

# Study of SEM/EDXS and FTIR for Fly Ash to Determine the Chemical Changes of Ash in Marine Environment

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**Abstract:** *In this paper, the chemical changes and impact of fly ash in contact with sea water in the earlier dumpsite near Tuticorin thermal power plant was characterized by SEM/EDXS and FTIR. The morphology and elemental composition of fly ash were characterized SEM/EDXS and functional group analysis was studied by FTIR spectrum. The chemical changes of ash in earlier dumpsite was determined by comparing with fresh ash taken from power plant and with sediment taken from 2 km away from dumpsite. The morphology of SEM showed fly ash has spherical particles and in ash from dump site few spherical balls were seen and confirmed the contamination of fly ash. The results of EDXS showed that all the three ash samples predominantly contributed the elements of oxygen, aluminium, silicon and low content of iron, calcium, and potassium in fly ash, iron, calcium, potassium, chloride in bottom ash and iron, calcium, potassium, chloride, and magnesium in ash from dump site. Calcium content in fresh fly ash showed less than 10%. FTIR spectra for all sediment samples showed peaks associated with quartz, feldspar, Montmorillonite, organic matter and nitrate. The present study revealed that the chemical changes occurred in ash in marine environment and thereby altered the quality of sea water.*

**Keywords:** Sea water, Thermal power plant, SEM/EDXS, FTIR, fly ash

## 1. Introduction

The leachability of elements from sub bituminous coal fly ash from India and revealed that the pre and post leached samples were analyzed for morphology specific surface areas and mineralogical changes. Analysis of post leached fly ash indicated changes in the specific surface area and morphology but no change in mineralogy [1]. Most of the studies in the literature that describe leaching from coal ash during contact with seawater were conducted under laboratory, small scale, controlled conditions [2], [3], [4], [5], [6]. Large scale leaching experiments, simulating natural environmental conditions were not performed to date in non stabilized coal ash. Laboratory experiments have shown that leaching from coal fly ash during contact with seawater is dominated by dissolution and desorption processes [3]. SEM can provide size and morphology information of particles at submicron scale [7]. The fact that the sample consisted mainly of respirable size particles is very important in point of view for health risk assessment [8], [9], [10]. Fourier transform infrared (FTIR) spectroscopy has been applied to analyze the environments of Al-O and Si-O bonds in fly ash, which are used as raw materials of geopolymer synthesis. It is noted that the relative intensities of the bands at around 1000, 910 and 700  $\text{cm}^{-1}$  are much higher in fly ash with higher reactivity was observed by [11]. In this present study the tentative physical and chemical changes of prolonged contact of ash (earlier it was dump in deep sea) in marine environment was determined by studying SEM-EDXS and FTIR/KBR.

### 1.1 Study Area

Tuticorin Bay is situated in the South east coast of India in the Gulf of Mannar along the Tamil Nadu coast. Tuticorin Thermal Power Station (TTPS) is located about 2 km to the

east of Tuticorin Port and the northern boundary of the complex is on the brim of the intertidal area of the Tuticorin Bay (Lat.08° 46' 20" N; Long. 78° 10' 46" E). TTPS is a coal – fired thermal power station and hence large amount of fly ash (6,000 Metric Tonnes per day) is generated during the process. Tuticorin Thermal Power Station functioning since 1976 and is generating 1050 MW of electricity. About 17,000 metric tons of coals are used as fuel for the power generation per day. Presently the hot water effluent generated by cooling the condenser has pumped directly into the Bay.

In this present investigation the study area is located near the earlier fly ash dumpsite in Tuticorin coastal water and this also contains the water outfall from the coolant. So this area received high temperature of water. Two stations (station 1 and 2) were fixed at distance of 500 meter and 2 km from the outfall of TTPS shown in Fig :1

**Station 1 :** 500 meters away from water outfall of power plant (Earlier ash dumpsite) (N 08° 46' 48.3" & E 078° 10' 76.3"). This area do not containing any biological system due to the water with high temperature from outfall of thermal power plant and the presence of fly ash.

**Station 2 :** 2 km away from the water outfall of power plant. (N 08° 47' 32.0" & E 078° 10' 80.3"). This area also do not containing any biological system. The impact of outfall water from power plant and fly ash extents over in this area too.

### 1.2 Sample Collection

For the determination of chemical changes of fly ash in marine environment, ash sample was collected from thermal power plant. Three types of fly ash were used for the

analysis. Fresh fly ash from electrostatic precipitator was collected. Second sample from earlier ash dumpsite of Tuticorin coast and third sediment sample from station 2 were also collected by deep grab sampling during May 2015.



**Figure 1:** Aerial view of Tuticorin Thermal Power Plant (TTPS) with 2 stations

## 2. Materials and Methods

### Characterization of fly ash samples by SEM-EDXS, FTIR/KBr

A Scanning Electron Microscope (SEM) (model-JEOL-JSM-6380LA, USA) with energy dispersive X-ray spectroscopy (EDXS) was used to evaluate the texture, morphology and elemental composition of fresh fly ash, ash from dumpsite and sediment from station 2. Fly ash samples of fresh fly ash, ash from dumpsite and sediment from dumpsite were investigated by different methods, as described. The Perkin Elmer FTIR spectrometer was used in the present work for recording the FTIR spectra of the samples at room temperature. The KBr pellet technique (1:20) was followed for the mineral analysis. To provide a good characterization of a mineral by infrared spectroscopy, the spectrum recorded in the range of  $4000-400\text{ cm}^{-1}$ .

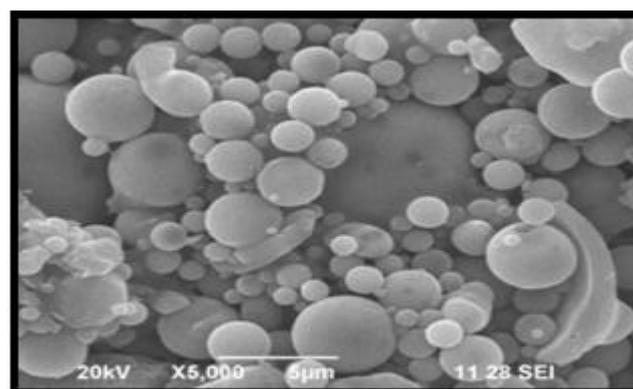
## 3. Results and Discussion

### 3.1 SEM-EDXS

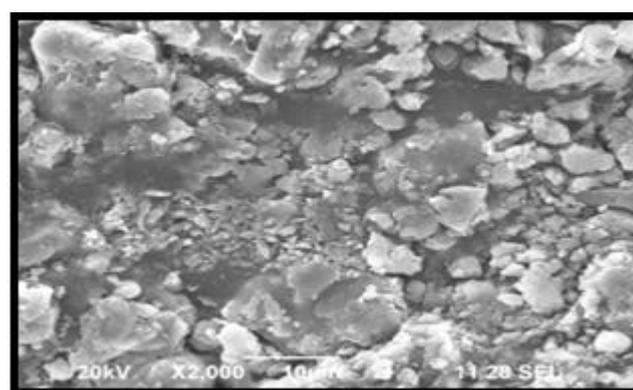
SEM is one of the best and most widely used techniques for the identification and characterization of mineral phases and morphology of fly ash. Fig. 2 showed the SEM image of dried fly ash. Fig. 3 showed the image of ash from dumpsite. Fig. 4 showed the SEM image of sediment from station 2. The SEM data indicated intermixing of Fe and Al-Si mineral phases and the predominance of Ca-nonsilicate minerals. The majority of the iron-rich spheres consisted of two phases an iron oxide mixed with amorphous aluminosilicate. The calcium rich material was distinct in both elemental composition and texture from the amorphous aluminosilicate spheres. Many spherical particles along with irregularly shaped are seen (Fig. 2). The rounded particles with a wide distribution in size are predominantly glassy. The angular particles are mostly comprised of crystalline solids such as quartz, mullite, magnetite and hematite. The spherical particles which correspond to magnetic fraction of any fly ash sample. The non-magnetic components have a general tendency to be spheroidal. With increase in particle

The inner part of the grab sample was taken for the analysis to avoid contamination and collected in polythene bags. The collected fly ash was air dried under the shade.

size this spheroid nature of the magnetic properties increases. The elemental composition of ash samples were determined and confirmed by EDXS shown in Table 1-3. All the three samples were predominantly contains oxygen, aluminium, silicon (Fig. 5-7). Ash from dumpsite showed the predominant value of calcium. Ash taken from sea dumpsite showed the major elements of oxygen, silicon, aluminium, and calcium. Lower elements were iron, potassium, magnesium and chloride. And it has the same elemental nature, except it has calcium as a major element and magnesium as a lower element. From sea water it gets adsorbed. The morphological nature was different from fresh fly ash. The particles were shapeless and fused together. Ash from dumpsite showed different composition due to contamination with marine sediment and get leached/adsorbed. Increase of element concentration may be due to chemical exchange processes, for example, Ca-Mg exchange [12], [13] or to adsorption [14]. It is known that coal ash has adsorption properties. Station 2, sediment showed silicon which was higher than ash from dumpsite and other elements were lower than ash from dumpsite.



**Figure 2:** SEM image of fresh fly ash



**Figure 3:** Ash from dumpsite

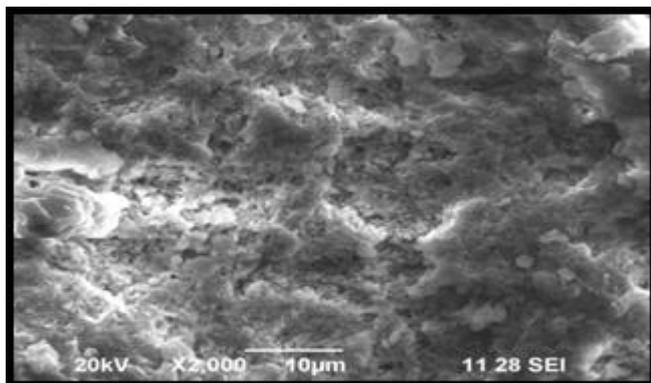


Figure 4: Ash from station 2 (Arrows showing the spherical particles)

Table 1: Elemental composition of fresh fly ash

Element	Wt %	Element	Wt %
O	50.95	Fe	2.97
Si	28.21	K	1.33
Al	15.44	Ca	1.10

Table 2: Elemental composition of Ash from dumpsite (Station 1)

Element	Wt %	Element	Wt %
O	54.64	Fe	3.48
Si	18.22	Mg	1.78
Ca	10.06	K	1.32
Al	9.06	Cl	0.66

Table 3: Elemental composition of sediment from station 2

Element	Wt %	Element	Wt %
O	55.69	Fe	2.77
Si	22.30	Na	2.34
Al	8.20	Mg	1.71
Ca	4.13	K	1.66
		Cl	1.20

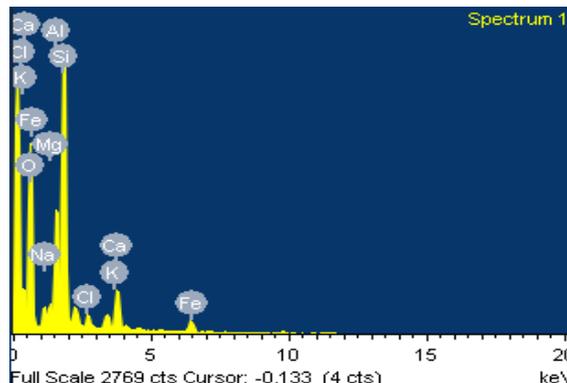


Figure 7: EDXS- Sediment from station

### 3.2 FTIR/KBr

Fig. 20 - 22 showed the FTIR spectra of fresh fly ash, ash from dumpsite and sediment from station 2. The important infrared (IR) bands of samples with their possible assignments are shown in Table 4-6. By comparing the observed frequencies with available literature, the minerals such as quartz, orthoclase, kaolinite, and montmorillonite have identified. Appearing peaks in the region 2850 to 2853 $\text{cm}^{-1}$  and 2923 to 2926  $\text{cm}^{-1}$  in all the samples show the presence of organic carbon [15]. Fresh fly ash sample showed the presence of organic carbon. The presence of the OH deformation band of the  $\text{AlFe}^{3+}\text{OH}$  grouping in the range 886 to 888  $\text{cm}^{-1}$  is observed in some of the sites which may be due to the presence of montmorillonite. All the three samples showed the presence of montmorillonite.

N-O stretching was present in all the three samples due to the presence of nitrate species. FTIR spectra for all sediment samples showed peaks associated with quartz, feldspar, Montmorillonite, organic matter. In addition to that station 2, and ash from dumpsite showed calcite. Fresh fly ash showed the presence of mullite. By comparing ash from dumpsite and station 2 sediment the frequencies obtained in FTIR were similar with few exception. By tidal waves and prolong exposure to sea water the ash in dumpsite is mixed with sea sediment.

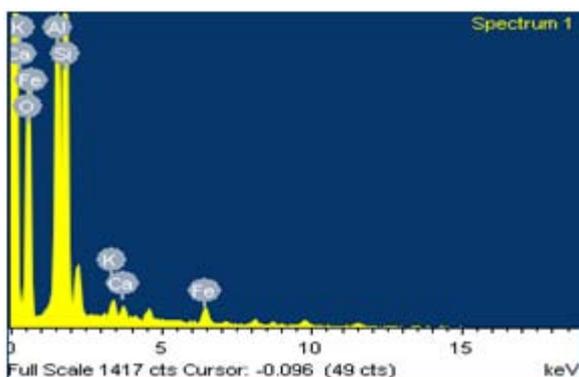


Figure 5: EDXS-Fresh Fly ash

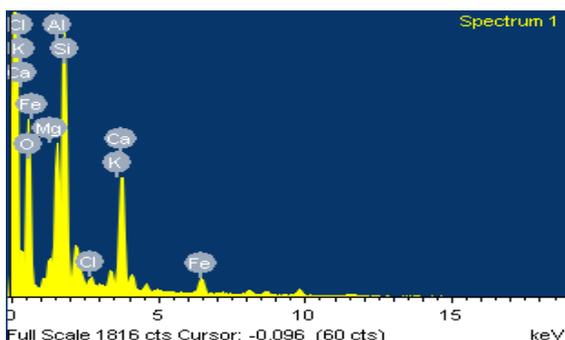


Figure 6: EDXS-Ash from dump site

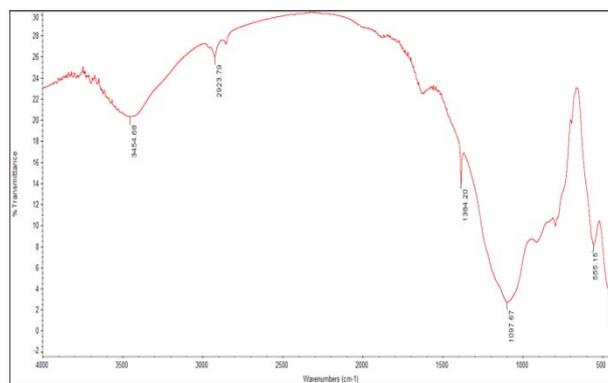


Figure 8: FTIR spectrum of fly ash

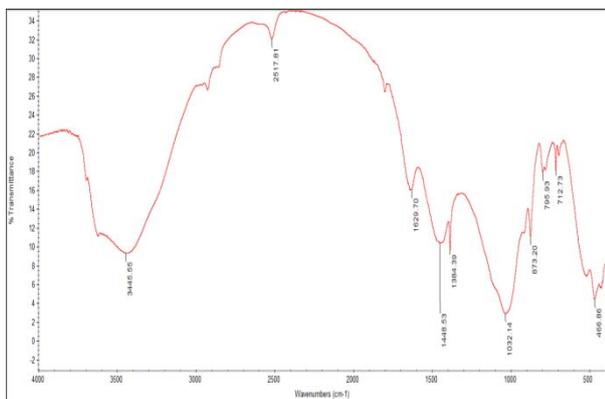


Figure 9: FTIR spectrum of ash from dumpsite

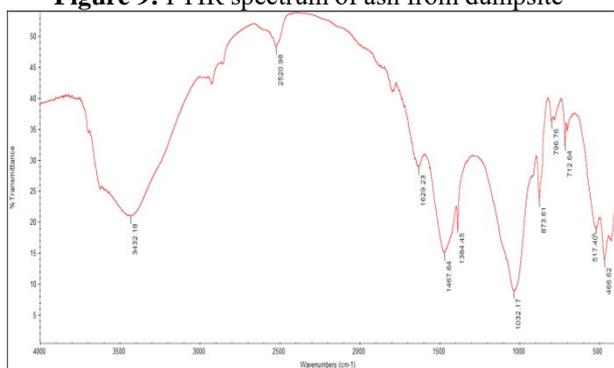


Figure 10: FTIR spectrum of sediment from station 2

All the samples were subjected to Fourier transform infrared spectroscopy analysis and observed wave numbers ( $\text{cm}^{-1}$ ) were tabulated with corresponding minerals (Table. 4-6). According to [16], the presence of quartz in the samples can be confirmed by the characteristic peaks at around 778 and  $796 \text{ cm}^{-1}$  with Si-O symmetrical stretching vibrations. In the presence study, the above-mentioned characteristic peaks were observed with well intensity in all the samples.

Table 4: Band assignments for different minerals of fly ash

Frequency ( $\text{cm}^{-1}$ )	Mineral Name/component	Tentative Assignment	Reference
3454	Montmorillonite	OH group of adsorbed water dust-stretching	[17]
2923	Organic carbon	C-H stretching vibration	[18]
1629	Organic matter	Stretching vibrations of C=O carboxylate group of organic matter	[19], [20], [21]
1384	Nitrate species	N-O stretching	[22]
1097	Quartz	Si-O-Si asymmetric stretching vibration	[23]
794	Quartz	Si-O symmetric	[16], [24]
463	Felspar	Amorphous silica Si-O-Si band	[25], [26], [27]

Table 5: Band assignments for different minerals of fly ash from dumpsite

Frequency ( $\text{cm}^{-1}$ )	Mineral Name/component	Tentative Assignment	Reference
3445	Montmorillonite	H-O-H stretching of water molecules	[17]
2517	Calcite	Vibrational mode of carbonate	[28]
1629	Organic matter	C=O carboxylate group of organic matter	[19], [20], [21]

1448	Calcite	C-O stretching for carbonate	[29]
1384	Nitrate species	N-O stretching	[22]
1032	Kaolinte	Si-O stretching of clay mineral	[30]
873	Calcite	C-O bending for carbonate	[31]
795	Quartz	Si-O symmetric	[16], [24]
712	Calcite	carbonate	[32], [33], [34]
466	Feldspar	Si-O-Si bending	[31], [35]

Table 6: Band assignments for different minerals of sediment from station 2

Frequency ( $\text{cm}^{-1}$ )	Mineral Name/component	Tentative Assignment	Reference
3432	Montmorillonite	Broad-O-H stretching of water molecules	[17]
2520	Calcite	Vibrational mode of carbonate	[28]
1629	Organic matter	C=O carboxylate group of organic matter	[19], [20], [21]
1467	Calcite	C-O stretching for carbonate	[29]
1384	Nitrate species	N-O stretching	[22]
1032	Kaolinte	Si-O stretching of clay mineral	[30]
873	Calcite	C-O bending for carbonate	[31]
796	Quartz	Si-O symmetric	[16], [24]
712	Calcite	carbonate	[33], [34], [35]
517	Hematite	Si-O-Al (or) $\text{Fe}_2\text{O}_3$	[36], [30]
466	Feldspar	Si-O-Si bending	[31], [35]

#### 4. Conclusion

Chemical changes of fly ash revealed that the ash was leached/adsorbed in the marine environment. Changes were occurred in the chemical composition of the ash during the experiment. Scanning electron microscope revealed that the contamination reduced as the distance increased from earlier dumpsite. Elemental composition study of EDXS showed that the fly ash taken from power plant belongs to class F. FTIR studies revealed that the frequencies were same in both samples from station1 which is located near water outfall and station 2 which is located 2 km away from the outfall. SEM and EDXS studies also confirmed that the impact of fly ash is in few kilometers. Further, it is necessary to study leaching test for the ash of Tuticorin thermal power plant, which will provide a clear idea about real chemical changes of ash, and the causes for chemical changes.

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#### References

[1] Proharaj, S.P., Swain, M.A., and Powell, 2002. Environment International, 27: 631-638.

- [2] Reuss, M., 1983. Comparison different methods for estimating the leaching of heavy metals from coal combustion waste. *Water Sci. Technol.*, 15: 193–205.
- [3] Van Der Sloot, H.A., Nieuwendijk, B.J.T., 1985. Release of trace elements from surface-enriched fly ash in seawater. In: Duedall, I.W., Kester, D.R., Park, P.K., Ketchum, B.H. (Eds.), *Wastes in the Ocean*, Vol. 4: Energy Wastes in the Ocean. Wiley, New York, pp. 449–464. Chapter 18.
- [4] Van Der Sloot, H.A., Wijkstra, J., Van Stigt, C.H., Hoede, D., 1985. Leaching of Trace Elements from Coal Ash and Coal Ash Products. In: Duedall, I.W., Kester, D.R., Park, P.K., Ketchum, B.H. (Eds.), *Wastes in the Ocean*, Vol. 4: Energy Wastes in the Ocean. Wiley, New York, pp. 467–497. Chapter 19.
- [5] Crecelius, E.A., 1985. Fly-ash disposal in the ocean: an alternative worth considering. In: Duedall, I.W., Kester, D.R., Park, P.K., Ketchum, B.H. (Eds.), *Wastes in the Ocean*, Energy Wastes in the Ocean. Wiley, New York, 5, Chapter (15): 379–388.
- [6] Kress, N., 1993. Chemical aspects of coal fly ash disposal at sea: predicting and monitoring environmental impact. *Water Sci. Technol.*, 27 (7–8): 449–455.
- [7] Utsunomiya, S., and Ewing, R.C., 2003. Application of high-angle annular dark field scanning transmission electron microscopy, scanning transmission electron microscopy energy dispersive X-ray spectrometry, and energy-filtered transmission electron microscopy to the characterization of nano particles in the environment, *Environ Sci & Technol.*, 37: 786–791.
- [8] Davison, R.L., Natusch, D.F.S, Wallance, J.R, and Evans, C.A. 1974. Trace elements in fly ash dependence of concentration on particle size. *Environ. Sci.& Technol.*, 8: 1107- 1113.
- [9] Gieré, R, Carleton, L.E, and Lumpkin, G.R. 2003. Micro- and nanochemistry of fly ash from a coal-fired power plant. *American Mineralogist*, 88: 1853– 1865.
- [10] Hansen, L.D., and Fisher, G.L., 1980. Elemental distribution in coal fly ash particles, *Environmental Science & Technology*, 14: 1111- 1117.
- [11] Zhang, Z., Hao Wang, John, L., and Provis, 2012. Quantitative study of the reactivity of fly ash in geopolymerization of FTIR. *Journal of sustainable cement based materials.*, 1(4).
- [12] Hockly, D.E., and Van Der Sloot, H.A., 1991. Long-term processes in a stabilized coal-waste block exposed to seawater. *Environ. Sci. Technol.*, 25: 1408–1414.
- [13] Kress, N., Galil, B., Herut, B., Hornung, H., Natan, Y., 1994. *Israel Oceanographic and Limnological Res. Report (H9/94)* (in Hebrew).
- [14] Roethel, F.J., and Oakley, S.A., 1985. Effects of seawater on the mineralogical and chemical composition of coal-waste blocks. In: Duedall, I.W., Kester, D.R., Park, P.K., Ketchum, B.H. (Eds.), *Wastes in the Ocean*, Energy Wastes in the Ocean. Wiley, New York, 4: 691–704.
- [15] Song, Z., Chouparova, E., Jones, K.W., Feng, H., and Marinkovic, N.S., 2001. FTIR Investigation of Sediments from NY/NJ Harbor, San Diego Bay, and the Venetian Lagoon. *NSLC Activity Report, Science Highlights.*, 112–116.
- [16] Hlavay, J., Jonas, K., Elek, S., and Inczedy, J., 1978. Characterization of the particle size and the crystallinity of certain minerals by infrared spectrophotometry and other instrumental methods-II. Investigation on quartz and feldspar, *Clay and Clay Minerals.*, 26: 139.
- [17] Summer, M.E., 1995. *Hand Book of Soil Science*. University of Georgia, Boca Raton Hondor press, New York.
- [18] Saikia B.J., Parthasarathy G., Sarmah N.C., and Baruah G.D., 2008. Fourier transform infrared spectroscopic characterization of naturally occurring glassy fulgurites, *Bull Mater Sci.*, 31(2): 155-158.
- [19] Socrates G., 2001. *Infrared and Raman characteristic group frequencies*, 3rd 233 Ed. Wiley and sons.
- [20] Matrajt, J., Borg, P.I., Ray nal, Z., Djouadi, d Herdecouirt, G., Flynn, D., and Deboffle, 2004. FTIR and Raman analyses of the Tagish lake meteorite, Relationship with the aliphatic hydrocarbon observed in tge diffuse interseller medium, *Astron. Astrphys.*, 416: 983-990.
- [21] Langford H., Hodson A., and Banwart S., 2011, Using FTIR spectroscopy to characterize the soil mineralogy and geochemistry of cryoconite from Aldegondabreen glacier. *Applied Geochemistry.*, 26: S206–S209.
- [22] Smidt, Katharina Böhm and Manfred Schwanninger BOKU, 2002. *The Application of FT-IR Spectroscopy in Waste Management - University of Natural Resources and Life Sciences, Vienna Austria, Fourier Transforms - New Analytical Approaches and FTIR Strategies*, 405- 430.
- [23] Katara, S., Sakshi Kabra, Anita Sharma, Renu Hada, and Ashu Rani, 2013. Surface modification of fly ash by thermal activation: A DR/FTIR study, *Intl. J. Pure & Applied Chem.*, 3(4): 299-307.
- [24] Coates J.P., 1977. *The IR Analysis of Quartz and Asbestos*, Neliioth Offset Ltd., Chesham, England.
- [25] Farmer, V.C., 1974. *The IR Spectra of Minerals*, Mineralogical Society, London, 182.
- [26] Clarence Karr, 1974. *Jr. Infrared and Raman Spectroscopy of Lunar and Terrestrial Minerals*, Academic Press: Newyork, 1.
- [27] Russell J.D., 1987. *Infrared methods, A Hand Book of Determinative Methods in Clay Mineralogy*, (M.J.Ed.Wilson,) Blackie and Son Ltd.
- [28] Ramasamy, V., Rajkumar, P., and Ponnusamy, V., 2009. Depth wise analysis of recently excavated Vellar river sediments through FTIR and XRD studies. *Indian J. Phys.*, 83 (9): 1295–1308.
- [29] Ramasamy, V., Suresh, G., Meenakshisundaram, V., and Ponnusamy, V., 2011. Horizontal and vertical characterization of radionuclides and minerals in river sediments. *Appl. Radiat. Isotopes.*, 69: 184–195.
- [30] Ramasamy, V., Rajkumar, P., and Ponnusamy, V., 2006. FT-IR Spectroscopic analysis and mineralogical characterization of Vellar river sediments. *Bull. Pure Appl. Sci.*, 25: 49– 55.
- [31] Dahlan, I., Gui Meei Mei, Azlina Harun Kamaruddin, Abdul Rahman Mohamed, and Keat Teong Lee, 2008. Removal of So<sub>2</sub> and no over rice husk ash(rha)/cao-supported metal oxides. *J.Eng. Sci. Technol.*, 3(2): 109 – 116.

- [32] Hunt, J.M., and Turner, D.S., 1953. Determination of mineral constituents of rocks by infrared spectroscopy. *Anal. Chem.*, 25: 1169-1174.
- [33] Adler, H.H., and Kerr, P.F., 1962. Infrared spectra symmetry and structure relations of some carbonate minerals. *Am. Min.*, 48: 839-853.
- [34] Chester, R., and Elderfield, H., 1967. The application of infrared absorption spectroscopy to carbonate mineralogy, *Sedimentology.*, 9: 5-21.
- [35] Sivakumar, S, Ravisankar, R., Raghu, Y., Chandrasekaran, A., and Chandramohan, J., 2012. FTIR Spectroscopic Studies on Coastal Sediment Samples from Cuddalore District, Tamilnadu, India. *Ind. J. of Advances in Chemical Sci.*, 1: 40-46.
- [36] Manoharan, C.P., Sutharsan, S., Dhanapandian, R., and Venkatachalapathy, 2012. *J. Mole. Struct.*, 1027: 99-103.