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Characterization of Various Flyash fractions for Adsorption processes

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Abstract

Flyash is a by-product of coal combustion processes for energy generation obtained from thermal power plants. It is defined as finest coal combustion residue generated during burning of pulverized coal from power generation. The emerging amount of flyash in the world is millions of tons per year. In our country, it is expected that nearly 28 million tons of flyash is generated per year. The flyash can be evaluated by using as adsorbent material for wastewater treatment. The purpose of this study is to investigate the possibility for the use of various fractions of flyash as cost effective material for organics as well as heavy metal adsorption. In this connection, flyash is first characterized to know its adsorptive characteristics. So chemical as well as instrumental like XRF, FT-IR, XRD, SEM and SEM- EDS analyses are performed.

Keywords: Flyash, characterization, XRF, FTIR, XRD, SEM/EDS

Introduction

Flyash is one of the significant wastes materials[1]. It is the finest coal combustion residue generated during the burning of pulverized coal for power generation. The quality of flyash is related with nature as well as composition of coal, size of coal particle, percentage of ash in coal, combustion technique used, air/fuel ratio, types of burners used and type of boiler. Now a days , different application areas are started to investigate about the nature and composition of flyash. The flyash is capable of removing organic as well as heavy metals pollutants because of high minerals content, a large surface area per unit volume and contained various elements responsible for the adsorption. Therefore, flyash can be used as an effective coagulant and adsorbent[2-4]. Organic compounds are known to have a toxic effect on aquatic life, plant as well as animals responsible for various diseases. Among them, Phenols are a basic structural unit for a variety of synthetic organic compounds, wastewater originating from many chemical plants and pesticide and dye manufacturing industries. Wastewater from other industrial sources like paper and pulp, resin manufacturing, tanning, textile, plastic, rubber, pharmaceutical and petroleum also contain others types of phenols. Phenols i.e. a class of organic compounds are known as a most common and hazardous contaminant in water environment. The concentration level of phenols from 10 to 240 mg/L for a prolonged period causes diarrhea, mouth sours, excretion of dark urine and impaired vision and other more diseases. Heavy metals are also one of the most important contaminants in water and soil[5]. Heavy metals are discharged to the environment by verities of industries like mining, metallurgical, electronic, electroplating, metal finishing etc. Heavy metals cannot be degraded nor destroyed[6] . The removal of heavy metals from wastewaters by adsorption is very important due to their high toxicity and having tendency to accumulate in living organisms causing a serious problem. So many studies are conducted to show the effectiveness of fly ash in the removal of organic materials[7-9] as well as heavy metals[10-12] from aqueous solutions.

The aim of investigation is to characterize the various fraction of flyash used as low cost adsorbents for their potential for organics as well as heavy metal adsorption. For this purpose; flyash is characterized in respect of their physicochemical, morphological and mineralogical properties to find the utilization of flyash as adsorbent.

Material and methods

Materials: The flyash is obtained from Thermal power station Chachai, Anooppur, Shahadol (M.P.) India and are fractionated into different fractions of varying particle sizes using standard sieves of mesh sizes having geometrical mean particle diameters 150, 106 and 45μm .The different fraction of flyash are dried for 2 hours at 110^0C in an electric oven and stored in a zip lock bags and placed in a desiccators for performing characterization studies. The sample is used as such without any pre treatment.

Physiochemical characterization of adsorbent: The characterization of flyash samples are carried out with a number of experimental approaches in order to investigate all the relevant features present in the samples. The Chemical constituents of flyash are determine by standard method[13] along with the other characteristics like lose of ignition (LOI) at 800^0C, specific gravity, surface area (Surface Area Analyzer, Quantasorb, USA) and porosity (Hg – porosity meter) and are shown in Table-1. Proximate analysis of flyash fractions are determined and are listed in table-2. Chemical composition of different fractions of flyash are also determined by standard method[13] and are presented in Table-3.

X-ray fluorescence spectrometer (XRF) patterns of different fractions of flyash samples are obtained by the Model Philips PW–2404 PANAlytica (Netherlands) for analysis of the chemical composition or elements present in the samples at 4 KW with 60 KV, 125 mA (in steps).

The identification of the mineralogical constituents and phase properties of different fractions of flyash are examined by X-ray diffracter on a model Bruker D-8 venture with CuKα radiation at operating parameters of 40 mA and 45 kV with step size 0.02° and speed of 1°/min over the range of 2θ from 0° to 100°. Phase identification is made by searching the ICDD powder diffraction file database with the help of JCPDS (Joint Committee on Power Diffraction Standards) files for inorganic compounds. Various inorganic compounds present in the flyash samples are identified with the help of JCPDS (Joint Committee on Powder Diffraction Standards) files.

Different fractions of flyash samples are subjected to Scanning Electron Microscopy on FEG- SEM (Model– JEOL JSM 7600F) coupled with Energy Dispersive X-Ray Spectroscopy (EDS) having XMAX 80 mm 2 as detector in order to investigate the morphology and chemical composition of the samples. Photomicrographs of the different fractions of flyash are taken at different magnifications i.e.×250, .×500, .×1000, .×1500, .×2000, .×2500. SEM is one of the important and widely used technique for the physicochemical characterization of samples. The EDX analysis is performed at each analysis point and the elements present are both qualitatively and quantitatively measured. Examining SEM images of different fractions of flyash and performing EDS measurements on areas of interest, elemental composition and its oxides are determined.

The flyash fractions are analyzed with Fourier transform infrared spectroscopy (FTIR) using Perkin Elmer 1800 model instrument in the range 400– 4000 cm^{-1} as potassium bromide pellet .

Results and Discussion

Fractionation and Characterization of FlyAsh: Physicochemical characteristics of are important parameters for deciding economic utilization of flyash which are analyzed and summarized in table-1. It is clear from the data that SiO_2 and Al_2O_3 are major constituents of flyash. It is also obvious that different constituents in flyash show greater variation in their chemical composition. This is due to variable quality of Indian coal and also due to lack of control and standardization in the plant machinery. The outcome of investigations reveals some interesting features about various flyash fractions. From proximate analysis of flyash fractions shown in table-2, it is observed that fraction of larger particle size have higher fixed carbon content and lower densities. A descending order of fixed carbon is followed with increase in densities of the fractions. This may be assigned to higher mineral matter content of the fractions with smaller particle size. Fractions having larger particle size obviously contain larger agglomerates of carbonaceous matter, thereby increasing the fixed carbon content and lowering the densities. Whereas fractions having smaller particle sizes contain lower amount of these agglomerates, and accordingly are low in fixed carbon content.

Table-1
Characteristics of flyash

Element as oxide	Weight %
SiO_2	59.54
Al_2O_3	27.20
Fe_2O_3	4.87
CaO	2.91
MgO	0.40
K_2O+Na_2O	1.00
LOI ($800\,^0$ C)	12.00
Specific gravity	1.80
Porosity	0.34 - 0.62
Surface Area	7000 – 9000 cm^2

Table-2
Proximate analysis of flyash fractions

S. No.	Particle Size	Specific Gravity	Moisture Contents (%)	Ash (%)	Volatile Matter (%)	Fixed Carbon (%)
S1	150 μm	1.80	1.16	86.96	2.10	9.84
S2	106 μm	1.86	0.99	92.00	1.00	5.01
S3	45 μm	2.12	0.95	97.00	1.00	0.05

Table–3
Chemical analysis of fractions of Flyash Chemical Composition (Percentage by weight)

Particle Size μm	SiO_2	AI2O_3	Fe_2O_3	CaO	MgO	LOI 800^0C
150 μm	59.54	27.20	4.87	2.91	0.40	12
106μm	67.00	30.00	6.10	3.80	1.10	08
45 μm	77.75	36.00	6.00	4.00	1.50	4.09

XRF characterization: The chemical composition of different fractions of flyash samples are determined by XRF and are shown in table-4. The data shown in table-4 shows that the alumina and silica oxide are present in major quantities while other minerals are present in trace amounts. This confirms the chemical analysis of flyash analysed by chemical analysis method. So the fraction of flyash samples mainly consists of SiO_2, Al_2O_3 and Fe_2O_3 which support the earlier results [14].

XRD Characterization: The X-ray diffractogram for the fractions of flyash are shown in figure-1-3. The presence of above minerals found through XRF analysis are further tested by XRD studies. It can be observed from figures-1 to figures-3 that the flyash consists mostly of quartz, alumina, mullite and small amount of hematite and calcium oxide with characteristic peaks of quartz (SiO_2). This result is similar finding to that reported for a flyash investigated by Sarkar et al.[15]. It can be seen from the diffractogram of different fractions of flyash samples that components are mainly present in their oxide form. XRD is utilized to determine the mineralogical composition of the raw material components as well as qualitative and quantitative phase analysis of multiphase mixtures. The occurrences of minerals in samples of flyash are identified by comparing' values[16-17]. The possible minerals with their'd' spacing values present in the different fractions of flyash samples are given in table-5. Further the occurrence of the above minerals in the flyash samples are confirmed by SEM/EDS as well as FTIR studies. The XRD patterns also supports the XRF.results that the major phases in flyash samples are silicon, aluminum and iron oxides.

SEM/ EDS Analysis: There is a great importance of detailed knowledge of the physical nature of the surfaces of solids in the fields of material science and surface chemistry. The characterization of surface morphology has a vital role in understanding the physical and chemical behavior of the material. SEM is a useful tool to study modes of particle association or for detection of surface irregularities. The scanning electron micrographs are shown in figure-4, figure -6 and figure-8 for fractions of flyash indicating that it consists largely of solid or hollow spherical particles of variable size with small bulgings of siliceous and aluminous glass with appearance of cracking at the tip of bulges. The photomicrographs also indicate that dark areas are organic material, light areas are mineral matter, gray sheet are mixtures of coal and ash and large angular grains are quartz. Solid and porous part indicate 'the presence of mineral matter probably quartz and hematite which is supported by earlier findings[18]. Irregular black parts of the micrographs which are porous indicate the presence of partially burnt coal particles, sometimes containing mineral matter. The image reveals that most of the particles present in the flyash are irregular in shape and covered with relatively smooth grains of quartz. It is observed that samples of flyash particles are mostly spherical in shape whereas irregular shaped particles are also present in small amount.

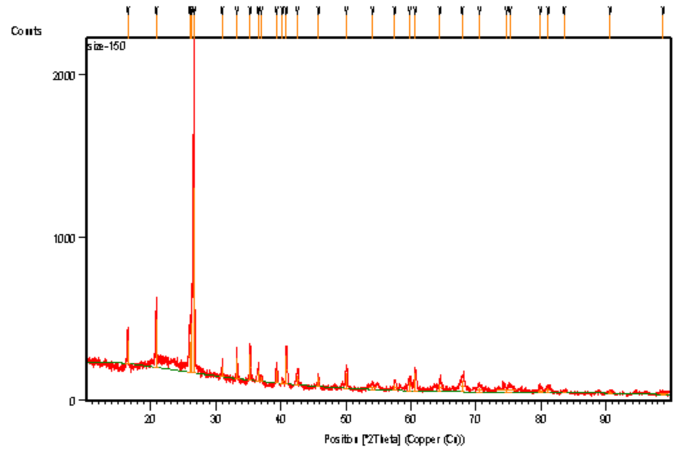

Figure-1
X-ray diffractogram of flyash (150 µm)

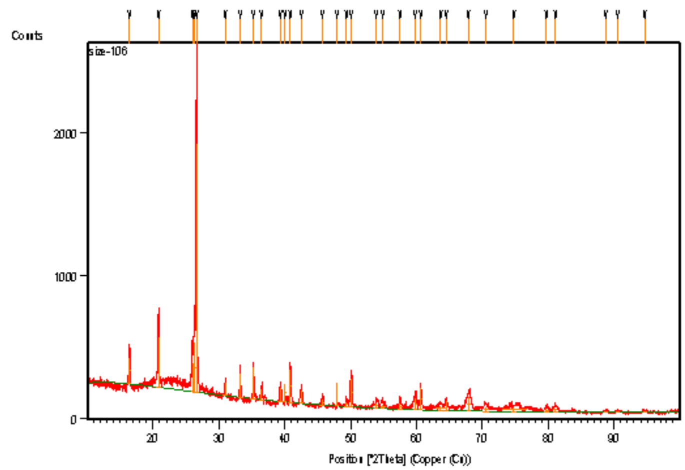

Figure-2
X-ray diffractogram of flyash(106 µm)

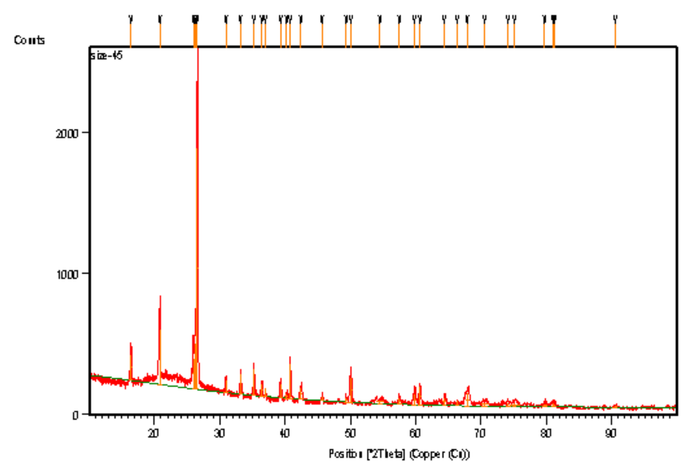

Figure-3
X-ray diffractogram of flyash(45 µm)

Energy-dispersive X-ray spectroscopy (EDS) is an important instrumental technique used for the elemental or chemical analysis of a sample. The EDX analysis results of flyash samples are represented in figure-5, figure-7and figure-9 (SEM images with corresponding EDS spectra). The EDS of flyash samples suggest the presence of aluminum, oxygen, carbon, iron, titanium and silicon as the primary elements. SEM/EDS provide detailed imaging information about the morphology and surface texture of individual particles as well as elemental composition of flyash samples which also confirms the earlier findings[19]. So SEM/EDS is one of the important and widely used techniques for the and physicochemical analysis of flyash samples. The identified elements in the flyash samples are C, O, Al, Si, Ti, Fe in various compounds (SiO_2, Al_2O_3, Fe_2O_3, Tio_2 etc.) as determined by EDS showing figure-5, figure-7 and figure-9,. The morphology and element showing in figures indicate presence of amorphous alumina-silicate spheres as well as a lesser amount of iron-rich spheres composition in flyash samples.

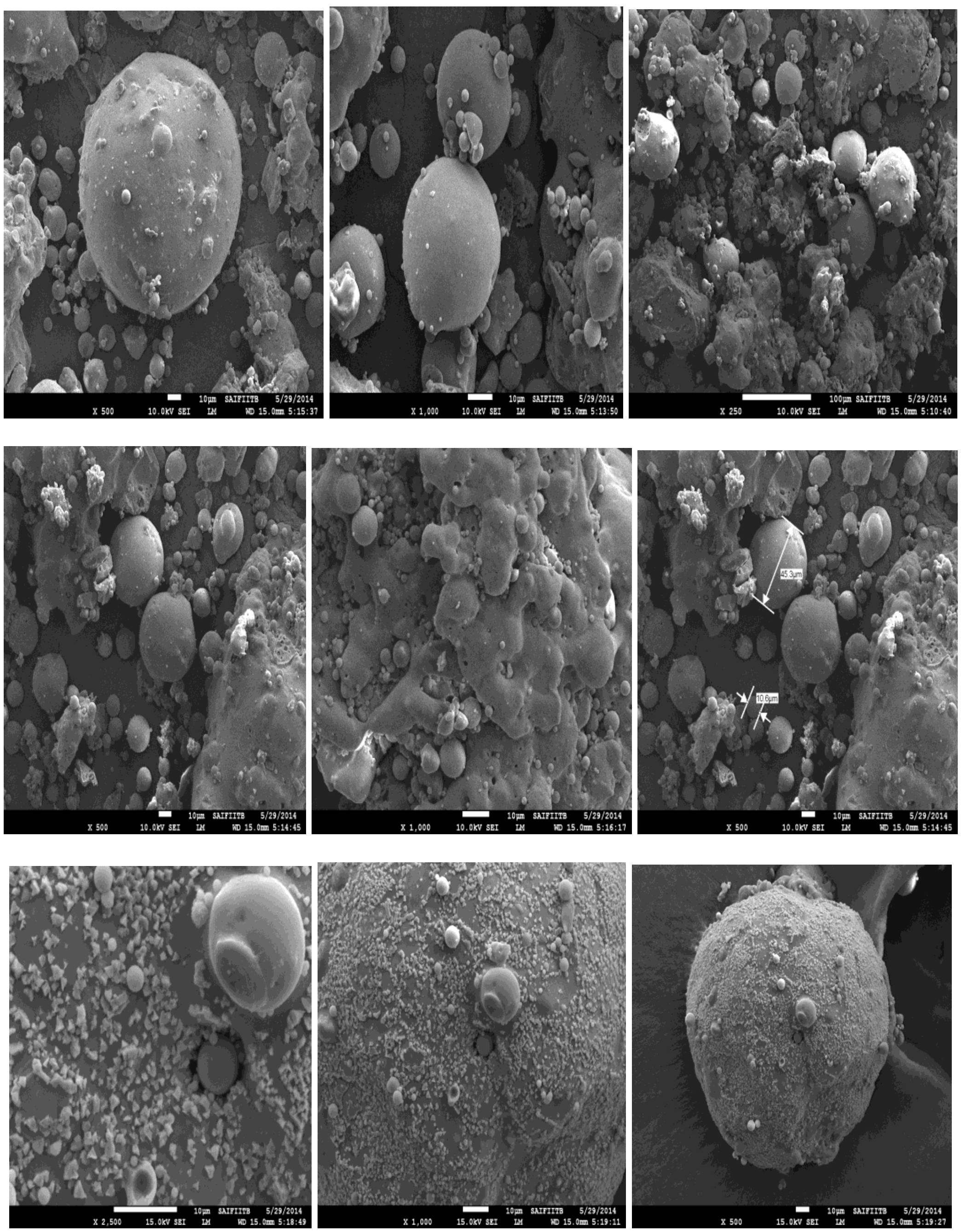

Figure-4
SEM photomicrograph of fly ash sample (size: 150 um). at different magnifications

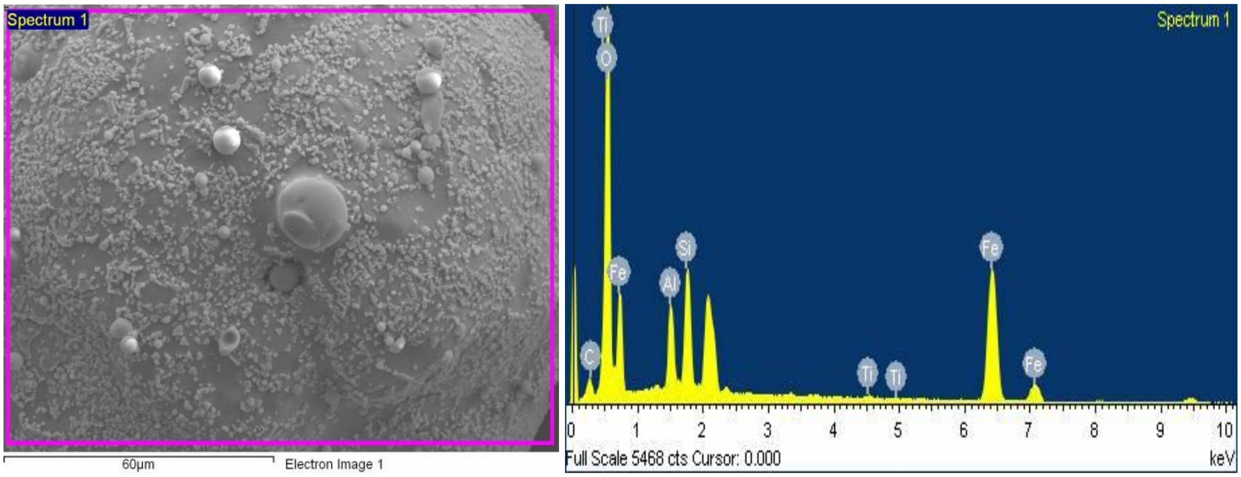

Figure-5
SEM-EDX photograph of flyash(150 μm)

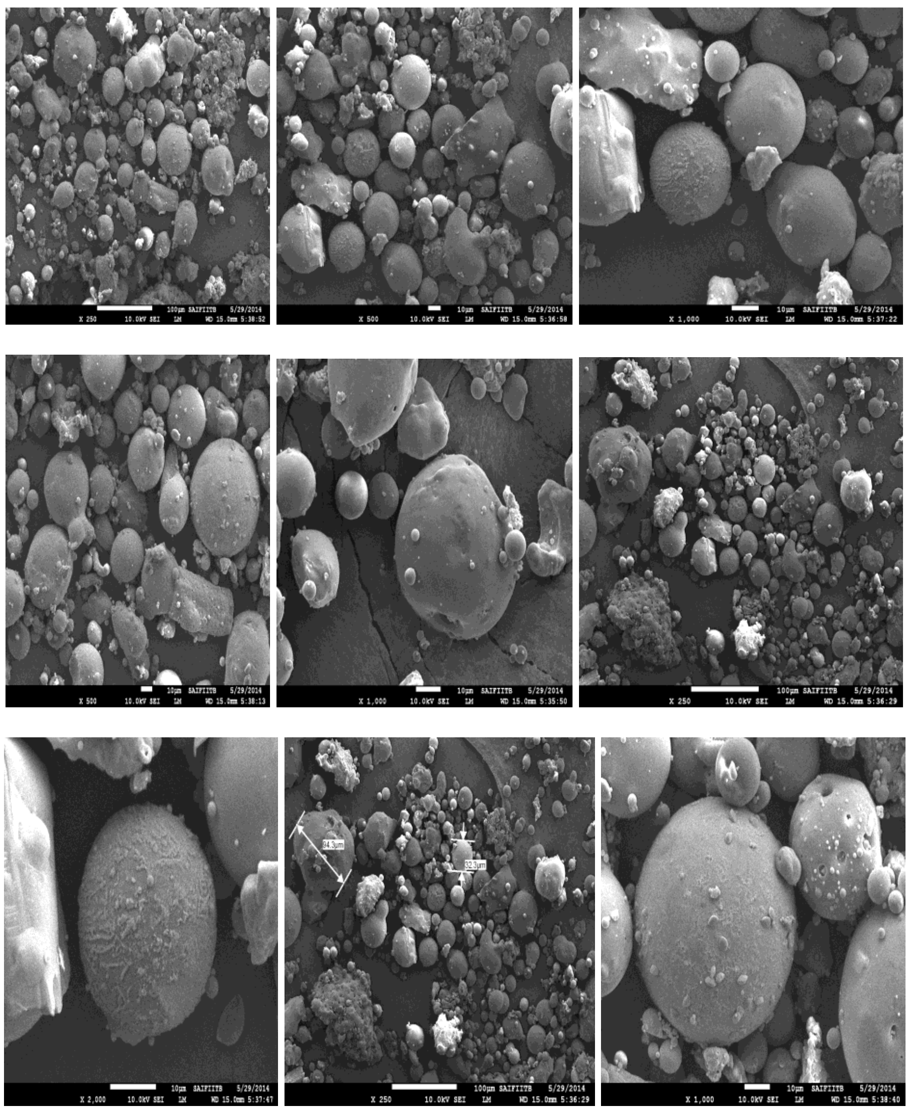

Figure-6
SEM photomicrograph of flyash sample (size: 106um) at different magnifications

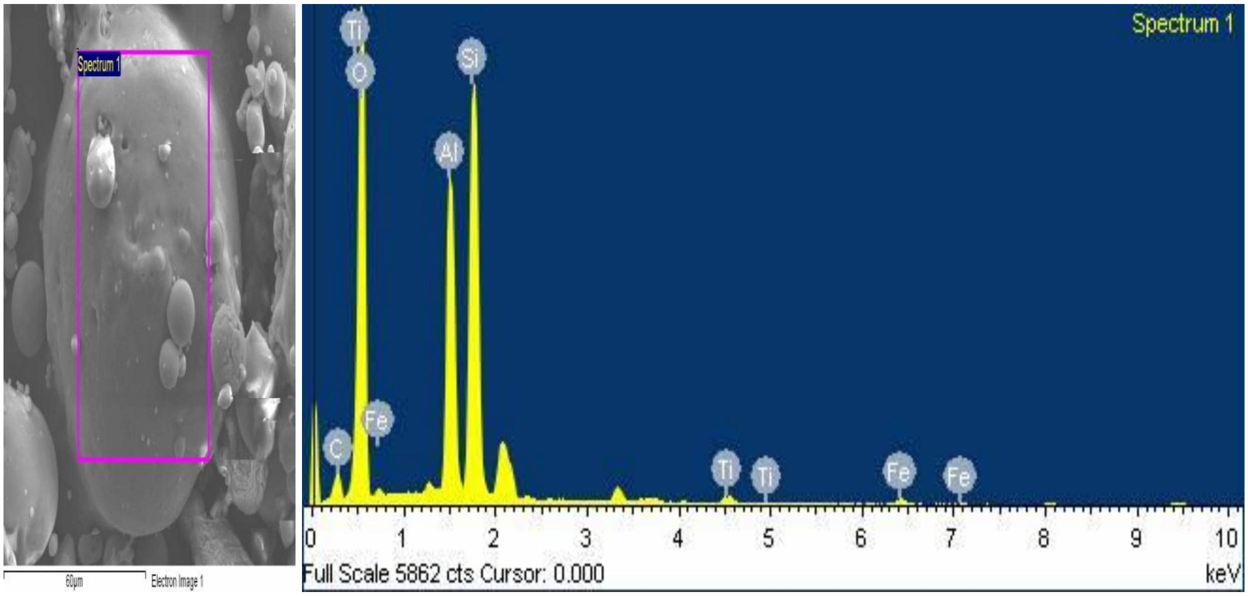

Figure-7
SEM-EDX photograph of flyash (106μm)

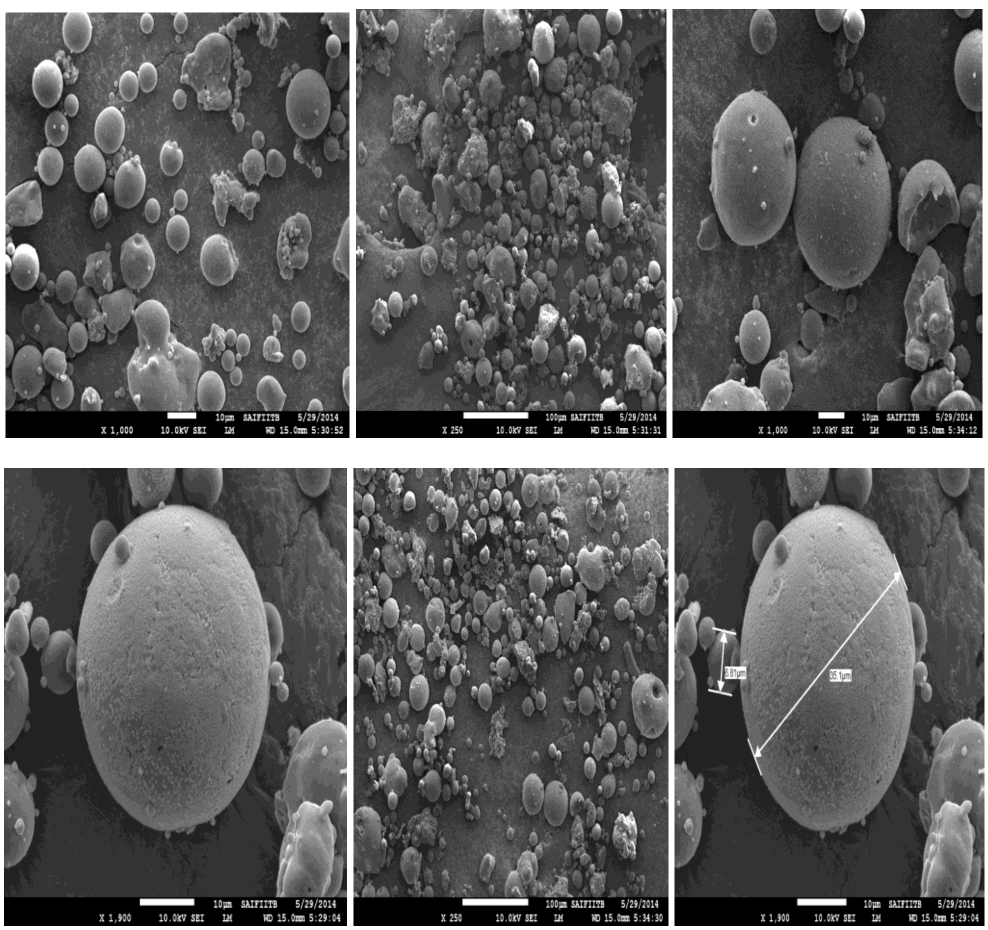

Figure-8
SEM photomicrograph of fly ash sample (size: 45um) at different magnifications

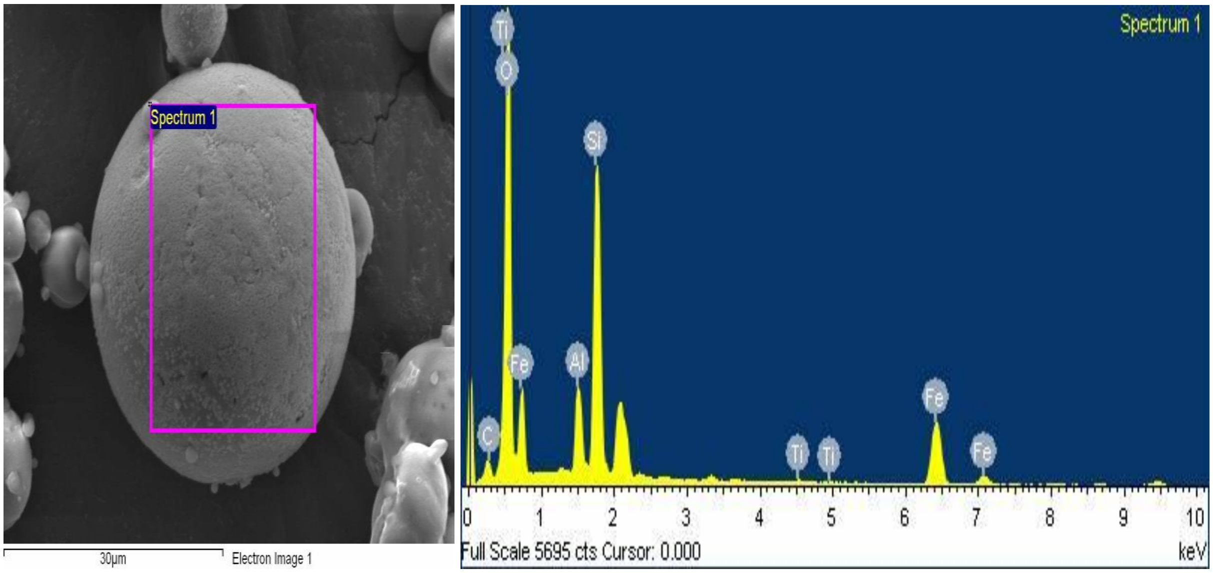

Figure-9
SEM-EDX photograph of flyash (45 μm)

FTIR Analysis: It has been shown that FTIR technique can be successfully applied to the characterization of coals, coal-derived materials and minerals[20]. The FTIR spectra for fractions of the flyash samples are shown in figure-10, figure -11 and figure-12. The FTIR data shows the presence of functional groups on the surface of flyash samples. FTIR spectra of flyash samples represent a broad band between 3700cm^{-1} - 3100cm^{-1} indicating the presence of -OH group on the samples surface. This stretching vibration is due to the silanol groups (Si-OH) present in the flyash samples. The band observed between 1250cm^{-1}- 850cm-^{1} of flyah samples show the presence of TO_4 (where T = Si, Al) asymmetric stretching vibrations of internal tetrahedral. The bands between 720cm^{-1}-650cm^{-1} and 420cm^{-1}-500cm^{-1} indicate about the presence of symmetric stretching and TO_4 bending mode of internal tetrahedral respectively present in flyash samples. In addition, bands appearing between 800-600 cm^{-1} are related with tetrahedral vibrations known as secondary building units as well as fragments of aluminosilicate of flyash samples. FTIR studies of these flyash fractions help in the identification of various forms of the minerals. The coupled vibrations are found due to the availability of various constituents found in the flyash samples. The important FTIR bands of flyash fractions along with their possible assignments[20, 21] are shown in table-6 shows the presence of minerals like alumina, silica, mullite, hametite which have been found through chemical analysis, XRF, XRD, SEM/EDS studies. This result is similar finding to that reported for a flyash investigated by Rajamannan et al. [22] .

Conclusion

With millions of tonnes of flyash produced in India, use of flyash as adsorbent for organics as well as heavy metals will in no way help in its bulk utilization. Still authors have made an effort towards the better utilization of flyash for water wastewater treatment. Here different fractions of flyash are characterized with a number of experimental approaches for adsorption studies. Therefore, the selection of proper flyash is very important task. Sieving, chemical analysis, XRF, XRD SEM/EDS and FT-IR analysis results show about adsorptive characteristics of flyash samples for organics as well as heavy metal adsorption. By this means, we can say that flyash samples are convenient for wastewater treatment through adsorption. The analysis of XRF, XRD, SEM/EDS and FTIR show that different fractions of flyash is mainly constituted of silica and alumina as major quantities and iron, calcium, magnesium, potassium oxides and other elements are as minor quantities. XRD studies show the presence of quartz, kaolinite, hematite, mullite and feldspar as major phases. The presences of above minerals are further confirmed by XRF and also by FTIR analysis. The SEM/EDS observations shows that silicon and aluminium are the major constituents of flyash samples. The flyash samples consisted mostly of amorphous alumina-silicate spheres with a lesser number of iron-rich spheres. The aluminium and silicon-rich spheres has minor elemental associations. So the presence of such minerals are responsible for adsorption processes.

Acknowledgment

The authors thank the authorities of the Central Drug Research Institute, Lucknow and Indian Institute of Technology, Roopar and Mumbai for providing FTIR, XRD, XRF and SEM/EDS analysis results respectively.

Table–4
XRF analysis for different fractions of flyash

Chemical composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	Sr	SO_3
Weight(%) 150 μm	59.817	24.290	6.664	1.599	0.254	0.120	2.082	4.314	0.044	0.001	0.056	0.001
Weight(%) 106 μm	60.250	24.373	6.576	1.513	0.248	0.077	1.841	1.841	0.042	0.001	0.054	0.001
Weight(%) 45 μm	60.420	25.339	6.192	1.473	0.306	0.071	1.711	3.505	0.040	0.017	0.052	0.012

Table-5
X- ray diffraction‘d’ values of flyash fractions

Flyash fractions	d (A°)	Possible mineral
S_1 (150µm)	4.2754,2.4668,3.3582	Quartz
	1.3781,2.1273,3.3582	Mullite
	1.6064,1.3804,1.7011	Hematite
	1.8236,2.2082,1.6947	Magnetite
	1.4452,1.3749,1.7011	Calcium oxide
S_2 (106µm)	5.3976, 3.3913, 3.4304	Mulite
	4.2699, 3.4304, 3.3513	Quartz
	2.5469, 2.4637, 1.5265	Magnetite
	2.6973, 2.2894, 2.2095	Hematite
	2.4637, 1.6725, 1.5265	Lime
S3 (45µm)	5.4033, 1.6820, 1.5462	Mulite
	4.2723, 1.5462,1.3799	Quartz
	2.5482, 1.6820, 1.3799	Magnetite
	2.6982,1.6820, 3.4308	Hematite
	2.6982, 1.6820, 1.3799	Lime

Table-6
Important FTIR bands of flyash fractions along with their possible assignments

Flyash fractions	Band, cm^{-1}	Assignments
S_1 (150µm)	3639	Al-O-H (inter-octahedral)
	3468	H-O-H str
	1646	H-O-H str
	1033	Si-O-Si, Si-O str
	795	Si-O str, Si-O-Al str. (Al,Mg)-O-H Al-O-(Mg,Al) str.
	664	Si-O str, Si-O-Al str.
	560	Si-O str, Si-O-Al str
	483	Si-O str., Si-O-Fe str
S_2 (106µm)	3669	Al-O-H st
	1648	H-O-H str.
	1024	Si-O-Si, Si-O str.
	775	Si-O str, Si-O-Al str. (Al,Mg)-O-H Ai-O-(Mg,Al) str.
	724	Si-O str, Si-O-Al str.
	535	Si-O str, Si-O-Al str
	497	Si-O str, Si-O-Fe str
S_3 (45µm)	3674	Al-O-H str
	3625	Al-O-H (inter-octahedral)
	1650	H-O-H str
	1034	Si-O-Si, Si-O str
	920	Al-O-H str
	772	Si-O str, Si-O-Al str. (Al,Mg)-O-H Ai-O-(Mg,Al) str.
	687	Si-O str, Si-O-Al str.
	580	Si-O str, Si-O-Al str
	481	Si-O str, Si-O-Fe str

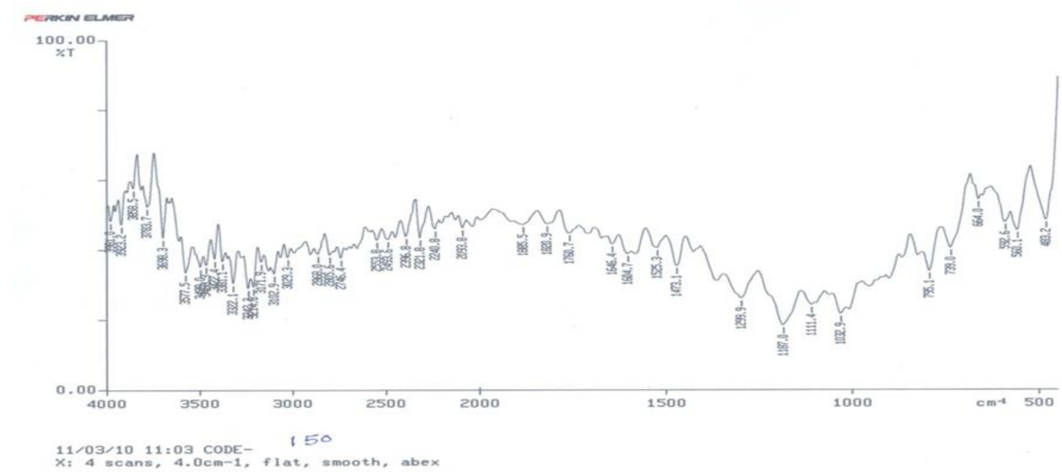

Figure-10
FTIR Spectrum of Flyash (150µm)

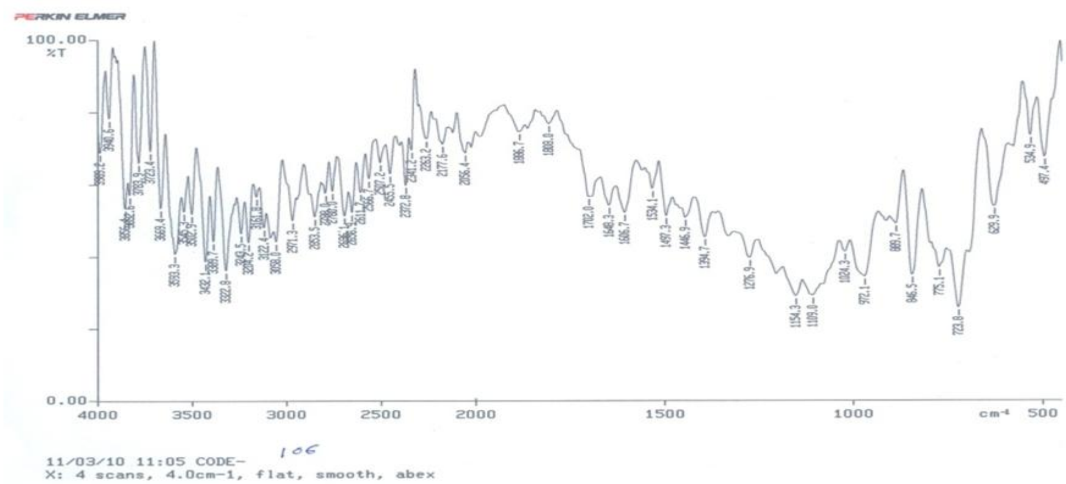

Figure-11
FTIR spectrum of Flyash(106µm)

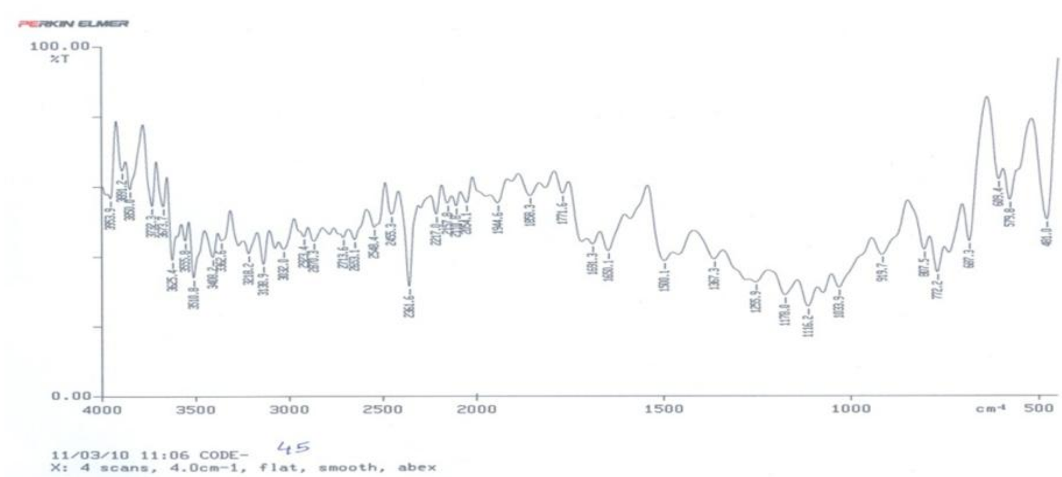

Figure-12
FTIR spectrum of Flyash (45µm)

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