Research Journal of Material Sciences E-ISSN 2320–6055
Vol. **4(7),** 6-14, August **(2016)** *Res. J. Material Sci.*

Synthesis and Characterization of Modified Coal Fly Ash (MCFA) as an Adsorbent from Coal Fly Ash (CFA)

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Available online at: www.isca.in, www.isca.me
Received 26th June 2016, revised 16th July 2016, accepted 8th August 2016

Abstract

CFA is the waste generated from Thermal Power Plants which is recognized as byproduct of it. Huge amount of CFA is generated worldwide as compared to its utilization. CFA can be utilize by modifying it as an adsorbent as modified coal fly ash (MCFA). In this paper synthesis of MCFA and its characterization is described. MCFA is synthesized by treating CFA with 5N NaOH at 80^0C for 48 hours with continuous stirring. MCFA is analyzed by SEM, FTIR, XRD and XRF for characterization of different parameters like surface morphology, chemical bonding, phase identification and chemical composition etc. SEM micrograph of MCFA is seen with large gelatinous mass formed due to the breaking and dissolution of alumino-silicate phases modifying the surface morphology greatly. XRD pattern shows the intensity of the quartz is more in MCF than CFA. FTIR spectra observed shaper at band length of 1058 cm^{-1} in MCFA which indicates more crystallization and higher absorbance than CFA. In XRF analysis, it was observed that the MCFA consists of 44.63% SiO_2 and 43.72% Al_2O_3 which are the main constituents of the zeolites. Al_2O_3 percentage is increased from 26 to 43.72 in MCFA which indicates the zeolitisation of CFA. Also it was observed that SiO_2 percentage is reduced from 61 to 44.63. Increased amount of Na_2O (0.620) in MCFA was observed because of the alkali treatment of CFA.

Keywords: MCFA, CFA, SEM, FTIR, XRD, XRF.

Introduction

CFA is the waste generated from Thermal Power Plants which is recognized as byproduct of it. Huge amount of CFA generated worldwide as compared to its utilization. The global annual production of coal fly ash is about 800 million tons and this amount is predicted to increase in the future. However, the global recycling rate of CFA is only 15% posing important challenges for researchers in waste management. At present, efficient disposal of CFA is a worldwide issue because of its massive production and its harmful effects on the environment[1]. Hence coal fly ash can be utilize by modifying it as an adsorbent as modified coal fly ash (MCFA).

To develop an adsorbents from coal fly ash, several development techniques such as mechanical and thermal treatment, acid and alkali treatment being used by different researchers. Proper development treatment in order to increase its adsorption properties is required for better results. Alkali treatment is one of the methods to improve the adsorption property of coal fly ash. The present work describes the modification of CFA in to MCFA by treating the CFA with alkali at moderate temperature and time to increase its silica content and surface property.

Materials and Methods

Materials: CFA was collected from the Paras Thermal Power Plant situated at Paras village in Akola district of Maharashtra State. This coal fly ash was washed with neutral water for three to four times to remove the contaminants present if any. The washed coal fly ash then dried for two days in sunlight. This dried coal fly ash then screened in sieve shaker and separated into different screen sizes. Then the coal fly ash of below 90 micron size has been taken for the development of adsorbent.

Screen analysis of coal fly ash: Screening of the washed coal fly ash has been done by sieve shaker. The different size sieves like 75, 90, 150, 300, 600 microns and pan are taken for the screening of the coal fly ash. The screened material are collected according to the size and stored for further experimentations. Following are the figures for the sieves and sieve shaker.

Figure-1
Sieve shaker for screening with different micron size sieves (75, 90, 150, 300, 600 microns and pan)

Method: Preparation of the MCFA from CFA: MCFA was prepared form coal fly ash by taking 100 gram of coal fly ash treated with 1000 ml of 5N NaOH solution in a beaker. Crystallization of coal fly ash was done for 48 hours with continuous stirring at 80^0C. The prepared MCFA was washed with distilled water several times until the pH of the washed distilled water reaches to neutral. Drying of MCFA was done at 100^0C for one hour to remove the moisture present in it. This prepared MCFA is stored in the air tight polyethylene bags for further experimentations. Following are some figures of MCFA preparation.

Figure-2
MCFA preparation from CFA

Characterization of the MCFA: The surface morphology for CFA and MCFA were studied with the help of Field Emission Scanning Electron Microscope (FESEM) (Hitachi, Japan model S-4800 type 2).

Mineralogical compositions were determined on X-ray diffractometer (XRD) (Bruker, Germany model D8 advance) with Cu-Ka radiation. FTIR spectra for the CFA and MCFA were recorded on Shimatzu FTIR-8400 Spectrophotometer using KBr pellet method. All above analysis was done at UICT, NMU Jalgaon. Qualitative identification and quantitative determination of elements present in MCFA was done by X-Ray Fluorescence Spectrometer (XRF) (Philips model PW 2404) at Sophisticated Analytical Instrument Facility (SAIF), IITB, Mumbai.

Results and Discussion

SEM Images: SEM images for CFA and MCFA are shown in Figures-3 and 4.

The morphology of the CFA is shown in Figure-3 (A-I). The SEM photograph of CFA shows the particles of different shapes and sizes, minerals and unburned carbon particles, whereas the typical SEM image of MCFA shows the structural break down of larger particles and increased surface roughness and pore volume Figure-4 (A-H). The smooth spherical cenospheres are affected most resulting remarkable changes in morphology. After treating with NaOH, rough cenospheres are transformed into agglomerations of more amorphous in nature with none of crystal formation as seen in SEM micrographs presented in Figure-4 (A-H).

SEM micrograph of MCFA is seen with large gelatinous mass formed due to the breaking and dissolution of alumino-silicate phases modifying the surface morphology greatly. Similar results are observed by Sharma A. et.al[2].

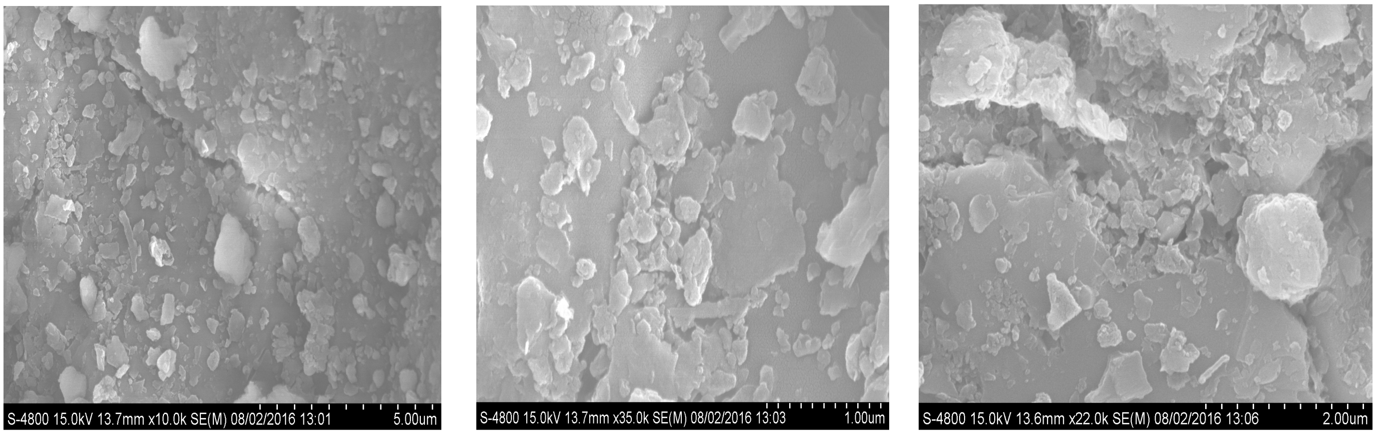
XRD Pattern: XRD pattern for CFA and MCFA are represented in the Figures-5 and 6.

The diffractogram (Figure-5 and 6) shows the X-ray diffraction pattern for CFA and MCFA having particle size below 90 micron. It was observed that CFA consisted of crystalline minerals, hematite, quartz, mullite and small amounts of ferrous and calcium oxide having large peaks of quartz (SiO_2).

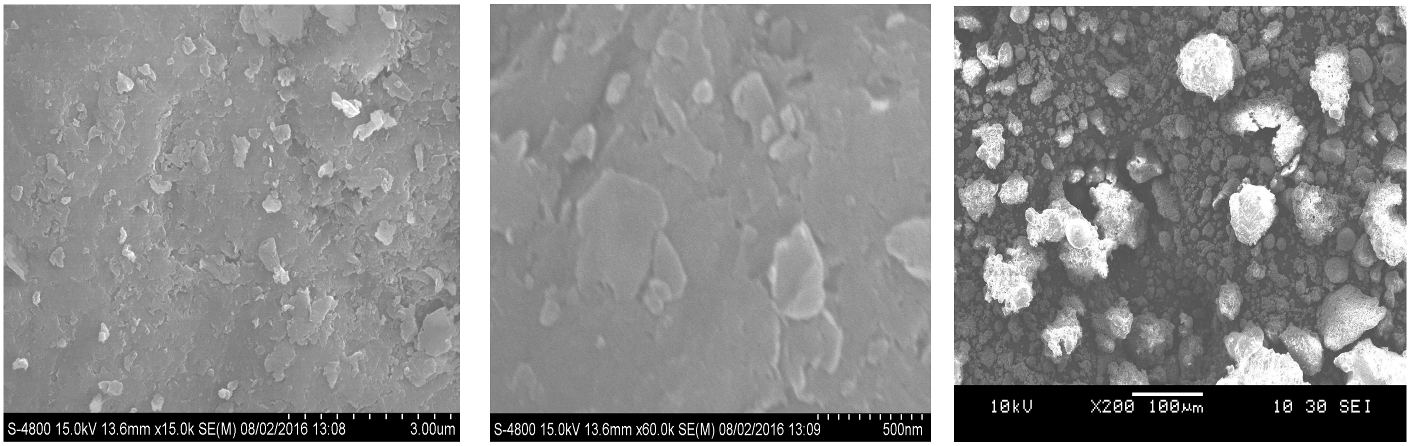
The peaks in Figure-5 (A) at 15.465º, 25.275º, 32.300^0 and 34.301° show mullite (alumino-silicate) phases while quartz (SiO_2) exhibits strong peaks at 19.927º, 25.695º, 38.511º, 41.574^0 and 49.217º of 2θ values. Peaks at 35.583^0, 39.901^0 and 54.527^0 indicates hematite phase. Similar results are observed by Sharma A. et.al[2]. The peaks in Figure-6 (A) at 30.046º, 32.259º, and 49.218º show mullite (alumino-silicate) phases while quartz (SiO_2) exhibits strong peaks at 19.901º, 25.697º, 34.356º, 35.650^0, 38.529^0, 44.893^0 and 53.058º of 2θ values.

A large SiO_2 concentration in MCFA than CFA is indicated by the large characteristic peaks of quartz (SiO_2). Due to the reaction of NaOH with Si-Al chain of CFA, breaking of the Si-Al chain occurs resulting increased volume of mircopore of the CFA as shown in Figure-4(D). The typical peak intensity of the quartz is more visible in Figure-5 and 6 which shows the concentration of quartz is more in this fragment.

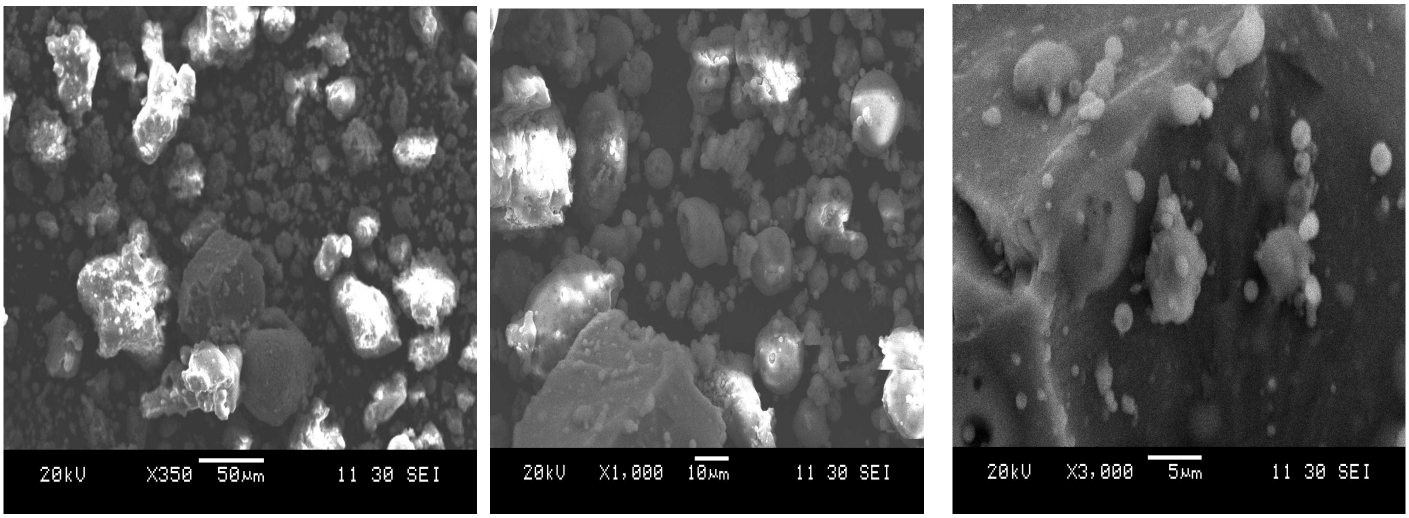
FTIR Spectra: FTIR spectra for coal fly ash and adsorbent (modified CFA) are represented in the Figures-7 and 8.



A. SEM image of CFA at 10.0k B. SEM image of CFA at 35.0k C. SEM image of CFA at 22.0k

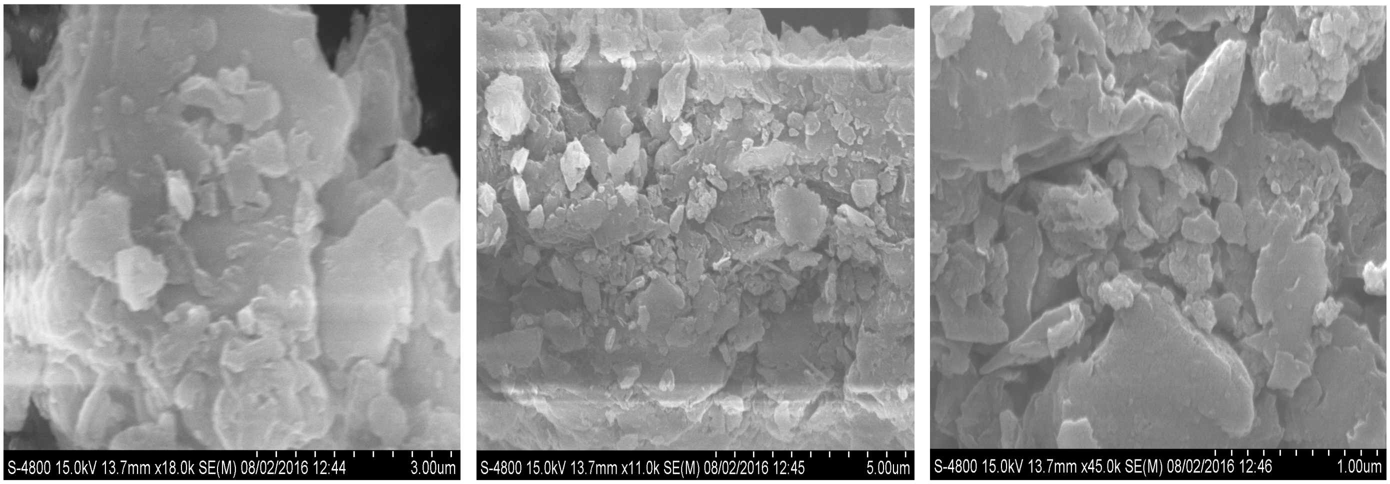


D. SEM image of CFA at 15.0k E. SEM image of CFA at 60.0k F. SEM image of CFA at 10.0kvx200

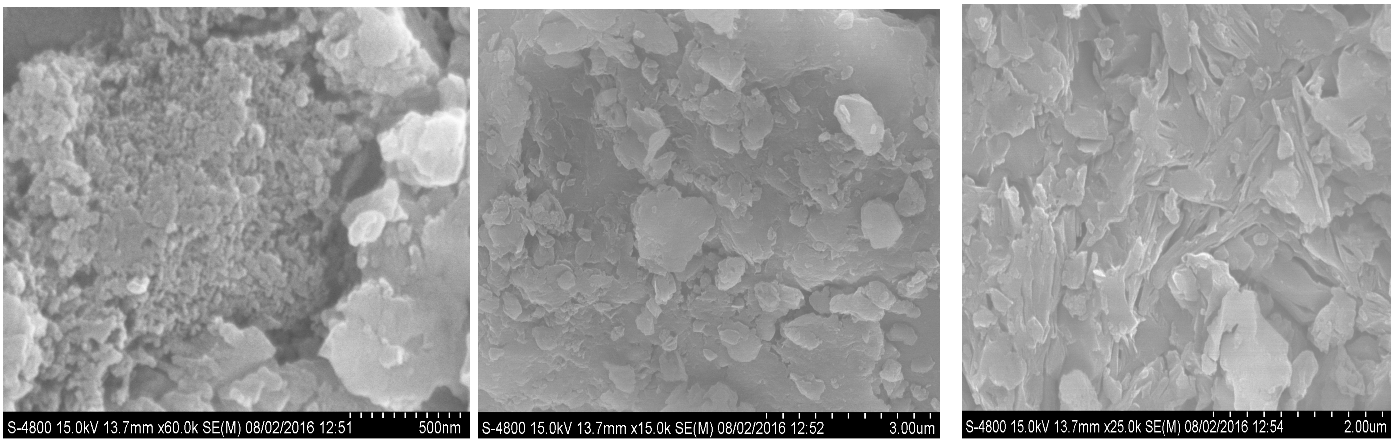


G. SEM image of CFA at 20.0kvx350 H. SEM image of CFA at 20.0kvx1000 I. SEM image of CFA at 20.0kvx3000

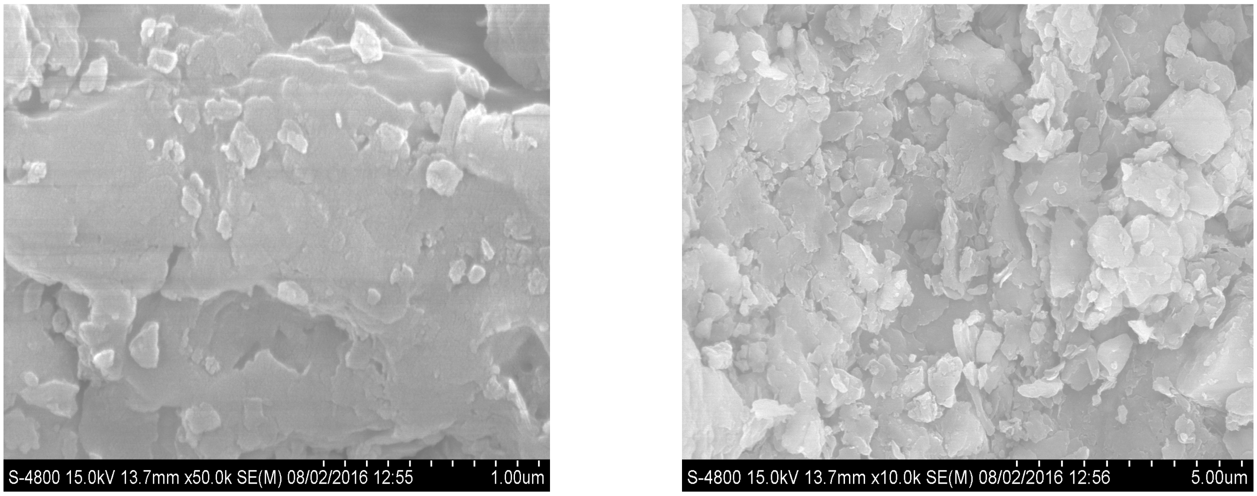
Figure-3
SEM images of CFA



A. SEM image of MCFA at 18.0k B. SEM image of MCFA at 11.0k. C. SEM image of MCFA at 45.0k

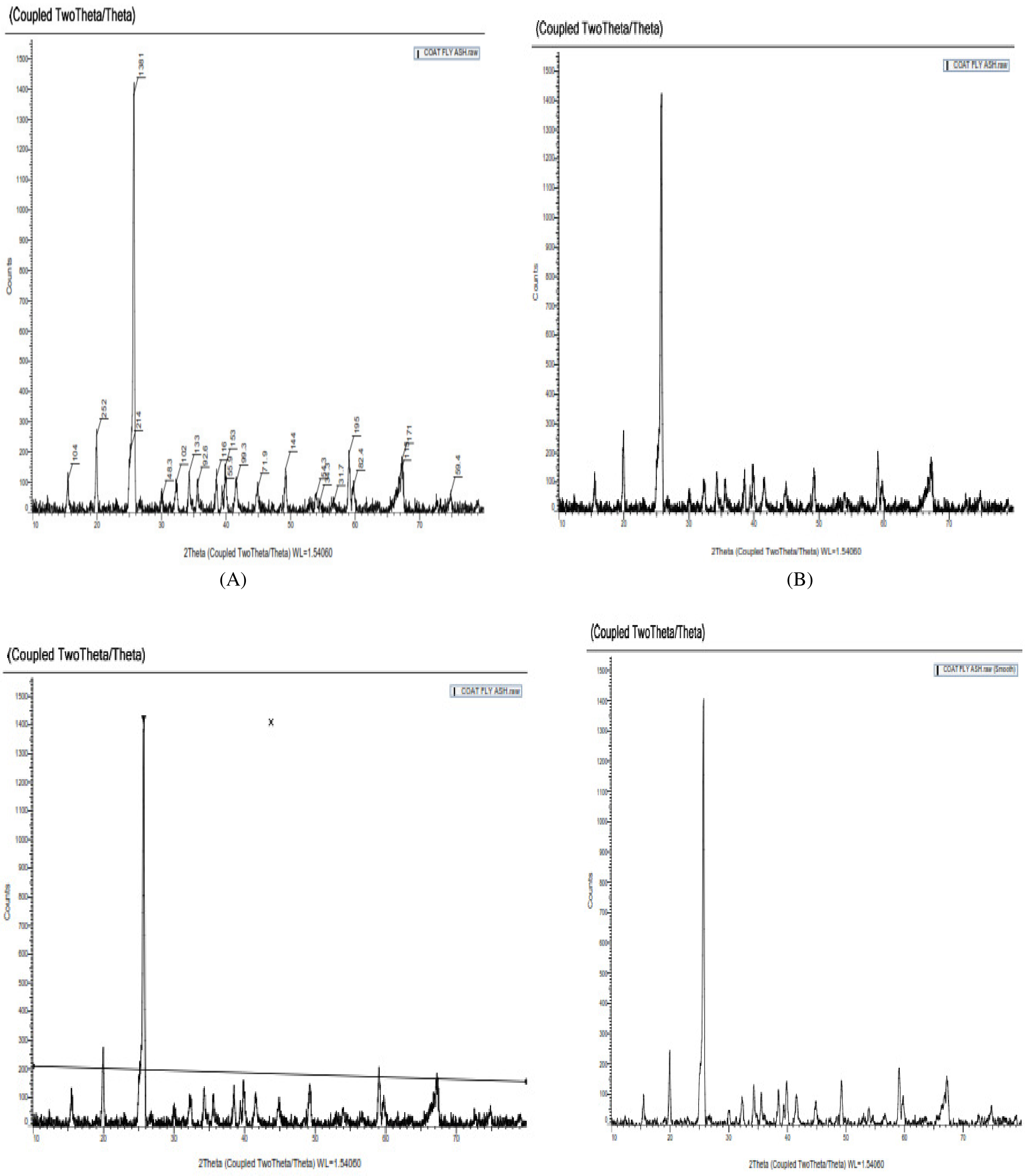


D. SEM image of MCFA at 60.0k E. SEM image of MCFA at 15.0k F. SEM image of MCFA at 25.0k



G. SEM image of MCFA at 50.0k H. SEM image of MCFA at 10.0k

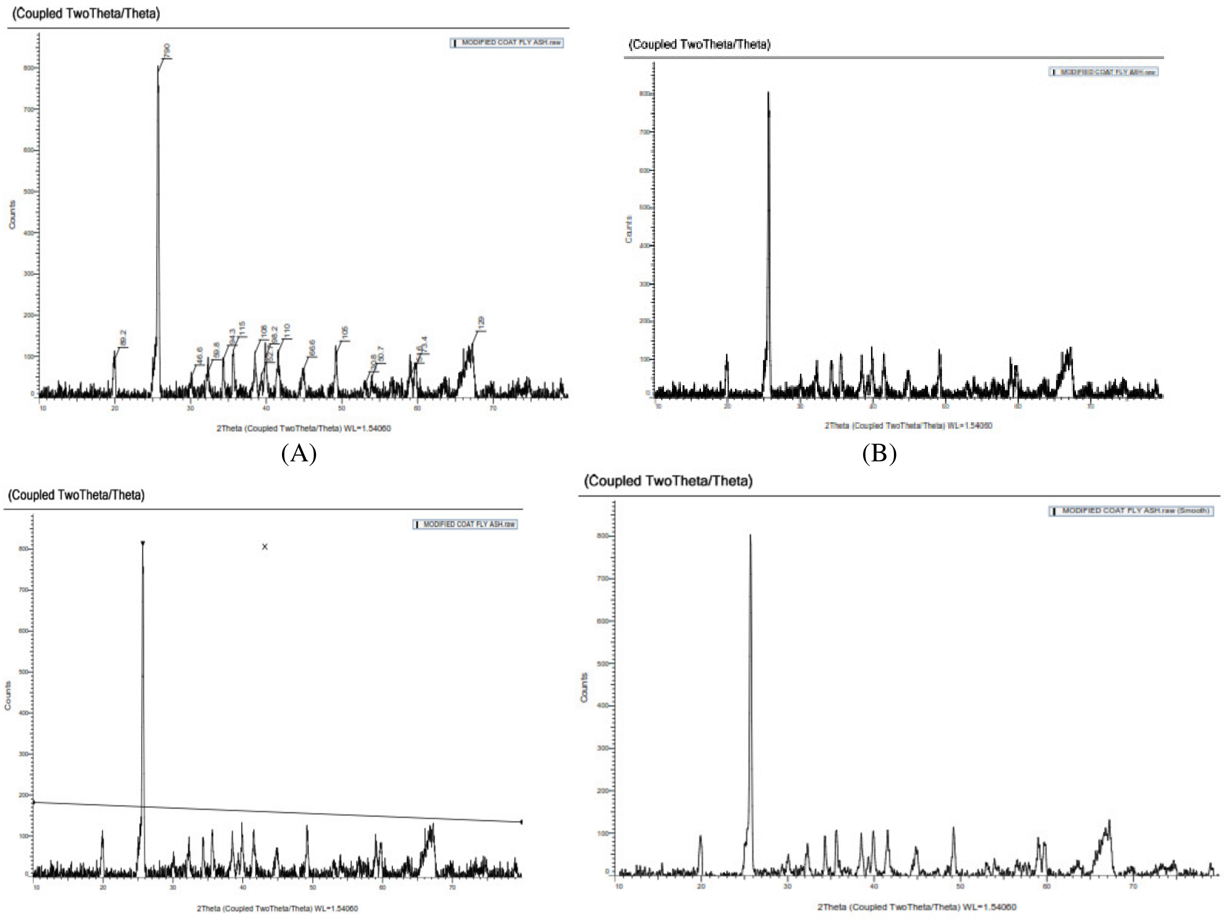
Figure-4
SEM images of MCFA



(A) (B)

(C) (D)

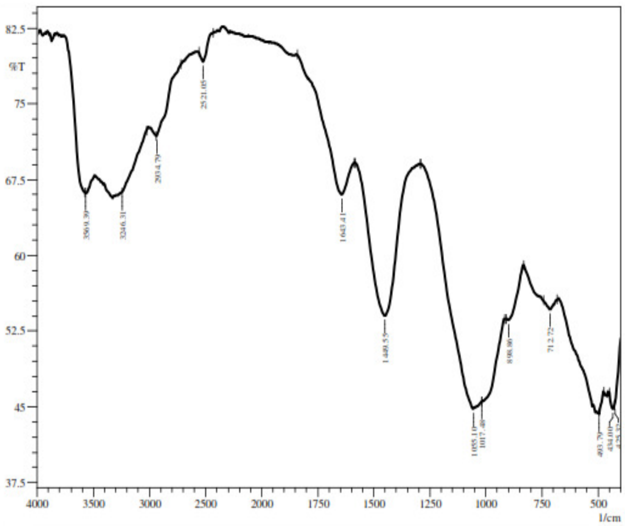
Figure-5
XRD of CFA



(A) (B)

(C) (D)

Figure-6
XRD of MCFA



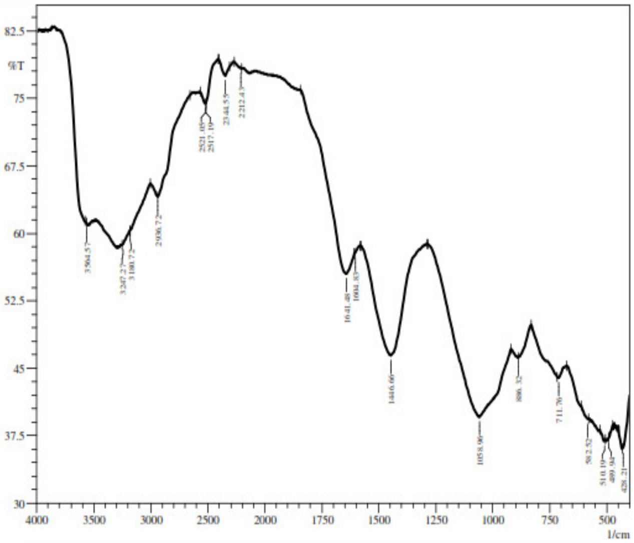


Figure-7
FTIR spectra for CFA

Figure-8
FTIR spectra for MCFA

Figures-7 and 8 represent the FTIR spectrum of CFA and MCFA. Fourier Transform Infrared spectroscopy (FTIR) is used to provide statistic about molecular structure. FTIR requires virtually no sample preparation. The scanning range was from 399 to 4000 cm^{-1}. The bands at 425 cm^{-1} – 428 cm^{-1} observed for both CFA and MCFA shows the aluminosilicate matrix present in both materials. In MCFA, the bands at 400 cm^{-1} – 420 cm^{-1} are associated to the pore opening of the modified coal fly ash. Band in the region 425 cm^{-1} – 510 cm^{-1} are assigns to Si-O and Al-O internal tetrahedron vibrations for CFA and MCFA. The shifting of the Si/Al-O band at 1065 cm^{-1}, analogous with stretching vibrations to lower frequencies (1058 cm^{-1}), indicates modification of the CFA. Shaper band at 1058 cm^{-1} (Figure-9) is observed which indicates increased crystallization in the MCFA have a higher absorbance than CFA. The bands in MCFA at 428 cm^{-1} – 510 cm^{-1} are also indicates that there is increased crystallization of MCFA than CFA. The peak at 2930 cm^{-1} and above indicates C–H stretching vibration of organic contaminants or some hydrocarbon present in CFA; whereas the peak observed at 3246-3569 cm^{-1} corresponds to O–H bonding.

Table-1 summarizes the observed infrared bands for PCC fly ash, FBC fly ash, and FBC spent bed ash by [3] and the present study indicated in bold figure. The observed frequencies are in cm^{-1}. (PCC-Pulverised coal combustion, FBC-Fluidized bed combustion).

Table-1
Summary of FTIR bands[3]

PCC Fly Ash	FBC Fly Ash	FBC Spent bed ash	CFA	MCFA	Comments	Assignments
3642	3642	3642	**3569.39**	**3564.57**	sharp	O-H stretch [Ca(OH),]
3448	3462	3448	**3246.31**	**3247.27**	broad	O-H stretch, adsorbed water
1631	--	1624	**1643.41**	**1641.48, 1604.83**	sharp, weak	H-O-H bend of water
--	1449	1448	**1449.55**	**1446.66**	broad, medium	Asymmetric CO_3^2 stretch [$CaCO_3$]
--	1144	1154	--	--	broad, strong	SO_4^{-2} stretch
--	1111	1122	--	--	broad, strong	[$CaSO_4$]
1072	1011	--	**1055.10**	**1058.96**	broad, strong	Si-O stretch
--	--	945	--	--	broad, weak	$CaSO_3$
--	--	920	**898.86**	**886.32**	sharp, weak	O-H bend [$Ca(OH)_2$]
--	885	--	--	--	sharp, weak	$CaCO_3$
794	795	--	**748**	--	sharp, medium	Quartz
778	--	--	**712.72**	**711.76**	sharp, weak	Quartz
694	--	--	**692**	**660**	sharp, weak	Quartz
--	681	680	--	--	sharp, weak	Anhydrite [$CaSO_4$]
613	616	615	--	**582.22**	sharp, weak	Anhydrite [$CaSO_4$]
--	602	605	--	--	sharp, weak	Anhydrite [$CaSO_4$]
593	--	595	--	--	sharp, weak	Anhydrite [$CaSO_4$]
560	--	560	--	--	broad, weak	Fe_2O_3 and Fe_3O_4
--	515		**493.79**	**510.19, 489.94**	broad, weak	Oxides
462	462	462	**434.00**	**428.21**	Broad, medium	quartz

XRF Analysis: MCFA was analysed for X-Ray fluorescence (XRF) test to determine the elemental composition of it. Table-2 represents the basic chemical composition of the CFA and MCFA. CFA values are taken from Nadaf M.B. et.al[4].

Table-2 shows that MCFA consists of 44.63% SiO_2 and 43.72% Al_2O_3 which are the main constituents of the zeolites. Al_2O_3 percentage is increased from 26 to 43.72 in MCFA which show the modification of CFA occurs. Also it is observed that SiO_2 percentage is reduced from 61 to 44.63. Increased amount of Na_2O (from 0.40 to 0.620 %) in MCFA was observed because of the alkali treatment of CFA. This agrees well with observations made by Khadse S. et.al[5] and Chigondo M. et.al[6].

The results of the other researchers are shown in Table-3.

It was observed from Table-3 that the compositions of MCFA of present study is comparable with ZOP-53, ZOP-57 and commercial (13X) zeolite and Khadse *et al*.[5].

Conclusion

The SEM photograph of CFA shows the particles of different shapes and sizes, minerals, unburned carbon particles, whereas the typical SEM image of MCFA shows the structural break down of larger particles and increased surface roughness. The XRD pattern for CFA and MCFA consists of crystalline minerals, hematite, quartz, mullite and small amounts of ferrous and calcium oxide having large peaks of quartz (SiO_2). It was observed that, large SiO_2 concentration in MCFA than CFA. The reaction of NaOH with Si-Al chain of CFA results in breaking of the Si-Al chain to increase the mircopore volume of CFA. FTIR spectra at 425 cm^{-1} – 428 cm^{-1} shows that aluminosilicate matrix present more in MCFA as compared to CFA. The bands at 400 cm^{-1} – 420 cm^{-1} are related to the pore opening of the MCFA. Band in the region 425 cm^{-1} – 510 cm^{-1} are assigns to Si-O and Al-O internal tetrahedron vibrations for CFA and MCFA. The shifting of the Si/Al-O band at 1065 cm^{-1}, analogous with stretching vibrations to lower frequencies (1058 cm^{-1}), indicates modification of the CFA. XRF results indicate that the MCFA consists of 44.63% SiO_2 and 43.72% Al_2O_3 which are the main constituents of the zeolites. Percentage of Al_2O_3 is increased from 26 to 43.72 in MCFA which indicates the modification of CFA occurs. In MCFA, it was observed that SiO_2 percentage is reduced from 61 to 44.63. Increased amount of Na_2O (from 0.40 to 0.620 %) in MCFA was observed because of the alkali treatment of CFA.

Table-2
Chemical composition of CFA and MCFA

Comp	**Al_2O_3**	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	**SiO_2**	TiO_2	Cr_2O_3	CuO	ZnO	CoO	NiO
Mass %	**CFA**														
	26.82	1.13	5.48	0.94	0.96	0.03	0.40	0.25	**61.32**	1.65	--	--	--	--	--
	MCFA														
	43.72	0.73	5.80	0.61	0.63	0.04	0.62	0.08	**44.63**	1.60	0.025	0.01	0.013	0.003	0.013

Table-3
Chemical composition for different zeolites[7]

Composition	**ZOP-21**	**ZOP-30**	**ZOP-31**	**ZOP-53**	**ZOP-57**	**Commercial (13X)**	**Khadse *et al.*[5]**	**Present work**
SiO_2	50.81	47.8	48.03	42.19	40.82	48.26	46.22	**44.63**
Al_2O_3	27.97	27.4	27.20	31.66	25.60	31.38	41.22	**43.72**
Fe_2O_3	2.11	2.9	3.57	5.41	1.73	3.00	2.254	**5.80**
Na_2O	13.21	17.6	15.57	8.94	15.22	15.67	0.75	**0.620**
CaO	1.14	1.0	1.47	2.67	4.16	0.37	3.621	**0.728**
K_2O	0.68	0.6	0.77	0.0	0.75	0.07	0.902	**0.606**
TiO_2	2.54	1.4	2.12	5.15	1.24	0.08	0.826	**1.60**
MgO	0.69	0.6	0.49	0.52	0.96	0.0	0.205	**0.628**

Acknowledgement

The authors are thankful to SAIF, IITB, Mumbai, for providing XRF analysis and also to UICT, NMU Jalgaon for providing SEM, XRD and FTIR analysis.

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