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RESEARCH ARTICLE

Comparative Study of Different Sorbents to Adsorb Various Components from Flue Gases and/or Exhaust Gases.

Kanagarethinam Selvaraj, Vishal Patel Haribhai
PG student, Amity Institute of Biotechnology, Amity University, Noida, Uttar Pradesh, India.

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Corresponding Author

Kanagarethinam Selvaraj.

Abstract

From 1960s till now numerous studies were taken in industrialized countries and those surveys confirm the antagonistic effects of air pollution on human fitness. In order to encounter rigorous environmental regulation there is need of fast track ensnaring approach that shrinks those emissions. Conferring to literature survey experimental line of attack for adsorbing toxic pollutants from emission is the best choice. From various physico- chemical test and characteristics of various pollutants from three major types of industrialized adsorbent. Oxygen based sorbent called molecular sieve and carbon based sorbent called activated carbon can be opted for the study. Comparative study of adsorbents was made and find out a particular type of molecular sieve 4A and activated carbon 1000IV compounds. Based on that a combination device was made with extended surface area through sieves. From this device field work has been done in order to find the emission control in both gasoline and diesel system through changes in their CO2, O2, HC, CO, HSU levels. The results show the effective trapping of these pollutants on the surface as well as in their internal pore opening. We also find the efficiency will increase drastically as we increase the reaction area on the surface of various sorbents.

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Introduction:-

Preliminary information about Air pollution:-

Our worry about air pollution and its effect on human health stemmed primarily from three major air pollution incidents- Meuse Valley of Belgium in 1930, Donora in Pennsylvania of USA in 1948, and London smog episode in 1952. These incidents stimulated many nations in Europe and North America to initiate legislative and regulatory actions to regulate open-air pollution. From the 1960s through 1980s several population-based studies were taken up in the industrialized countries and these investigations confirmed the adverse effects of air pollution on human health (Pope CA III (2000), Lave LB (1970)).

The world's reckless rising financial prudence has turned out to be the biggest polluters. As nations contest ahead to boost growth and development, their need on fossil fuels also upsurge. To support the growth, a country needs to set up more infrastructure projects, transport more goods, sale of automobiles rises, and all these, in turn, increase the fuel demand. The most polluting countries are typically nations with high population, biggest industries and production capabilities.

The main pollutants emitted from the automobiles are hydrocarbons, lead/benzene, carbon monoxide, sulphur dioxide, nitrogen dioxide and particulate matter. The main cause of vehicular pollution is the rapidly growing number of vehicles. The other factors of vehicular pollution in the urban areas are 2-stroke engines, poor fuel quality, old vehicles, inadequate maintenance, congested traffic, poor road condition and old automotive technologies and traffic management system.

Epidemiological studies of gaseous pollutants:-

A series of epidemiological studies that followed in a short period of six years from 1989 to 1995 unveiled the role of particulate matter as the chief mediator of toxic effects of air pollution (Pope CA (1995), Dockery DW (1993), Schwartz J (1992)). This finding opened a floodgate of epidemiological and toxicological investigations on fine and ultrafine particulate air pollution (Pope CA III (2004a), Brook RD (2004)). The United Nations Environment Programme has estimated that globally 1.1 billion people breathe unhealthy air (UNEP (2002)).

Epidemiological studies have shown that concentrations of ambient air particles are associated with a wide range of effects on human health, especially on the cardio-respiratory system. The WHO has estimated that urban air pollution is responsible for approximately 800,000 deaths and 4.6 million lost life-years each year around the globe (WHO (2002)). Several studies have shown that maintenance is a significant factor in vehicular emissions.

Epidemiological studies of outdoor air pollution in Western countries, in general, have not considered indoor sources and total exposures. Residents of slum households, who tend to have more health problems due to poverty, might also experience higher outdoor exposure because they live in road-side slums. In such cases, the effect of poverty on health can be confused with the effect of vehicular air pollution.

Sources of air pollution in vehicles:

In general, combustion is the chief donor to outdoor air pollution. In most cities, the major source of combustion is fuel use, which tends to increase along with population size and economic activity (Badami MG (2005)).

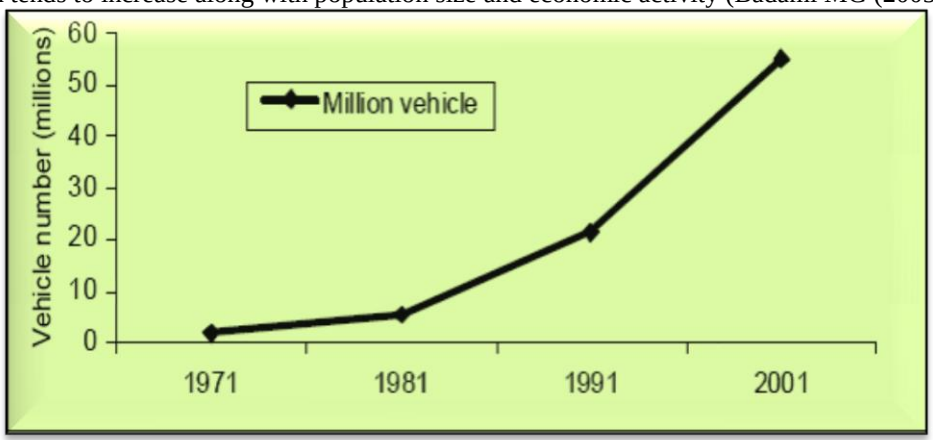


Fig 1. Motor vehicle growth in India, (Badami MG (2005)

Motor vehicles have internal combustion engine which burns a mixture of air and fuel to produce energy that propels the vehicle. The type and quantity of the pollutants released during this combustion is influenced by more than a dozen factors. The kind of fuel- petrol, diesel or CNG is just one of them.

However, fuel type is a useful indicator of potential emissions. Coal and biomass are high emitting solid fuels, petrol, diesel and kerosene are mid-emitting liquid fuels and LPG and CNG are low-emitting gaseous fuels. Transport sector consumes half of the petroleum products in the world, and same is true for India. Petroleum product consumption by motorized vehicles has nearly doubled in India in the last decade. Indian gasolines have a high volatility, and the vast majority of gasoline vehicles are carburetted, not fuel-injected.

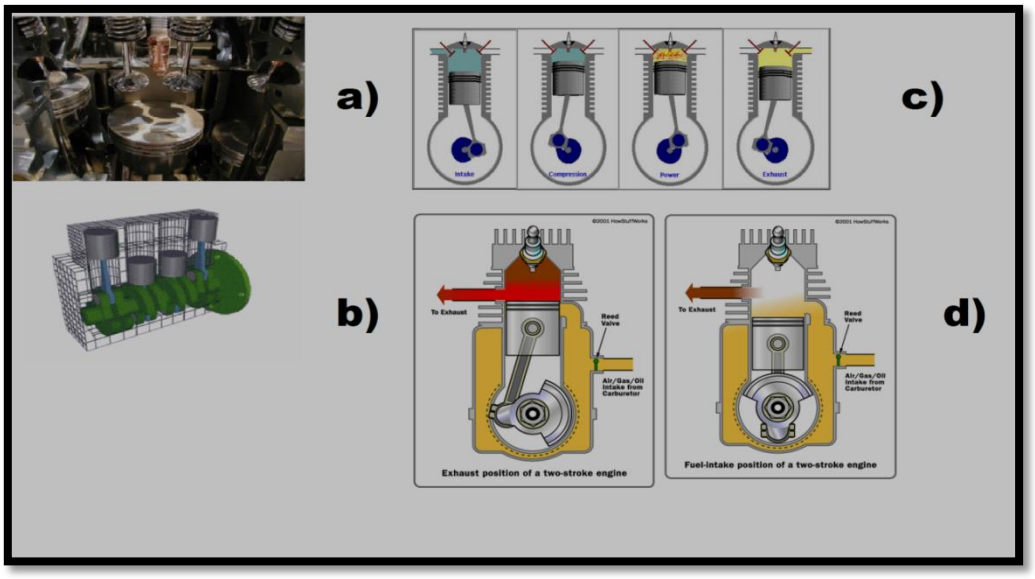


Fig2. Type of engine Used. a) Engine operation, b) Working principle of Engine Motors, c) Four Stroke Engine Operation, d) Two Stroke Engine Operation (science.howstuffworks.com)

These facts coupled with India's high ambient temperatures increases the potential for evaporating emissions rich in reactive hydrocarbons with the potential to generate ground-level ozone. Traffic congestion is yet another problem leading to high vehicular emissions. In Delhi, for example, the average speed for public transport vehicles ranged from 12 to 20 km/hr in the 1990's .Besides causing loss of time and productivity, traffic congestion increases fuel consumption and carbon monoxide and hydrocarbon emissions per vehicle-km by 200% or more (Faiz, A. et al. (1990)) Several studies have shown that maintenance is a significant factor in vehicular emissions.

Major pollutants:-

Particulate pollutants: the major toxic component of urban air:-

PM is a complex mixture of suspended solid and liquid particle in semi equilibrium with surrounding gases (Brook RD (2003)). PM may be classified as primary (particles emitted directly by emission sources) and secondary (particles formed through the atmospheric reaction of gases). The size distributions of airborne particles are important for health impact. Outdoor (ambient) PM size ranges from approximately 0.001-100 μm in aerodynamic diameter. PM is considered as the single best indicator of potential harm. There are three main size categories for PM measured in urban air:

PM10:-

They consist of PM with a diameter up to 10 μm. However, for toxicity studies, the most important particles are those having a diameter of less than 10 μm because they are respirable whereas the larger particles are not. PM10 deposit relatively quickly with a lifetime of less than 2 days, and exposure may lead to adverse responses in the lungs triggering an array of cardio-pulmonary problems (Brunekreef B (2005), Harrabi I (2006)). For every 10-μg/m3 increase of PM10, mortality from all causes increases by 0.51% and from cardiopulmonary diseases by 0.68% (Samet JM (2000)). Moreover, the rise in daily mortality from increased concentrations of PM10 persists for several days (Zeka A (2005)).

Accumulation mode or fine particles (PM2.5):-

They consist of PM with a diameter up to 2.5 μm. Airborne particles smaller than 2.5 μm are usually called fine particles. These particles may penetrate deep inside the airways and are more strongly linked to adverse health effects. Fine particles are composed mainly of carbonaceous materials (organic and elemental), inorganic compounds (sulphate, nitrate, and ammonium), and trace metal compounds (iron, aluminium, nickel, copper, zinc, and lead). There are potentially thousands of different compounds existing on fine particles that may exert harmful biological effects. The relationship between PM10 or PM2.5 exposure and acute health effects is linear at concentrations below 100 μg/m3 (Zeka A (2005)) a modest rise in PM10 or PM2.5 level has been shown to be

associated with small changes in cardiac function. Exposure to the fine particles induces oxidative stress (Schwela D (2000)).

Nuclei mode or ultra-fine particles (UFP):-

The particles in this category are smaller than 0.1 μm. They are also known as UFP. UFP are present in great number in polluted urban air. They have a carbonaceous core with attached inorganic and organic materials that can cause adverse health effects (Oberdorster G (2000)). The UFPs have less mass than course particle fraction but they are much greater in number and have a relatively large surface area to mass ratio, making them potential carriers of harmful gaseous compounds. Exposure to high doses of UFP can cause severe pulmonary inflammation and haemorrhage, high degree of alveolar and interstitial oedema, disruption of epithelial and endothelial cell layers and even death (Oberdorster G (1992), Peters A (1997)). UFPs cause health effects like cardiovascular problems, pulmonary disease, and development of cancer (Vinzents PS (2005)).

Fate of the particles:-

Following inhalation, the size of the particles determines where they are likely to deposit in the respiratory tract. Particles larger than 10 micrometre are mainly deposited in the nose and throat and are less likely to affect the health beyond the point of deposition. PM2.5 and UFPs are able to penetrate into the airways all the way to the terminal alveoli. Smaller particles are present in larger numbers and have more total surface area and bioavailability, eliciting greater biological effect.

Other pollutants:-

Sulphur dioxide (SO2):-

Sulphur dioxide (SO2) is emitted in direct proportion to the amount of sulphur in fuel. It is an acidic gas, which combines with water vapour in the atmosphere to produce acid rain. SO2 in ambient air can also affect human health (Routledge HC (2006)), particularly in those suffering from asthma and chronic lung diseases and exacerbates respiratory symptoms and impaired breathing in sensitive individuals (Lipfert FW (1994)). It can also attach to particle surfaces and may form acidic coatings. It is considered more harmful when particulate and other pollution concentrations are high.

Oxides of nitrogen (NOx):-

Nitrogen oxides are formed during combustion processes at high temperatures from oxidation of nitrogen in air. The major types of oxides of nitrogen are NO and NO_2. They are collectively known as NOx. The main source of NO is road traffic, which accounts for 49% of total NO emissions in Europe and 32% in the USA. It is emitted from both petrol- and diesel engine motor vehicles. Almost all NOx is emitted as NO, which is rapidly oxidized to more toxic NO2. NOx is a precursor of ozone formed in the troposphere. Oxides of nitrogen are immune toxic and increase the susceptibility to respiratory tract infection such as influenza. Continued or frequent exposures to high concentrations of NOx in breathing air may cause irritation of the lungs and consequent acute respiratory illness. In addition, NOx is a potent and selective vasodilator in pulmonary arterial hypertension (Perez-Penate G (2005)).

Carbon monoxide (CO):-

It is a toxic gas emitted into the atmosphere as a result of combustion processes. CO is also formed by the oxidation of hydrocarbons and other organic compounds. CO is produced almost entirely (90%) from road traffic in European cities. It remains in the atmosphere for approximately one month before being oxidized to CO2. The largest contributors of CO are petrol-fuelled vehicles. CO binds strongly to haemoglobin in red blood corpuscles resulting in the production of carboxyhemoglobin (COHb). This impairs the transport of oxygen within the blood and can result in adverse effect on tissues with high oxygen needs such as the cardiovascular and nervous systems. High concentration (>1000 ppm) for prolonged hours (>8 hr) can give rise to hypoxia. A recent study has shown that chronic exposures to CO may cause adverse birth outcomes such as reduced birth weight and intrauterine growth retardation (Hrudkova M (2004)).

Polycyclic aromatic hydrocarbons (PAHs):-

About 200 different kinds of hydrocarbons are emitted from combustion of petrol and diesel. Of these, the polycyclic aromatic hydrocarbons (PAHs) are of particular interest due to their carcinogenic potential. They enter the body through inhalation of these respirable particles. These compounds are semi-volatile in nature. Several PAHs like benzo (a) pyrene [B (a) P] are highly carcinogenic (Cohen AR(1999)).Incidence of lung cancer has been

reported in persons directly exposed to B (a) P from automobile exhausts and biomass (wood, dung, agricultural wastes) fuel burning during household cooking (Wallace LA(1984)).

Volatile organic compounds (VOCs):-

VOCs consist of various classes of carbon-containing chemicals that are gases at room temperature. They are released into the environment from petrol and diesel, especially by evaporation or as combustion products. Some VOCs (e.g. benzene) are human carcinogens while others are either respiratory tract irritants or neurotoxic (e.g. toluene, xylene). Benzene, a VOC, is a minor constituent of petrol. It is produced from combustion and evaporation of both petrol and diesel, especially the former. Combustion of petrol is the largest source (70% of total emissions) of benzene in air. Airborne benzene is primarily absorbed through the respiratory tract and then transported by blood to critical target organs. Therefore, it is possible that cumulative exposure to benzene could lead to systemic changes. Benzene has been found very harmful for human health for its hematotoxic, neurotoxic, leukemogenic and carcinogenic effects (Wallace LA (1989), Midzenski MA (1992), Farris GM (1993)). Because of this, a sustained worldwide effort is on to reduce benzene exposure as far as possible.

Health effects of air pollution:-

Table1.Pollutants and its impact on health:-

Pollutants	Local Impacts	Global Impacts	Comments
CO	Aggravates existing cardiovascular diseases, impairs visual perception and dexterity	Indirect influence on warming through competition with methane for oxidation	Transportation can be responsible for up to 95% of CO emissions in urban areas. Globally distributed gas
HC	Range of health impacts including respiratory, neurological & carcinogenic Photochemical smog precursor	Class of compounds includes methane, a potent greenhouse gas Indirect warming influence through ozone formation	A range of natural and anthropogenic sources ensures that HC species are generally available as ozone precursors
NO_x	Respiratory irritant Visibility impairment Acid precursor Photochemical smog precursor	Indirect warming influence through ozone formation	Acid and ozone production impacts of NO_x can be widely distributed through long-range transport of reservoir species
O_3	Primary constituent of photochemical smog Severe respiratory impacts Material & crop damage	Global warming impacts due to increasing background concentrations	O_3 has no direct emissions sources—NO_x, HC, and sunlight are required for production
SO_x	Respiratory irritant Visibility impairment Acid precursor	Sulfate has some cooling impact due to light scattering	SO_2 has a relatively long atmospheric lifetime leading to widespread acid impacts
PM	Cardiovascular & respiratory impacts Visibility impairment Includes acid species	Particles can influence warming or cooling, depending on carbon content & scattering abilities	Atmospheric lifetime varies with particle size
GHG		Leading to global warming through long-term atmospheric accumulation	Transportation is a major source of CO_2 but less important for methane & N_2O

Harmful effects of air pollution on human health are recognized for centuries. It has been estimated that globally 8,000 people die every day from diseases related to air pollution exposure. Each year 60,000 deaths in the United States and 500,000 deaths in China occur due to air pollution.

Global warming potential of pollutant gases:-

All greenhouse gases (GHGs) are not equal. In fact, each greenhouse gas has a unique atmospheric lifetime and heat-trapping potential. The concept of a Global Warming Potential (GWP) has been developed to allow the comparison of the ability of each greenhouse gas to trap heat in the atmosphere relative to carbon dioxide (CO2) over a specified time horizon. Often, greenhouse gas emissions are calculated in terms of how much CO2 would be required to produce a similar warming effect oven the chosen time horizon. This is called the **carbon dioxide equivalent** (CO2 eq) value and is calculated by multiplying the amount of gas by its associated global warming potential (GWP).

Table2. Global Warming Potential of GHGs:-

Global Warming Potential of Green House Gases (GHGs)

Green House Gases	Formula	Pre-industrial conc.	1995 conc.	Global Warming Potential (Over Time Horizon of 100 years)
Carbon Dioxide	CO2	278 ppm	360 ppm	1
Methane	CH4	700 ppb	1721 ppb	23
Nitrous Oxide	N2O	275 ppb	315 ppb	296
Dichlorodifluoro Methane (CFC-12)	CCI2F2	0	0.5 ppb	6200 - 7100
Chlorodifluoro Methane (HCFC-22)	CHCIF2	0	0.1 ppb	1300 - 1400
Perfluoro Methane	CF4	0	0.07 ppb	6500
Sulfur hexa fluoride	SF6	0	0.03 ppb	23900

Norms opted for controlling pollutants:-

The Journey Began in 1984 when the State of Maharashtra introduced norms for idling CO and free acceleration smoke. In 1989 the above norms were extended for the entire country. In 1991 Exhaust mass emission norms for gasoline for only CO & HC for vehicles below 3.5 ton GVW were introduced followed by Full load and free acceleration smoke regulations for diesel vehicles also introduced. In 1992 Exhaust mass emission norms for diesel vehicles / engines above 3.5 ton GVW introduced.

In 1995 Mandatory fitment of catalytic converter for gasoline Passenger cars in Metropolitan cities. In 1996 stringent norms for gasoline (CO, HC+NOx) and diesel vehicles introduced, Cold start emission test for diesel vehicles below 3.5 ton GVW. In 1998 Cold start emission test for gasoline passenger cars introduced. In 1999 India 2000 (Equivalent to Euro-I) norms introduced for passenger cars in National Capital Region (Delhi).

In 2000 Bharat Stage I norms for all category of vehicles introduced, Bharat Stage II (Equivalent to Euro-II) norms for gasoline and diesel passenger cars introduced in National Capital Region (Delhi) ,Particulate limit values introduced for diesel vehicles. In April 2005 Bharat Stage II (Equivalent to Euro-II) norms for gasoline and diesel passenger cars a will be introduced in entire country Bharat Stage II norms for 2 and 3 Wheelers will come into force in entire country Bharat Stage III (Equivalent to Euro-III) norms for gasoline and Diesel vehicles will be introduced in 11 cities

Table3. Emission Norms for 2/3 wheeler :-

Norms	CO(g/km)	HC+ NOx)(g/km)
1991Norms	12-30	8-12 (only HC)
1996 Norms	4.5	3.6
India stage 2000 norms	2.0	2.0
Bharat stage-II	1.6	1.5
Bharat Stage-III	1.0	1.0

Table4. Emission norms for passenger cars:-

Norms	CO(g/km)	HC+ NOx(g/km)
1991Norms	14.3-27.1	2.0(Only HC)
1996 Norms	8.68-12.40	3.00-4.36
1998Norms	4.34-6.20	1.50-2.18
India stage 2000 norms	2.72	0.97
Bharat stage-II	2.2	0.5
Bharat Stage-III	2.3	0.35(combined)
Bharat Stage-IV	1.0	0.18(combined)

Table5. Emission norms for Heavy Diesel vehicles:-

Norms	CO(g/kmhr)	HC (g/kmhr)	NOx (g/kmhr)	PM(g/kwhr)
1991Norms	14	3.5	18	-
1996 Norms	11.2	2.4	14.4	-
India stage 2000 norms	4.5	1.1	8.0	0.36
Bharatstage-II	4.0	1.1	7.0	0.15
BharatStage-III	2.1	1.6	5.0	0.10
BharatStage-IV	1.5	0.96	3.5	0.02

Techniques available to control gaseous pollutants:-

Various approaches have been made to remove pollutants from effluent streams. They are Absorption, Adsorption, Condensation, Incineration, etc. In general, absorbers can achieve removal efficiencies greater than 95 percent. One potential problem with absorption is the generation of waste-water, which converts an air pollution problem to a water pollution problem. So in my work I focused on adsorbents of carbon based compounds & O_2 containing compounds.

Adsorbent used in my work:-

Adsorbent Selection:-

Adsorption can perform many separations that are impossible or impractical by conventional techniques, such as distillation, absorption, and even membrane-based systems. Lately, applications for adsorption have expanded rapidly because of sharply rising environmental or quality requirements. The most important attributes of an adsorbent for any application are: capacity, selectivity, regenerability, kinetics, compatibility, and cost. Rarely will a single adsorbent be optimal in all these respects.

To evaluate those attributes a number of different approaches can be taken. First, vendors can be contacted, and if the compound is relatively common, they may be able to provide information quickly. Otherwise, especially for a relatively large application, they may be willing to do measurements. Second, you might use a database, such as one that was mentioned earlier in this article. Third, you might arrange to conduct the measurements, either yourself or by someone else in your firm. Fourth, you might arrange to have tests conducted by an independent firm, since they could offer an unbiased and cost efficient assessment.

Molecular sieves:-

Molecular Sieves are crystalline, three-dimensional molecules made up of silicon and aluminum atoms. It contain surface pores and channels which selectively absorb only molecules of a certain size and shape. Positive ions, most commonly sodium, calcium, or potassium are added in order to balance the molecule. The specific cation chosen influences the pore diameter and therefore the adsorptive properties of the molecular sieve. There are four basic grades of molecular sieves. These grades differ from one another due to their chemical composition and pore size.

Type 3A - potassium form of the compound. It will adsorb those molecules that have a critical diameter of less than three angstroms. For example: WATER, Helium, Hydrogen, and Carbon Monoxide.

Composition:- 0.6 K_2O: 4.0 Na_2O: 1 Al_2O_3: 2.0 " 0.1 SiO_2: x H_2O

Type 4A - sodium form of molecular sieves. It will absorb those molecules having a critical diameter of less than four angstroms. For example: Arzan and Ammonia. And those of 3Å.

Composition:- 1 Na_2O: 1 Al_2O_3: 2.0 " 0.1 SiO_2: x H_2O

Type 5A - calcium form of molecular sieves. It will absorb those molecules having a critical diameter of less than 5 angstroms. For example: Methanol, Ethane, and Propane, as well as species adsorbed by 3Å and 4Å resins.

Composition:- 0.8 K_2O: 0.2 Na_2O: 1 Al_2O_3: 2.0 " 0.1 SiO_2: x H_2O

Type 13X - sodium modified molecular sieve, with a pore diameter of ten angstroms. It will absorb those molecules with a critical diameter of less than 10 angstroms. For example: Chloroform, Carbon Tetrachloride, and Benzene.

Composition:- 1 Na_2O: 1 Al_2O_3: 2.8 " 0.2 SiO_2: x H_2O

Applications:-Molecular sieves are suitable for drying, purifying, and separating a wide variety of compounds, such as inorganic gases, hydrocarbons, halogenated hydrocarbons, alcohols, esters, ethers, amines, and ketones. They are being used to adsorb, and temporarily isolate molecules. When loaded on a molecular sieve. A chemical's toxicity can be reduced, its vapor pressure lowered, its corrosiveness eliminated.

Activated Carbon:-

Activated Carbon is a black, solid (powdered, granular or palletized) material resembling charcoal. It has a large internal surface area which accounts for hold impurities, contaminants or colour bodies by a process known as adsorption. Interestingly, one kg of Activated Carbon can have a surface area of as much as 500 Acres. Activated Carbon can be manufactured from any carbonaceous material like wood, saw dust coal, lignite's, fruit shells etc. either by Chemical activation which entails impregnation of a chemical on the raw material and heating it to temperature above 450 °C or by steam activation wherein superheated steam is reacted with a carbonised material at a high temperature (900-10000 °C) in a rotary kiln.

Since Activated Carbon is absolutely opaque and can neither be melted nor dissolved and it is not possible to subject it to various analytical techniques. The process of Adsorption depends on several factors like pH temperature, solvent-salute interactions, pore-size distribution etc. Performance of an activated carbon will depend on several

factors like its raw material, method of activation, temperatures of carbonisation

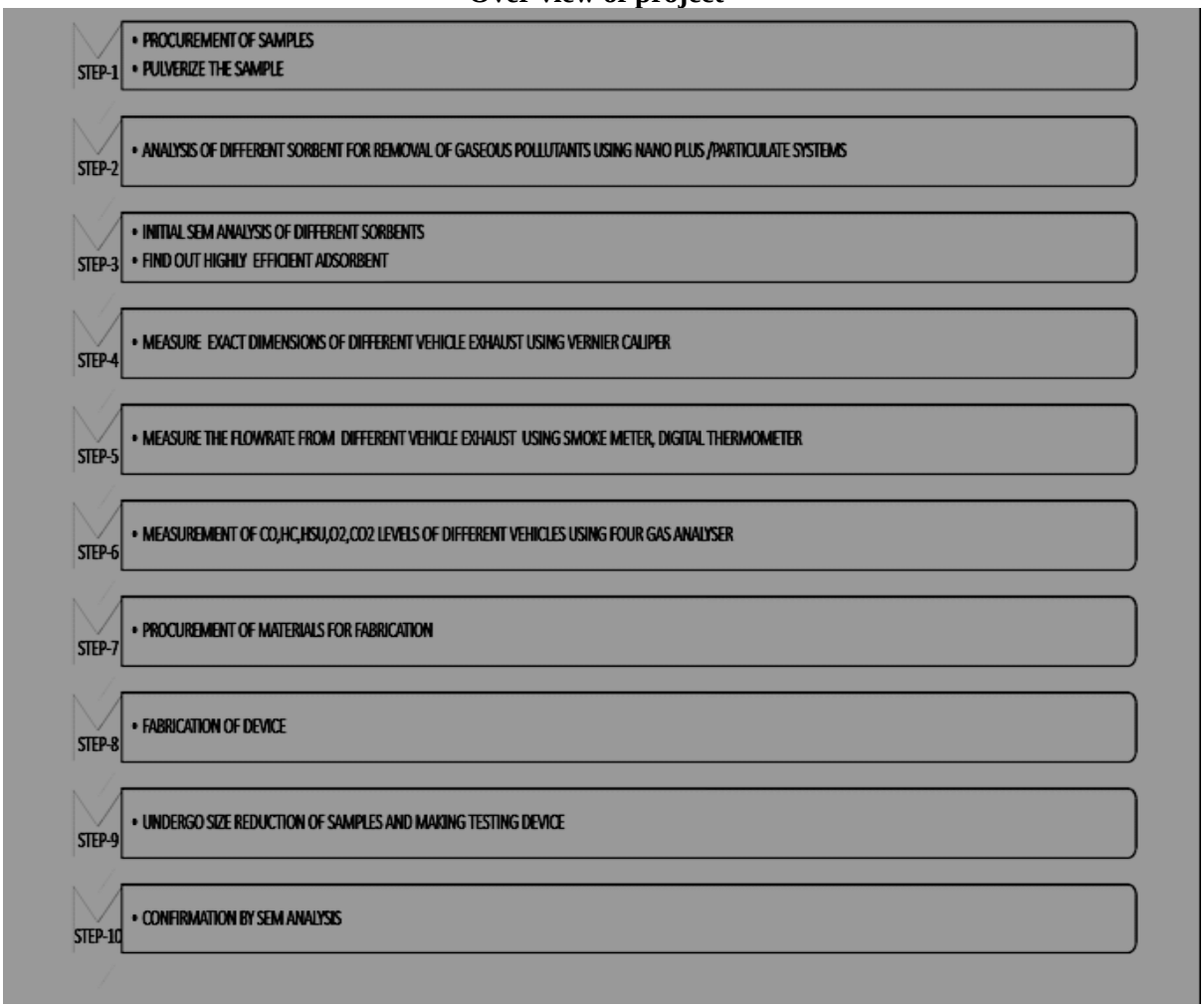
Table 6. Properties of Different Grades of Activated Carbon:-

Properties	Unit	Grades of granular activated carbon				
		KGr-4	KGr-3	KGr-2	KGr-1	KGr-1 Super
Iodine Value	mg/g.	350	550	600	950	1100
Apparent Density	kg/m3	620	580	550	510	480
CTC Adsorption	%	15	25	35	45	60
Hardness	%	95	95	90	90	85
Ash Content	%	5	5	4	4	4
pH Value		8-10				
Sieve Size		Any Desired Size				

Objective of the study:-

1. Checking the different adsorption properties (physical & chemical test).
2. Measure different dimensions of vehicle exhaust.
3. Measure the flow rate of different vehicles.
4. Measure the CO_2, CO, O2, HC, HSU levels of different vehicles.
5. Calculate total pollutants coming from different vehicles at 1000Km, 2000Km, 3000Km, 4000Km, and 5000 Km.
6. Development of cocktail of different adsorbent to adsorb pollutants (exhaust gases).
7. Confirmation of results by SEM analysis.

Over view of project



Materials and methodology:-

Instruments used:-

1. **Vernier caliper**- Measure the diameter of an exhaust pipe.
2. **Digital Anemometer**- Used for measuring the wind speed or air velocity of vehicle exhaust.
3. **Four gas analyser**- Used to measure the contents of CO, HC and CO2 in automotive emissions by the principle of NDIR detectors.
4. **Smoke meter**- Used for the analysis of pollution under control for in-use vehicle in terms of HSU%.
5. **Muffle furnace**- Used for moisture content analysis of a sample
6. **Mechanical Sieve Shaker**- Used to assess the particle size distribution (also called gradation) of a granular material. It is based on inclusion-exclusion principle.
7. **Scanning Electron Microscopy**- Used for high resolution and magnification imaging with enhanced depth of field for trace
8. the elements present
9. **Glass stoppered flask**
10. **Filters**
11. **Desiccator** with an efficient drying agent such as anhydrous calcium chloride or equivalent
12. **Digital balance** (accurate to 0.1mg)
13. **Thermocouple**
14. **Crucibles**
15. **Oven** (constant temperature between 145 and 155^0c**)**

Units for the measurement of concentration of air pollutants:-
There are two units of measurement. They are as follows:-
µg/m3
ppm (parts per million)
One ppm is 1 part in 1,000,000; Density = (Molecular weight of pollutant in gm/mol) / (Volume in l/mol)
Concentration in ppm = Concentration in mg/m3 / Density in mg/ml

Methodology:-

Procurement of samples:-
The major adsorbents available in markets include molecular sieves, activated carbon, silica gel, activated alumina, clay, and others. On the basis of application (gaseous pollutants removal) of those adsorbent the major material type molecular sieves and activated carbon are procured and then testing has to be done to find out the quality and efficiency of those samples.

Fig3: commercially available adsorbents procured for analysis.

Procurement of sample is the initial and most important step in comparative study. It is depends on the application and physical characteristics of those adsorbents and also it satisfy our requirement.

Analysis of different sorbent for gaseous pollutant removal:-

Iodine number test:
The iodine number is determined according to the ASTM D4607-94 method. The iodine number is defined as the milligrams of iodine adsorbed by 1.0 g of carbon when the iodine concentration of the filtrate is 0.02 N (0.02 mol L-1). This method is based upon a three-point isotherm. A standard iodine solution is treated with three different weights of activated carbon under specified conditions. The experiment consists of treating the activated carbon sample with 10.0 mL of 5% HCl. This mixture is boiled for 30 s and then cooled. Soon afterwards, 100.0 mL of 0.1 N (0.1 mol L-1) iodine solution is added to the mixture and stirred for 30 s. The resulting solution is filtered and 50.0 mL of the filtrate is titrated with 0.1 N (0.1 mol L-1) sodium thiosulfate, using starch as indicator.The iodine amount adsorbed per gram of carbon (X/M) is ploted against the iodine concentration in the filtrate (C), using logarithmic axes. If the residual iodine concentration (C) is not within the range of 0.008 to 0.04 N (0.008 to 0.04 mol L-1),the whole procedure should be repeated using different carbon masses for each isotherm point.A least squares fitting regression is applied for the three points.

The iodine number is the X/M value when the residual concentration (C) is 0.02 N (0.02 mol L-1). The X/M and C values are calculated by the Equations 2 and 3 respectively.

$$X/M = \{(N_1 \times 126.93 \times V_1) - [(V_1 + V_{Hcl})/V_F] \times (N_{Na2S2O3} \times 126.93) \times V_{Na2S2O3}\}/Mc$$

$$C = (N_{Na2S2O3} \times V_{Na2S2O3})$$

where N_I is the iodine solution normality, V_I is the added volume of iodine solution, VHCl is the added volume of 5% HCl, VF is the filtrate volume used in titration, NNa2S2O3 is the sodium thiosulfate solution normality, VNa2S2O3 is the consumed volume of sodium thiosulfate solution and MC is the mass of activated carbon.

Methylene blue Value test:-

Methylene blue value gives an indication of the adsorption capacity of an sample having similar dimensions to methylene blue. It is a quick method for compairing different batches of samples of same quality.Methylene blue value is defined as the number of millilitres standard methylene blue solution decolourized by 0.1g of samples in dry basis.

Methylene blue test solution:-

Dissolve a quantity, equivalent to 1200mg of pure dye to 1000ml in avolumetric flask. Allow the solution to stand several hours or over night. Check the solution by diluting 5.0ml with 0.25%(v/v) acetic acid to 1L in a volumetric flask and measuring the absorbance at 620nm for 1cm. The absorbance must be 0.840 ± 0.01. If the absorbance is higher, dilute with the calculated amount of water. If lower, discard the solution and start over. Exactly 0.1g of sample with 25(5)*** ml of themethylene blue test solution in a glass stoppered flask. Shake until decolourization occurs. Then add a further 5 (1)** ml of methylene blue test solution and shake to decolourization. Repeat the additon of the methylene blue test solution in 5 (1) ml portions as long as decolourization occurs with in 5 minutes. Note the entire volume of test solution decolourized by the sample. Repeat the test to confirm the result obtained.

Volatile matter content analysis:-

To determine the volatile matter content of samples, so as to know the amount of devolatlization required to produce a good

adsorbent.The sampleis heated at 900^0c for 7minutes. The percentage of volatile matter is calculated from the lossin the mass of

the sample,correctedfor moisture content. Granular activated carbon is pulverized (<0.1mm). Adjust the temperature in the reaction zone of the muffle furnace, containing empty crucibles, to 900 ± 10^0C.Maintain steady temperature conditions in the furnace.Weigh 1.000± 0.010g of the sample into each crucible, place the lidson the crucibles, transfer to the muffle furnace and leave for exactly 7min at 900 ± 10^0C.Remove , allow to cool and weigh the crucibles

Moisture Content Analysis:-

Determination of moisture content of samples using oven dry method. Heating the sample air in an oven at constant temperature to constant weight. Put the sample into a pre-dried crucible with lid; close and weigh at once to the nearest 0.5mg. the depth of the sample in the container must not exceed 1.25cm. Remove the lid and place the container and lid in a preheated forced circulation oven . close the oven and dry to constant weight for 3 hours. Open the oven and close the container quickly. Cool in a desiccator to ambient temperature and weigh.

The methylene blue test and iodine test are done to check the adsorption capacity of those samples. Iodine test is an indication of internal surface area of the sample was as methylene blue gives an indication of adsorption capacity of a molecule having similar dimensions to methylene blue. The chemical and physic chemical tests are performed through volatile matter content and moisture content analysis. In that sample 3, 4 has high value than any other samples.

Material used	Shape of particles	Methylene blue Test,ml	Iodine value test(ASTM Method)			Moisture content Test %	Volatile mattent content test,%
			0.7g	1g	1.5g		
Sample-1	Granules	44	452.342	474.959	422.186	4.89	19.770
Sample-2	Granules	47	565.427	474.450	369.410	5.9	11.052
Sample-3	Globules	52	678.513	554.119	422.186	3.6	30.601
Sample-4	Globules	48	452.342	395.799	369.410	3.396	16.256
Sample-5	Cylindrical	45	339.256	316.639	316.639	7..392	17.717
Sample-6	Granules	43	324.431	314.632	312.429	12	6.818
Sample-7	Globules	38	424.321	388.461	341.243	13.4	7.852
Sample-8	Globules	30	421.370	392.411	388.421	16.3	6.452
Sample-9	Cylindrical	28	422.341	388.231	384.261	10.9	3.030

Table6: Analysis of different sorbent

Measurement of Exhaust tail pipe dimensions:-

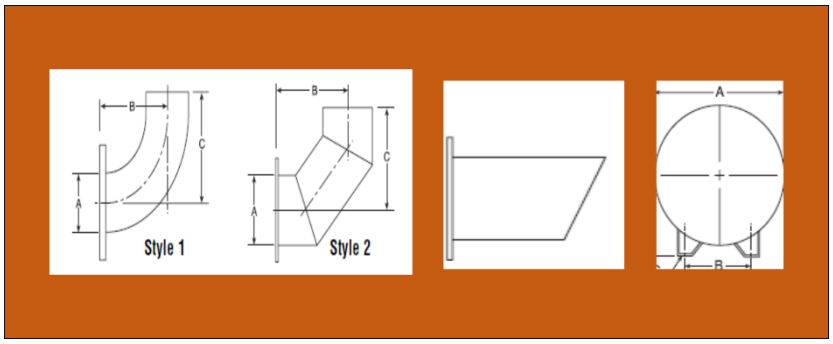


Fig4. Different Vehicle Exhaust Dimensions.

Basically the exhaust dimensions are belongs to 4 0r 5 different styles but the size will be vary based on the engine capacity and ignition rate. In the above models dimensions has to be measured has to be measured at different sides and positions in order to get concordant reading.

Flow measurement using Anemometer:-

Using anemometer the flow rate at three different times has been measured in that there might be a steady increase at start and rising. Based on these data the volume can be calculated. All data has to be plotted in terms of m/s. In the chart X-axis is belongs to vehicles and Y-axis belongs to flow rate. The red colour plot indicates the flow at rising and blue colour indicates the flow at start.

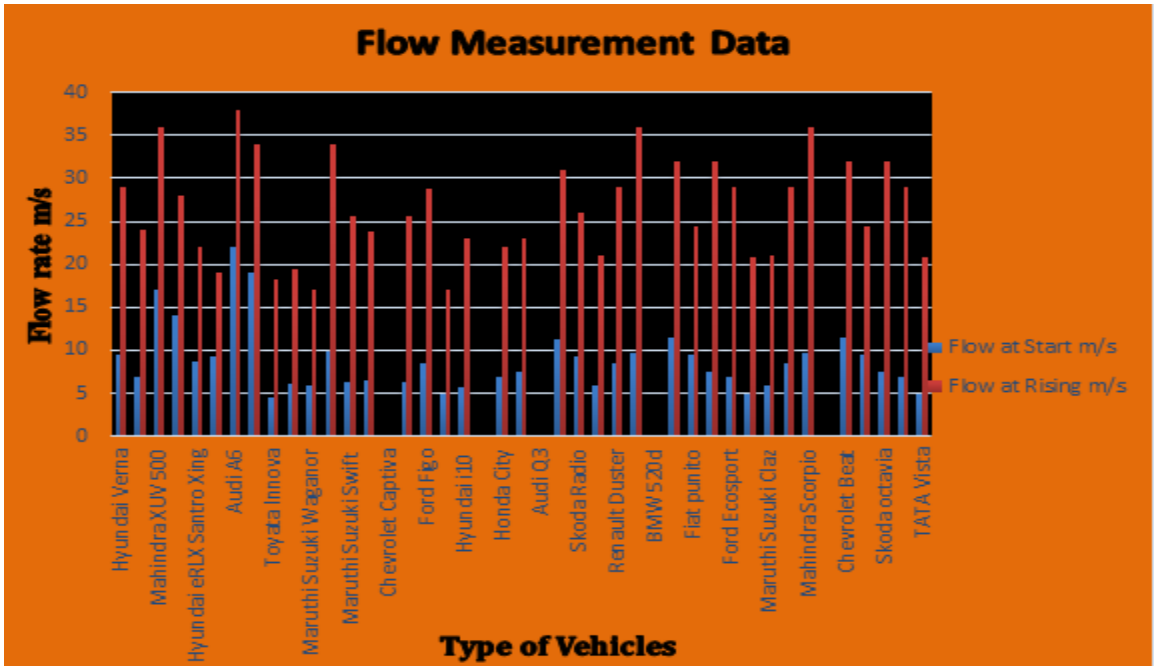


Fig5. flow measurement using Anemometer

Measurement of HSU% using smoke meter:-

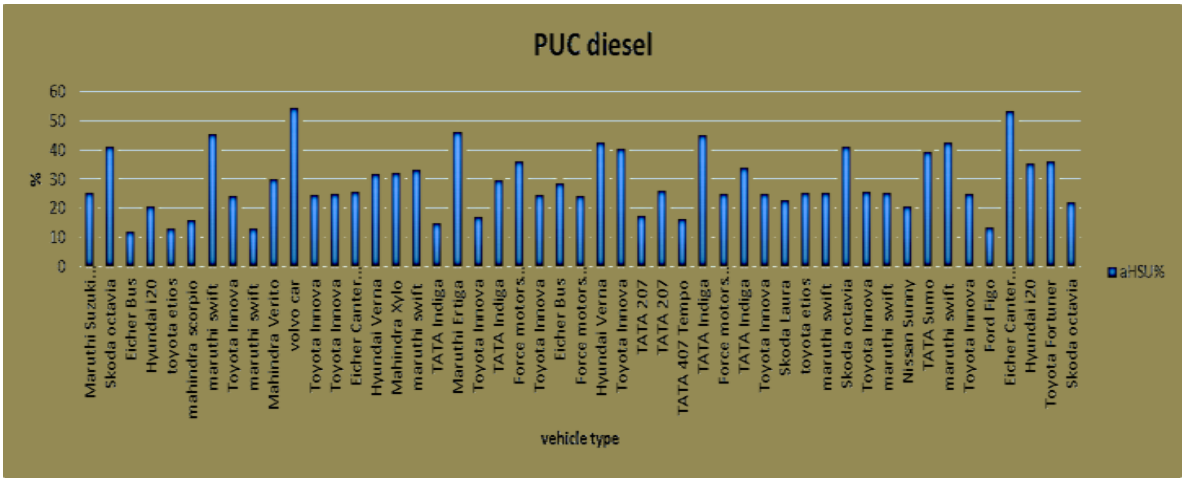


Fig6. Measurement of HSU% using Smoke Meter

As per Indian norms for diesel engines the HSU% won't be exceed 45. These plots are basically an initial data collected before fabrication. In the plot the X-axis represent the vehicle type and Y-axis represent the HSU %. In the plot the Volvo and eicher vehicle are emit more pollutant than other and more over it exceeds the level of release.

Total pollutant volume from the each vehicle analysis:-

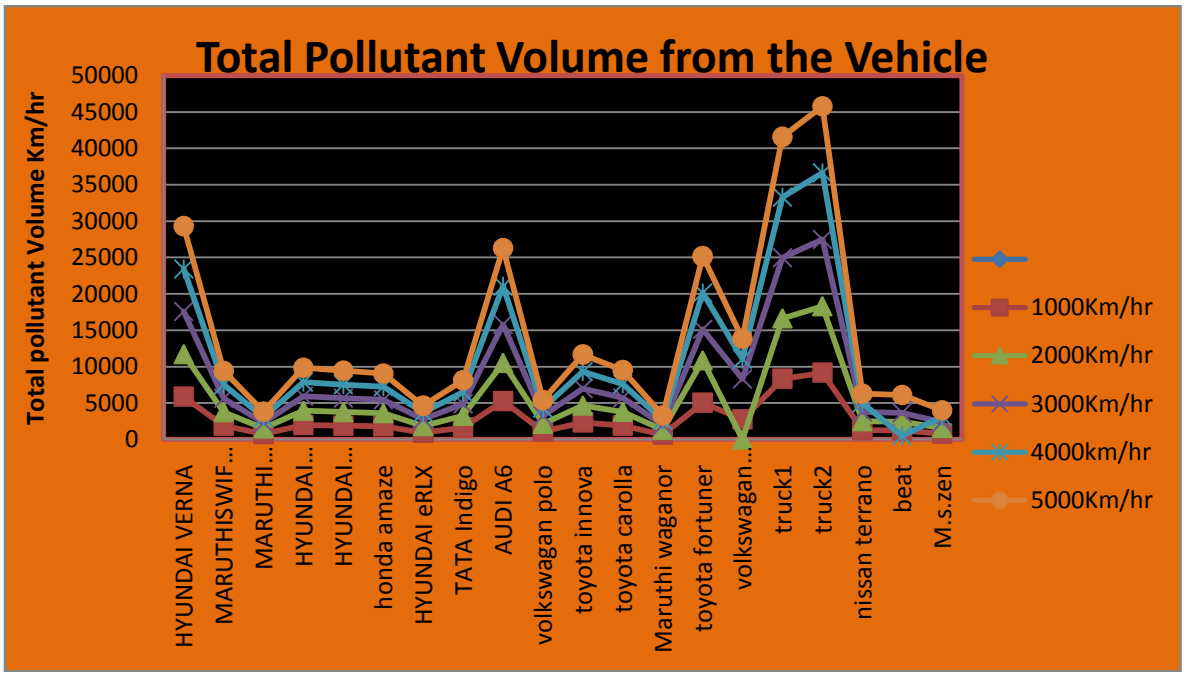


Fig 7. Total pollutant volume from the each vehicle

Inference:

These plot shows that at moderate speed the total number pollutants released from each vehicles at 1000, 2000, 3000, 4000, 5000 km/hr. In the plot at different KM/hr there might be a steady increase in release of pollutants

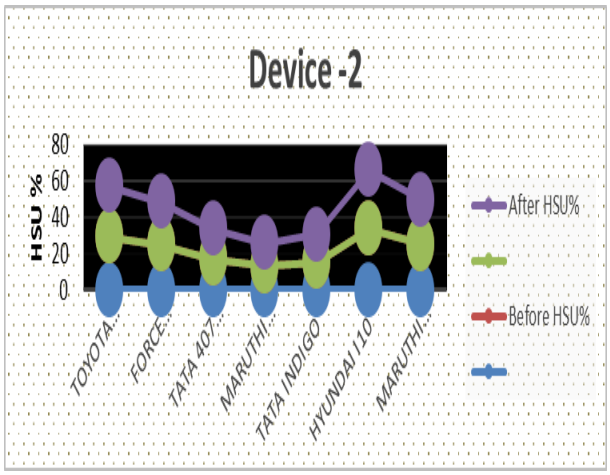
Particle size reduction analysis:

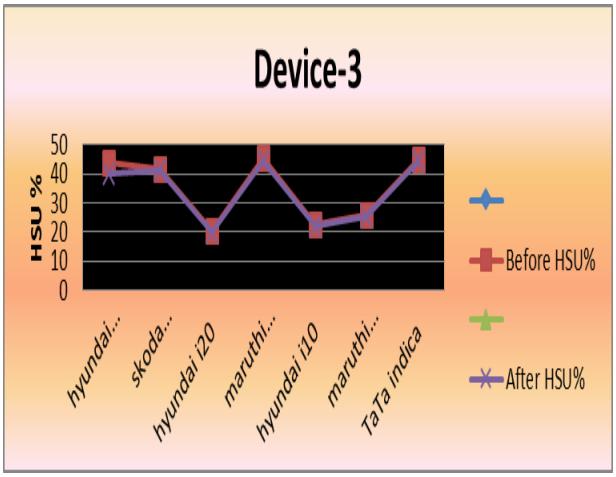
Size of particle (dia)mm	Volume of the particle (m^3)	Surface area of the particle (m^2)	Number of particle	Number of particle in 1 gram	Total surface area	Ultimate Surface Area	Increase in reaction area (times)
2mm diameter	$4.1887x10^{-9}$	$1.25663x10^{-5}$	1	$3.7x10^{5}$	$1.25x10^{-5}$	4.685	-
0.149mm diameter (100 mesh)	$1.7316x10^{-12}$	$6.9742x10^{-8}$	$2.4190x10^{3}$	$9.0x10^{7}$	$1.687x10^{-4}$	$1.522x10^{5}$	32486.659
0.074mm diameter (200 mesh)	$2.1217x10^{-13}$	$1.7203x10^{-8}$	$1.9742x10^{4}$	$7.3x10^{9}$	$3.392x10^{-4}$	$2.501x10^{6}$	533831.3
0.044mm diameter (325 mesh)	$4.4602x10^{-14}$	$6.082x10^{-9}$	$9.3912x10^{4}$	$3.5032x10^{10}$	$5.7117x10^{-4}$	$2x10^{7}$	428943.4
0.037 mm diameter (400 mesh)	$2.6521x10^{-14}$	$4.300x10^{-9}$	$1.5794x10^{5}$	$5.8915x10^{10}$	$6.791x10^{-4}$	$4x10^{7}$	8537886.8

Table 8.Particle size reduction analysis

In this analysis due to reduction of size of the particle the surface area will become increased in many folds in the table the last column shows the increase in terms of times. The value of the 2mm sample is having very small space when compared to other which means by size reduction the number of particle present in reaction area has to be increased million times.

Performance chart of each device:-





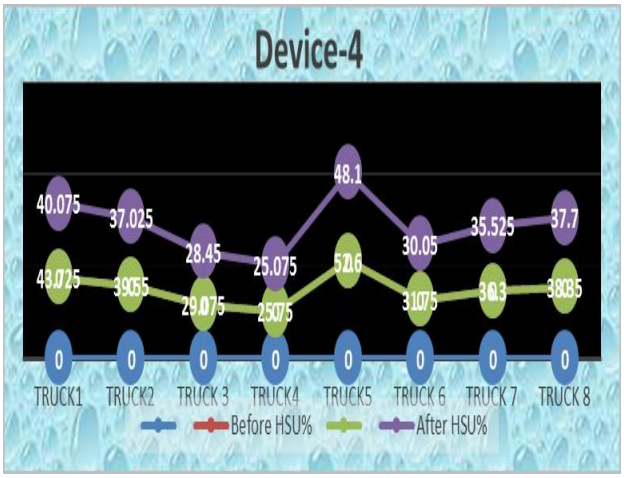


Fig 9:Performance chart of Different Devices

In each study there might be a reduction of pollutants coming out from vehicle exhaust. In the chart the there are two lines one indicates the before HSU% and other will be After HSU%. In all graph it is showing there might be a steady decrease in their pollutant level it means the adsorbent start adsorbing those pollutants on its surface

Composition of foreign particles analysis using EDX-SEM analysis:

The principle behind is Energy Dispersive (X-ray) Spectroscopy (EDS). It is a type of X-ray Fluorescence Spectroscopy. The EDAX X-ray detector is a Lithium Drifted Silicon detector. To avoid Li migration under the influence of bias and temperature, the detector is chilled to liquid nitrogen temperatures. If the liquid nitrogen evaporates and the detector warms up above a threshold set in the software, the detector is turned off to reduce the bias to zero. This helps prevent deterioration of sensitivity because of the thermal and bias drift of the Lithium impurities.

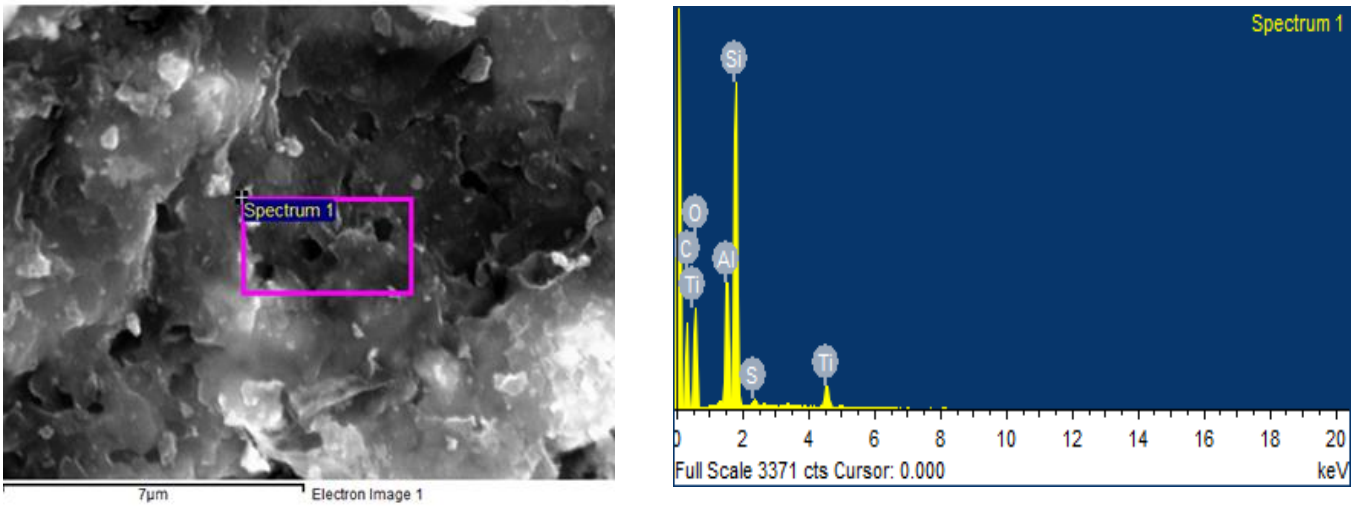


Fig10. EDX analysis of the sample at the pore size.

Inference:

The spectrum processing with peak possibly omitted 3.311 KeV with 5 iterations and shows the composition of those elements in terms of weight % and in terms of atomic%.

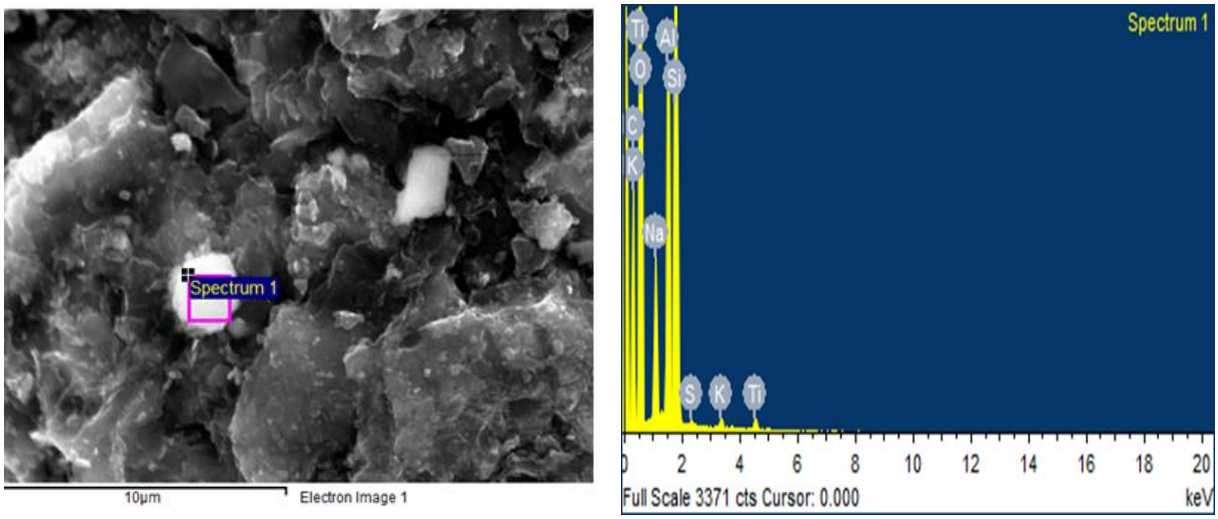


FIG11. EDX analysis of the sample at the white region

Inference:-

The spectrum processing with peak possibly omitted is 6.390 KeV with 7 iterations and show the composition of those elements in terms of weight % and in terms of atomic%.

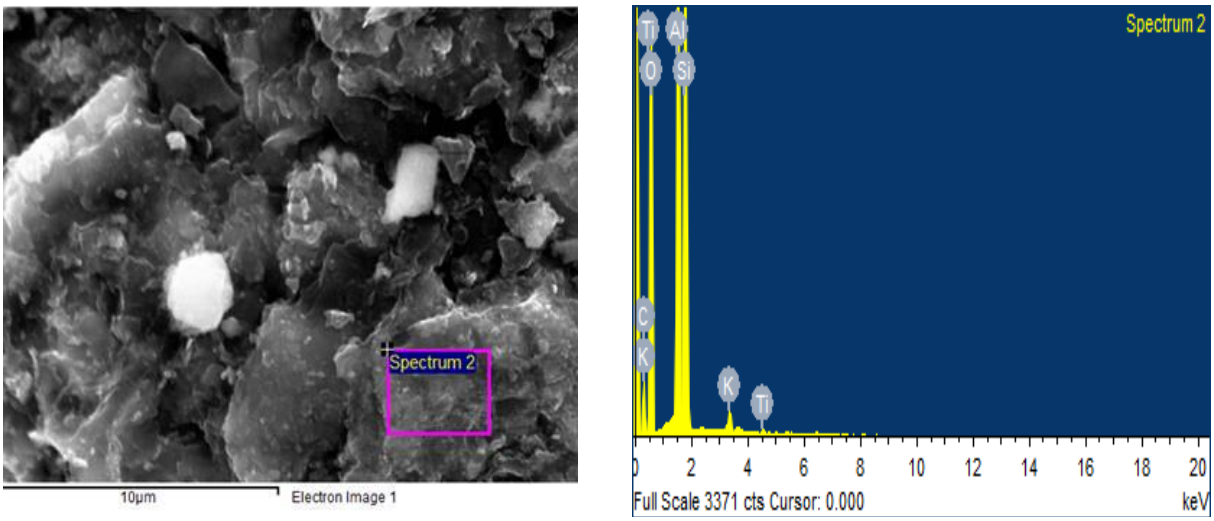


FIG12. EDX analysis of the sample at the bulk region

Inference:-

The spectrum processing with No peaks omitted with 6 iterations and show the composition of those elements in terms of weight % and in terms of atomic%.

Confirmation by Sem Analysis:-

Sem-edx analysis:-

It is used for high resolution and magnification imaging with enhanced depth of field for trace the elements present. The EDAX material analysis system can identify properties of highly localized features in thin samples.

Fig13. SEM instrument

Your sample can be mounted on one of a number of sample mounts. The simplest mount is the pin mount made of Aluminum. Before mounting the sample it is necessary to check the sample is conductive or not . If not coating has to be done before the sample mounting.

After the sample is properly mounted onto the SEM stage and inspected, gently close the chamber door and click to pump.

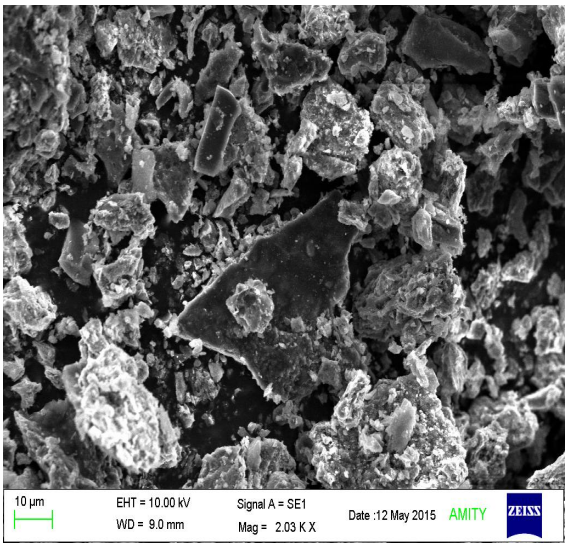
eter	Value
EHT	19.79 kV
Extractor V	4.40 kV
Extractor I	157 micro A
Fil I	2.410 A
Fil I Target	2.410 A
Extractor Target	4.40 A
EHT Target	19.79 Kv

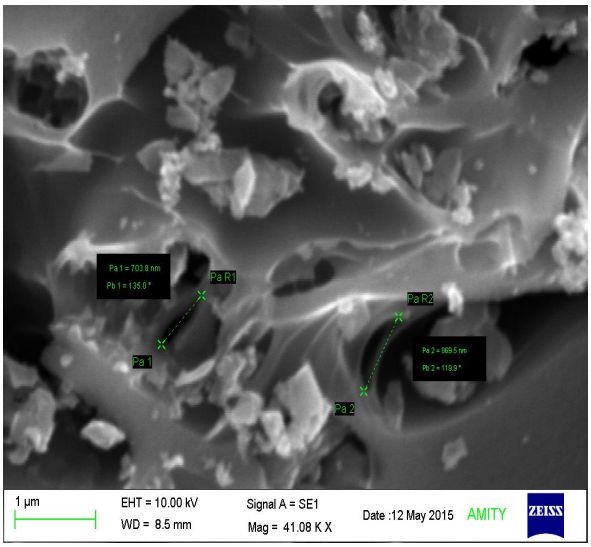
Table13: Normal gun conditions

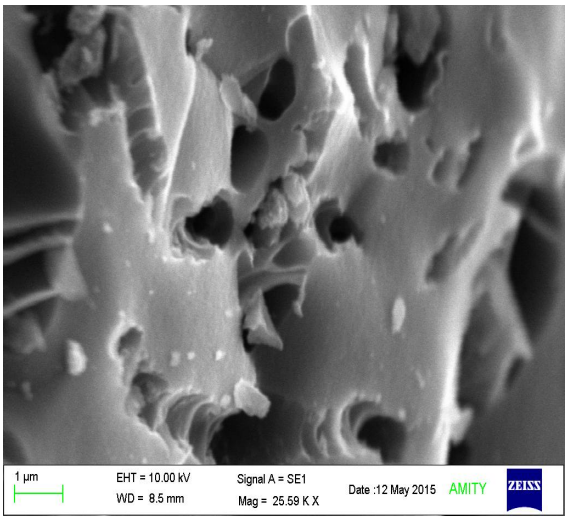
Once vacuum level in the chamber drops below 7.5x10-5 Torr, the column valve will open and the gun EHT (High Voltage) will “Run Up.”

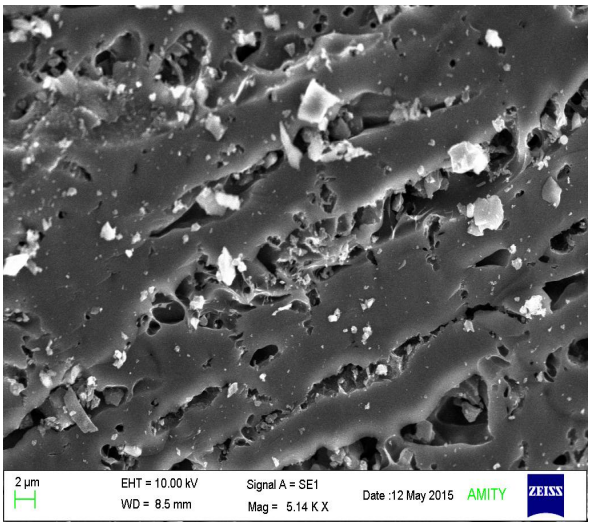
Procedure:

Prepare Sample and Mount Sample on Pin Mount. Log-in to SEM software Jump to Login.Vent SEM sample chamber. Jump to Loading.Open door and mount sample on stage. Jump to Loading. Close door and pump down chamber.Position stage under objective lens with joystick – watching stage in the Video window.Use joystick to raise stage to focus point to avoid collision with lens.When system is ready (Scanning operational at EHT), drive stage to target location at low magnification.Focus and correct astigmatism.Optimize image (brightness, contrast, scan speed).Capture image and save it in proper format.Exchange Sample (Vent, open door, change or remove sample, close door, pump down chamber). Never leave sample chamber at atmospheric pressure for very long.Log-Off SEM software to stop your session cost timer.Clean up the SEM and the sample prep table.









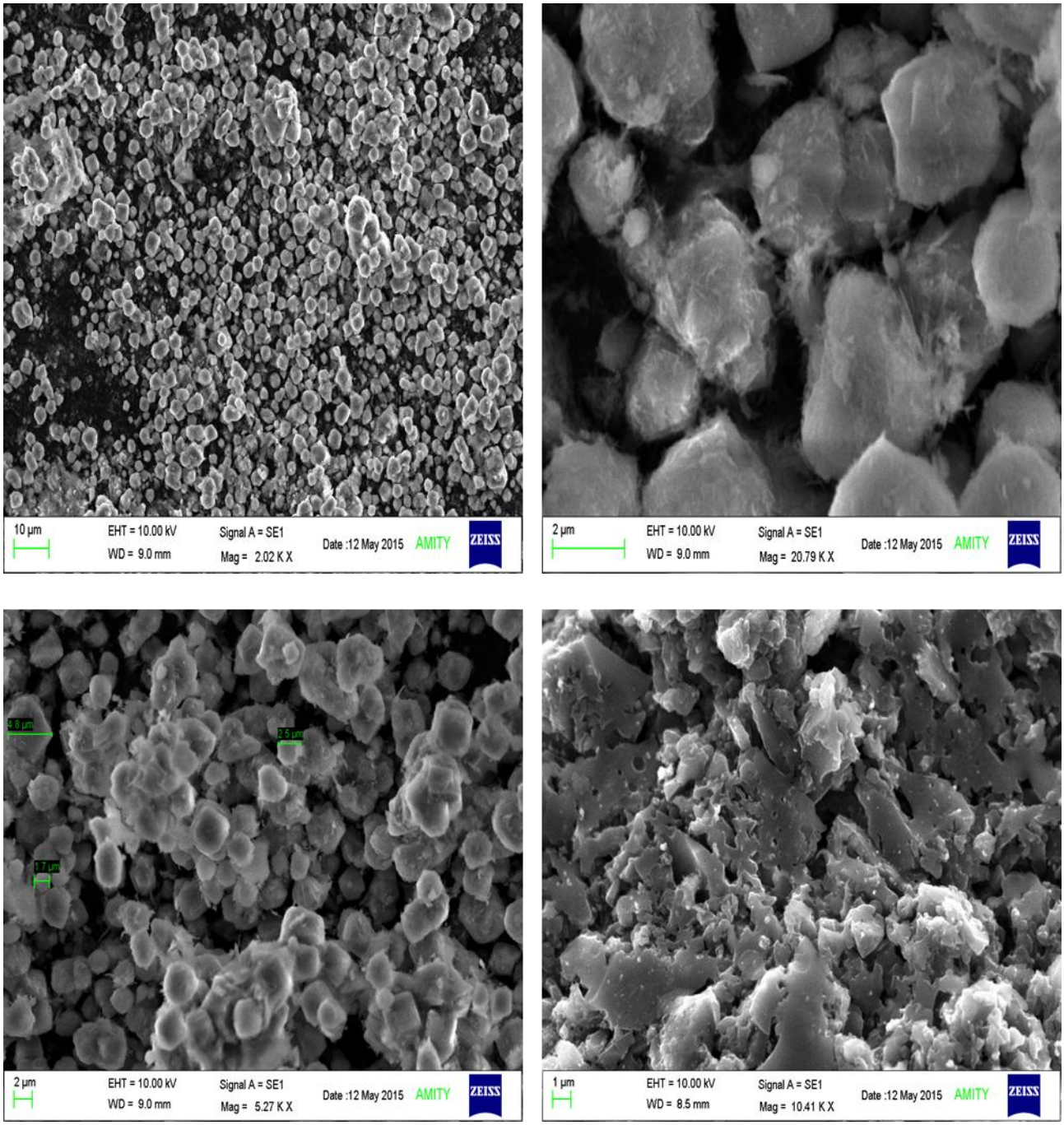


Fig13. SEM images of Sorbent Used for Comparative Study:-

Inference:

From SEM analysis it is seen that the foreign particles accumulation on the surface of the adsorbent the pore size of the sample can be noted in terms of µm. More over from EDX analysis we can see that major component is of C & O which means more CO_2 and CO adsorbed on its surface.

Conclusion:-

As preliminary data shows that the considerable reduction in pollutant, which results in lesser load on environment by adsorbing various gases on the surface of sorbents. The molecular sieve 4A has higher capacity to sorb pollutants of exhaust gases compared to others.

Moreover we can employ a further size reduction so increases a reaction area many fold as high as million times, thus we may achieve increased retention of pollutants on the various sorbents. Further, we check the exact quantification of various pollutant in the 4A pore of sorbents by FE-SEM Analysis.

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