J Domingo, E Garcia-Rojo, Synthesis of zeolites from fly ash at pilot plant scale. Examples of potential applications, Fuel, Volume 80, Issue 6, 2001.
- [26] **Ojha, K., Pradhan, N.C. & Samanta, A.N. Zeolite from fly ash: synthesis and n characterization. Bull Mater Sci 27, 555–564 (2004).** .
- [27] Role of Fly Ash in the Removal of Organic Pollutants from Wastewater M. Ahmaruzzaman , Energy & Fuels 2009 23 (3), 1494-151.
- [28] Gupta VK, Ali I. Removal of DDD and DDE from wastewater using bagasse fly ash, a sugar industry waste. Water Res. 2001 Jan;35(1):33-40. PMID: 11257890.
- [29] Ozturk, D. Kavak, Adsorption of boron from aqueous solutions using fly ash: batch and column studies, J. Hazard. Mater. 127 (2005) 81-88

- [30] Boron Release and Sorption by Fly Ash as Affected by pH and Particle Size J. F.Hollis, R. Keren, M. Gal First published: 01 April 1988 .
- [31] Adsorption of heavy metal ions from aqueous solution by fly ash I.J. Alinnor Department of Pure and Industrial Chemistry, Federal University of Technology,P.M.B. 1526, Owerri,Imo State, Nigeria .
- [32] Jianlong Wang, Xuan Guo, Adsorption kinetic models: Physical meanings, applications, and solving methods, Journal of Hazardous Materials, Volume 390,2020.
- [33] K.K. Panday, Gur Prasad, V.N. Singh,Copper(II) removal from aqueous solutions by fly ash, Water Research, Volume 19, Issue 7, 1985.
- [34] C R, Ramakrishnaiah & Naikar, Deepika. (2016). ARSENIC REMOVAL FROM DRINKING WATER USING FLYASH AS AN ADSORBENT. International Journal of Research in Engineering and Technology. 5. 1-4.
- [35] Maria Visa; Luminita Isac; Anca Duta (2012). Fly ash adsorbents for multi-cation wastewater treatment. , 258(17), 0–6352.
- [36] S. Golbad, P. Khoshnoud, N. Abu-Zahra. "Hydrothermal synthesis of hydroxy sodalite from fly ash for the removal of lead ions from water", International Journal of Environmental Science and Technology, 2016.
- [37] Bishweshwar Pant, Gunendra Prasad Ojha, Hak-Yong Kim, Mira Park, Soo-Jin Park. "Fly-ash-incorporated electrospun zinc oxide nanofibers: Potential material for environmental remediation", Environmental Pollution, 2018.
- [38] **Alzeer, M.I.M.; MacKenzie, K.J.D. Synthesis and Catalytic Properties of New Sustainable Aluminosilicate Heterogeneous Catalysts Derived from Fly Ash. ACS Sustain. Chem. Eng. 2018, 6, 5273–5282. [CrossRef].**
- [39] Al-Zeer MIM, MacKenzie KJD. Fly Ash-Based Geopolymers as Sustainable Bifunctional Heterogeneous Catalysts and Their Reactivity in Friedel-Crafts Acylation Reactions. Catalysts. 2019; 9(4):372. <https://doi.org/10.3390/catal9040372>.
- [40] Pande G, Selvakumar S, Batra VS, Gardoll O, Lamonier JF. Unburned carbon from bagasse fly ash as a support for a VOC oxidation catalyst. Catal Today 012;190(1):47–53.
- [41] Yang J, Zhao Y, Zhang J, Zheng C. Removal of elemental mercury from flue gas by recyclable CuCl₂ modified magnetospheres catalyst from flfly ash. Part 1. Catalyst characterization and performance evaluation. Fuel 2016;164:419–28.