



APPLICATIONS OF COAL FLY ASH BASED CFA-MCM-41 IN WASTEWATER TREATMENT

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ABSTRACT

Coal fly ash (CFA) production and its organization have turn out to be a significant vicinity of anxiety with increasing dependence on coal based power production units. Along with a variety of impending relevance of CFA, its utilization in surface water pollution control is emerging as an appealing theme of research. CFA based mesoporous materials such as MCM-41 is expansively studied for the removal of heavy metals and several organic/inorganic components frequently encountered in contaminated waters. The potential applications of contaminated water treatment involving use of CFA-MCM-41 synthesized from coal fly ash engendered from coal fired thermal plants.

Key words: CFA, CFA-MCM-41, waste water, Thermal power plants, XRD.

1. INTRODUCTION

About total power engendered in our country, almost 72% is produced by thermal power plants. With a 73 billion tons coal reserve, almost all the thermal power plants are working on coal and very few on gas and oil. About 2.8 billion tons of coal is being used by thermal power plants [1-2].

A massive quantity of coal fly ash (CFA) is being engendered by thermal power plants as a byproduct of coal combustion. The distinctive chemical and physical characteristics of Indian CFA collected from Chandrapur thermal power plant [3] are given in table A and B respectively. The pozzolanic properties and uses of CFA as a replacement for cement in concrete applications have made it a valuable material for the market. Increased ash utilization will not only solve its disposal problem, but also bring about other environmental benefits.

CFA is classified as Class C (high CaO content >20%) and Class F (low CaO content

<20%). It is also classified based on pH, slightly alkaline, moderately alkaline and highly alkaline. In India CFA generated is normally highly alkaline because of low sulphur content of coal and presence of hydroxides and carbonates of calcium and magnesium [4].

Table A: Typical chemical Characteristics of Indian CFA

Name	Formula	Percentage
Silica	SiO ₂	71
Iron oxide	Fe ₂ O ₃	2.26
Alumina	Al ₂ O ₃	21
Titanium dioxide	TiO ₂	1.82
Potassium dioxide	K ₂ O	1.27
Calcium oxide	CaO	1.12
Magnesium oxide	MgO	0.46
Phosphorus pentoxide	P ₂ O ₅	0.41
Sulfate	SO ₄	0.37
Disodium oxide	Na ₂ O	0.29

Due its high silica (>70%) content, it can be a renewable resource for making high value, versatile mesoporous material like MCM-41[5]. The molecular structure of MCM-41 performs a

uniformly and highly ordered network of silicon with hexagonal pore diameter in a range of 2–50 nm. These outstanding characteristics such as high surface area and high thermal stability results in various applications of MCM-41. For example, it can be used in a basic catalyzed reactions or being a catalyst support. This paper reports effective and eco-friendly utilization of CFA as an active silica source for synthesis of mesoporous materials such as MCM-41, its characterization and application in adsorption[6].

2. MATERIALS AND METHODS

Cetyl-tri-methyl-ammonium bromide (CTAB), sodium hydroxide and conc. hydrochloric acid were purchased from SD fine chemicals, India.

The acid pretreated (2.0 M HCl at 110°C) CFA was washed with water to remove the excess acid on the surface and dried in oven overnight at 150°C.

This was then calcined at 800°C in air for 4.5h to obtain the extracted silica from CFA. Silica extracted from CFA was first fused with 2M NaOH solution and was stirred for 2.5h to extract the silicate from the ash.

A clear solution of CTAB (Cetyl tri methyl ammonium bromide template) prepared in water was then slowly transferred into silicate supernatant solution and kept under stirring for 2.5h at temperature 90°C.

The p^H value of the gel was then adjusted to 6.9 by adding 2M H_2SO_4 solution. This homogeneous gel was heated under autogenous pressure at 80°C for 2h in a teflon coated autoclave.

After cooling, the solid product was filtered and washed repeatedly by de-ionized water.

The solid thus obtained was then dried in a muffle furnace at 100°C and calcined at 550°C

for 4.5h. This sample was named as CFA-MCM-41 which was evaluated for applications in adsorption

Table B: Typical Physical Characteristics of Indian CFA

Quantity	Value	Quantity	Value
Moisture retention	5.98to 12.8%	Density	1.98-2.75 g/cc
BET surface area	0.4- 1.0m ² /g	Particle diameter	9-24 microns

3. CHARACTERIZATION

Every natural or synthetic material (viz. zeolites and other solid porous materials) need to be completely characterized by a number of physical, chemical and spectroscopic techniques to elucidate their structural features, morphology, pore architecture, thermal stability, adsorptive and catalytic behavior, surface area etc. Synthesized samples are characterized by techniques such as XRD, N_2 -sorption, SEM, TGA/DTA, FTIR, NH_3 and CO_2 -temperature programmed desorption, etc. Among these, X-ray diffraction is of primary importance which provides information on the phase purity and some evidence for heteroatom incorporation. The sorption capacity data provide surface area, pore volume and pore size. SEM is an established technique to obtain the morphological information.

I) XRD-studies:

The X-ray pattern of the As-Synthesized and synthesized mesoporous silica material is an highly periodic silica phases which is normally reflected by the distinct XRD signatures at low 2θ angles from 2° to 10° as shown in (Fig.1a, b). Sharp signal in XRD spectra indicates the presence of long range order of uniform hexagonal phase in the mesoporous materials.

The well defined reflections from [100] plane are a prime characteristics of the hexagonal

lattice symmetry of the MCM-41 structure with d_{100} value = 35.3099, $2\theta = 2.500$, Intensity: 40163 cps $I/I_0 = 100$ Unit cell parameter

$$a_0 = \frac{2}{\sqrt{3}} d_{100} \quad a_0 = 40.8$$

The observation of three higher angle reflections other than d_{100} indicates that the product is likely to possess the symmetrical hexagonal pore structure typical of MCM-41. X-ray diffraction data therefore indicates that the supernatant of the CFA can be successfully used in the synthesis gel to prepare mesoporous materials. However, it is evident that CFA-MCM-41 samples synthesized using surfactant CTAB in a range from 0.9g to 1.2g showed the corresponding peaks for the planes (100), (110) and (200) located at 2.5, 4.2 and 4.9° of 2θ respectively.

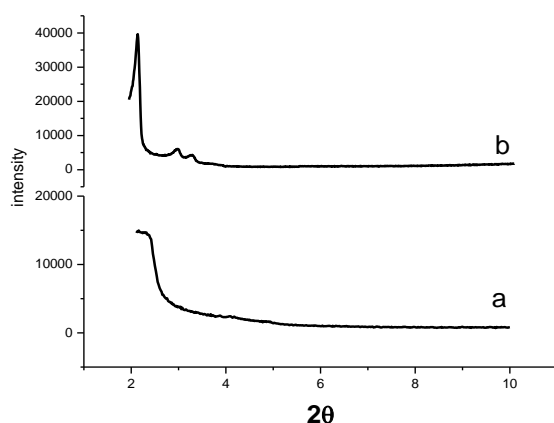


Fig. 1 : XRD pattern of optimized CFA-MCM-41 As-Synthesized and Synthesized Material

As-synthesized forms of CFA-MCM-41 shown in Fig1-a exhibit a typical pattern of XRD with a very strong (100) reflection at low angle but no other peaks at (110), (200) and (210) reflections as in calcined sample (Fig.1-b) are viewed this is because of the fact of undevelopment of well defined, well ordered mesophases of a sample. According to Beck *et.al* these four reflection lines can be indexed based on a hexagonal unit cell

parameter ($a_0 = 2d_{100}/\sqrt{3}$). The maximum contraction is observed in the case of As-synthesized CFA-MCM-41, which may be due to the poorly ordered arrangement of the mesopores. A significant increase in the intensity of this peak in calcined samples indicates that an atomic reorganization occurs during the removal of the surfactant molecules in the calcinations process.

II) FTIR-studies:

Fourier Transformed Infrared (FTIR) spectroscopy can capitulate information concerning structural details of the material. The two most intense bands for mesoporous materials usually occur during 860–1230 cm^{-1} , which is shown more clearly in Fig.2-a. The first is assigned to an asymmetric stretching mode and the second one to a bending mode of the T–O bond. All these bands are more or less dependent on the crystal structure. The mid infrared region of the spectrum contains the fundamental framework vibration of $\text{Si}(\text{Al})\text{O}_4$ groupings. The IR spectral data for the absorbance band in between the wave numbers 980–1320 cm^{-1} in the IR spectrum confirms the formation of CFA-MCM-41 on alkali and hydrothermal treatments of CFA.

From FT-IR spectra, the absorption bands around 2921 and 2851 cm^{-1} correspond to n-C-H and d-C-H vibrations of the surfactant molecules, such bands disappeared in the calcined sample indicating the total removal of organic material during calcinations Fig2-b. The broad band around 3392.65 cm^{-1} as observed due to surface silanols and O-H stretching frequency of adsorbed water molecule. Moreover the peaks in the range of 1500-1600 cm^{-1} are because of the deformation mode of surface hydroxyl group. A peak at 1070.63 cm^{-1} and 964.44 cm^{-1} corresponds to the asymmetric and symmetric Si-O groups, respectively.

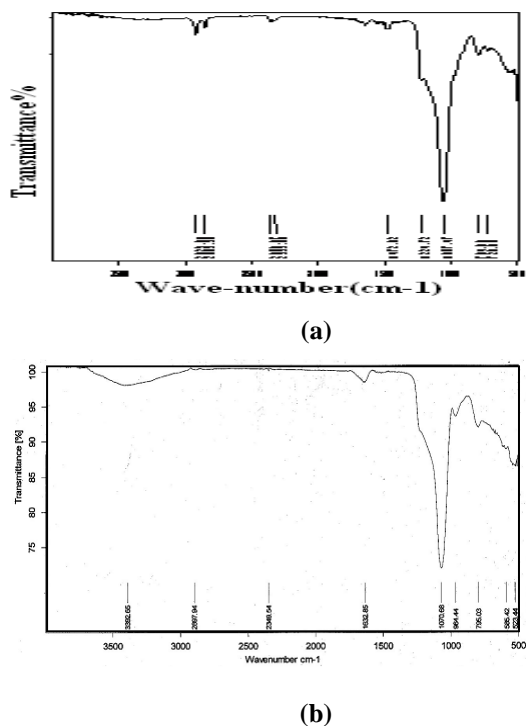


Fig.2: FT-IR of As-Synthesized and Synthesized Material (CFA-MCM-41)

III) SEM-analysis:

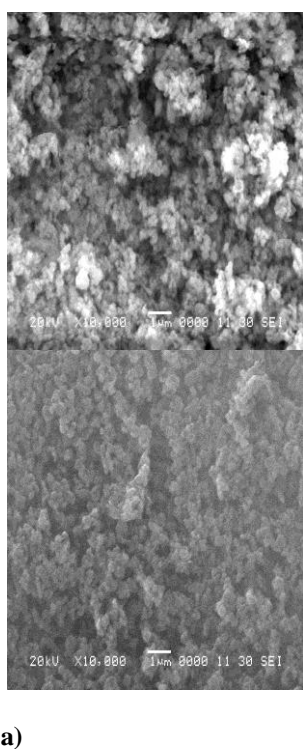


Fig.3: SEM images of As-Synthesized and Synthesized Material (CFA-MCM-41)

Fig.3(a, b) presents typical micrographs of the as-synthesized and calcined CFA-MCM-41 samples. Formation of the CFA-MCM-41 phase at

hydrothermal conditions under autogenic pressure is seen to result, in shorter time, in a solid consisting of small agglomerates Fig.3-b. The CFA-MCM-41 samples exhibit agglomerates with sizes between 30 and 200 nm. Sample ‘b’ exhibited uniform spherical shaped particles, with very small variations in the morphology and size might be associated with the differences in the synthesis gel conditions and hence in nucleation and crystallization.

IV) Sorption studies:

The adsorption/desorption isotherms of N₂ shown in Fig.4 and the values of specific BET surface area, mean diameter of the mesopores, total volume of pores and wall thickness obtained for calcined CFA-MCM-41 are presented in Table D are well in agreement with XRD analysis. Curves in Fig.4 and data from Table D shows an increase in the adsorption capacity of N₂ with time for the CFA-MCM-41 samples synthesized, indicating an improvement in the order of the mesoporous phase, already observed by the increase in the XRD peak intensity (Fig. 1).

According to IUPAC classification, the isotherm of CFA-MCM-41 is of type IV, which is the characteristic of mesoporous material. The isotherms exhibit three stages. The first stage is a linear part nearly going through the origin, which is due to monolayer adsorption of nitrogen on the walls of the mesopores ($p/p_0 < 0.2$). The second stage is characterized by a steep increase in adsorption (within the relative pressure p/p_0 range of 0.2-0.4) due to capillary condensation of N₂ in the pore channels. This part shows hysteresis.

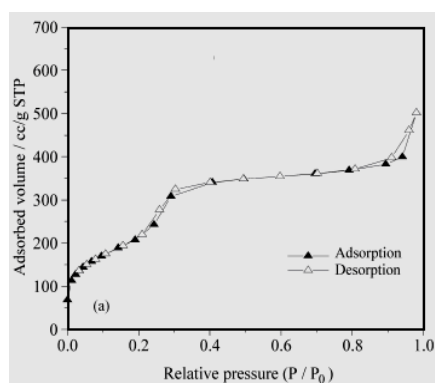


Fig. 4 : N₂ adsorption-desorption isotherms of optimized CFA-MCM-41

We noted that the surface areas of calcined CFA-MCM-41 samples are comparatively more than as synthesized CFA-MCM-41. The more surface area (1276.6 m²/g) is an indication of well dispersion of active sites.

V) TGA / DTG studies:

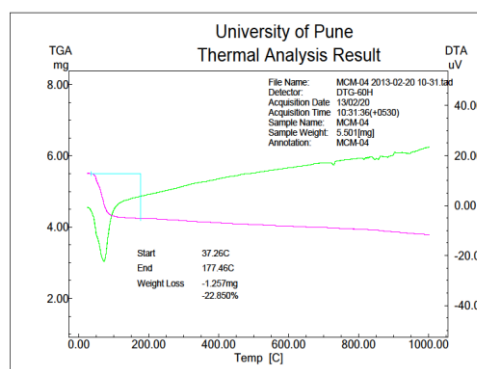


Fig. 5 : TGA-DTG analysis of the optimized CFA-MCM-41 sample

Thermogravimetric analysis of the synthesized CFA-MCM-41 sample presented a DTG curve typical of MCM-41 (Fig. 5). The as synthesized material presents approximately 50wt% of the MCM-41 phase. The remaining part corresponds to organic material whose mass loss is related to three exothermal stages: (a) between 100-285^oC: decomposition of the surfactant; (b) between 285-400^oC: breaking of the hydrocarbon chain, and (c) between 500-700^oC: combustion of

the surfactant and water loss associated with condensation of silanol groups.

5. APPLICATION AS AN ADSORBANT

CFA-MCM-41, being a blend of oxides has a predominant (-)ve surface charge and characterizes a promising adsorbent. Prior observations demonstrated that auxiliary conditioning by alkalization improves the adsorption effectiveness of heavy metals.

5.1 ELIMINATION OF ORGANIC COMPOUNDS

CFA-MCM-41 has been effectively used as an adsorbent to remove a variety of organic pollutants, dyes, phenols and phenolic compounds and pesticides. A maximum uptake of upto 0.73 mg phenol per gm of CFA-MCM-41 has been reported.

Phenolic derivatives such as 2-nitrophenol and, 4-nitrophenol recorded relatively lower uptakes. CFA-MCM-41 was successfully used to remove derivatives of phenol from aqueous solutions were efficiently with the rate of adsorption following first order kinetics before attaining equilibrium.

It was also reported that equilibrium adsorption data satisfies both Freundlich and Langmuir isotherms [7].

Several investigations explored the use of CFA-MCM-41 as an adsorbent for the treatment of wastewater to remove a variety of organic compounds and dyes.

We have reported the removal of copper from wastewater and removal of Methelene blue dye from aqueous solutions by taking CFA-MCM-41 as an adsorbent.

Recovery of phenol from industrial waste waters by CFA-MCM-41 has been reported and phenol concentration has been reduced from 4700 mg/l to 196 mg/l.

5.2 REMOVAL OF INORGANIC COMPONENTS

A number of studies have been reported on the removal of inorganic compounds from waste waters using CFA-MCM-41. Chromium has been separated from an aqueous solution by CFA-MCM-41. The adsorption properties of CFA-MCM-41 were investigated for some heavy metal cations like Pb, Mn, Zn etc). The adsorption increases as cation concentrations in aqueous solution increases and order of adsorption is $Pb > Zn > Mn$ [8].

5.3 REMOVAL OF DYE

The removal of some common textile dyes using the CFA-MCM-41 samples has been investigated spectrophotometrically as a function of its dosage, dye concentration, and contact time at ambient conditions.

Adsorption studies using a visible light irradiated system have been performed, and the spectral analysis of the photolyzed solution revealed that decoloration of the concerned dyes was greater compared to that observed in the dark under identical experimental conditions. The removal of Methylene blue dye from its aqueous solutions by adsorption on a homogeneous mixture of CFA-MCM-41 and effluent in different proportions has been carried out and 100% removal of the dye were achieved. Adsorption studies were made in treating textile dyeing industrial effluent containing Methylene blue by using CFA-MCM-41. The first-order adsorption rate constants were determined and found decreasing with temperature[9].

The effects of pH, stirring time, sedimentation time and temperature on color, COD, turbidity etc removal were determined. Potential of CFA-MCM-41

Starting with an initial COD concentration of 1177 mg/l the maximum COD reduction

achieved for CFA-MCM-41 was around 91.04%. These values were achieved when the wastewater was treated with CFA-MCM-41 for 2h with the adsorbent dose was 28g/l.

5.4 WASTEWATER TREATMENT

The use of CFA-MCM-41 in removing contaminants from wastewater is examined with special reference to the removal of COD, color, organic compounds, and heavy metals. Laboratory work carried out showed that the CFA-MCM-41 filter had the ability to reduce BOD and turbidity[10,11]

6. CONCLUSION:

Based upon the experimental study it was concluded that pure and well ordered CFA-MCM-41 material could be successfully synthesized from coal fly ash as the silica source instead of commercial expensive silica sources. The parametric variations such as change of synthesis temperature and pH of gel helps to optimize the synthesis conditions. The well ordered mesoporous material CFA-MCM-41 can be synthesized at 130°C for 4.5h keeping pH of gel 6.9 and calcined at 550°C.

The following conclusions can be drawn from this research work:

1. In an average more than 80% of phenol, 2-NP and 4-NP were adsorbed within the first hour of agitation, after which there was a slow approach to equilibrium. Among them 4-NP has the highest adsorption capacity is observed.
2. The amount of adsorbate adsorbed was found to increase with an increase in contact time and the adsorbent dosage.
3. It was shown the CFA generated from Chandrapur thermal power plant could be successfully utilized as an adsorbent for the

removal of phenols and other toxic contaminants from waste water.

ACKNOWLEDGMENT

The authors are grateful to University Grants Commission, New Delhi for Financial support.

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