Green Approach towards the Synthesis of MCM-41 from Siliceous Sugar Industry Waste


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Abstract

The Mesoporous material has been given great attention for diverse application in the different field of chemistry. The synthesis of MCM-41 derived from organo based silicon sources which are more expensive for small scale industries and toxic for large scale production. The main aim of this work is to deduct the cost of production of MCM-41 with utilization of siliceous sugar industry waste bagasse fly ash as silica source. The BFA is used as silica source by adopting multistep conventional refluxing with aqueous alkali solution. The extract contains large amount of silicone for synthesis of MCM-41. The hydrothermal synthesis of MCM-41 was done in open vessel with molar gel composition of Si: CTAB: Water is 1:0.09738:408.31. The synthesized material was analyzed by Inductively Coupled Plasma Atomic-Emission Spectroscopy (ICP-AES), Powder X-ray Fluorescence (XRF) X-ray diffraction (XRD), Fourier transformation infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), Transmission Electron Microscopy (TEM), Energy dispersive spectroscopy (EDS) and N₂ adsorption and desorption. The result confirmed that the as synthesized material exhibits well-ordered structure with hexagonal cell dimension 43.02 Å, surface area 901 m²/g, large pore volume of 0.723 cc/g, and BJH average pore diameter of 3.21 nm. The results are the same like the MCM-41
synthesized from reagent grade silica sources. Siliceous Sugar industry waste bagasse fly ash was successfully utilized for getting silicate precursor for MCM-41 synthesis.

Keywords- Bagasse Fly Ash, Multistep Silicate Dissolution, MCM-41, Advance analysis.

INTRODUCTION

The mesoporous materials have been given a significant attention by material scientists of the world after the discovery of MCM (Mobil Composition of Matter) by scientists of Mobil Oil Corporation in 1992 [1-3]. They named it as new family of Zeolite: M41S. Some of the representative zeolites of the family are MCM-41, MCM-48 and MCM-50. These materials have larger pore diameter in nanometer scale, larger surface area and large pore volume [1-4]. These distinct properties made them good candidate for catalysis [5-7], catalytic supports [8], sensors [9,10], adsorbents [11], host–guest chemistry [12,13], energy [14,15], and drug carrier [16,17].

The MCM-41 is highly studied amongst the zeolites of M41S family because it shows extraordinary thermal, hydrothermal, and hydrolytic stabilities [18,19]. Researchers have typically used two sources of silicon: tetraethlyorthosilicate (TEOS) and sodium silicate (Na$_2$SiO$_3$) to synthesize mesoporous silica [20,21]. However, expensive TEOS reagents increase the cost of mass production. Commercial fabrication of sodium silicate from quartz sand and sodium carbonate at 1300°C requires a large amount of energy [22]. These silicate precursors not only increase the cost of production but also result in environmental pollution, which restrict their application in large scale production. Therefore, new synthetic procedures are developed to prepare this kind of material either by non-hydrothermal or room temperature synthesis routes [23-25]. These new routes tend to be simple, time saving and low-energy consumption. Also it is now indisputable that the rapid increase in consumption of mesoporous materials calls for further work seeking cheaper raw materials for their synthesis. Researchers successfully made the mesoporous silica material MCM-41 from various cheaper materials such as natural zeolite [26], clay [27,28], ore tailoring [29,30], agriculture slag waste [31], E-waste [32], wheat husk [33], rice husk [34,35], coal fly ash [36,37].

Among these alternatives, Bagasse fly ash is favorable candidate for the synthesis of mesoporous silica material as it contains good amount of amorphous silica. Bagasse fly ash is generated as waste product after using Bagasse as boiler fuel in sugar industries. It is of increasing interest to search for possible alternative use before their final discharge, including adsorbents [38], filler for building materials [39], and high-purity mesoporous silica gels [40]. Our method for producing high-purity MCM-41 from bagasse ash was based on the unique solubility properties of silica [40].
solubility of amorphous silica is very low at pH bellow 10, but increases sharply above pH 10 \[41\]. Therefore, the silica in bagasse ash could be dissolved in a boiling alkali solution to form sodium silicate. Owing the high contents of useful silica and dissolvability, it makes perfect economic approach for industrial application. In this situation, it is a very useful research to utilize bagasse fly ash for synthesis of mesoporous materials such as MCM-41.

The aim of the present study was to synthesize MCM-41 materials through a green approach by using bagasse fly ash as silicone source. A green synthesis approach was designed to reduce the use or generation of hazardous materials associated with the synthesis of MCM-41. Moreover, recycling of an agricultural sugar industry waste material has been performed during synthesis of MCM-41. The material was characterized by various sophisticated analytical techniques such as ICP-AES, XRF, XRD, FTIR, SEM, TEM, EDS, BET and BJH.

**EXPERIMENTAL**

**Materials**

Bagasse fly ash was collected from a local Sugar Mill “Shree Khedut Sahkari Khand Udhyog Mandal Ltd.”, Bardoli, Gujarat, India as silica source and n-Hexadecyltrimethylammonium bromide(CTAB:>95% Sigma Aldrich), as the structure-directing agent were used as the reagents for the synthesis of MCM-41. Ethyl acetate, sodium hydroxide (NaOH: >99%), aqueous ammonia (25% NH\textsubscript{3}) and other chemical were all supplied by Aldrich and Merck and used without further modification.

**Methods**

**Pretreatment to BFA**

The native BFA was thoroughly washed with deionized water to remove foreign impurities as suspension materials on water surface. Then, the BFA was dried in a hot air oven at 353 ± 5 K for 5 h. The dried BFA was sieved in mesh size 75-90 µm and was used for silicon extraction.

**Silicon Extraction**

Silicon extraction was done by many researchers using fusion with alkali \[42\] by refluxing the silicate material with aqueous alkali solution \[43\] and applying microwave dissolution of silicate in aqueous alkali solutions \[44,45\]. These methods lead to extraction of silicon as aqueous sodium silicate from which pure silica is precipitated with mineral acid.
In this study, multistep dissolution of silica was adopted with partial modification of conventional method. The process of multistep dissolution of silica was done by alkali using conventional heating. Previously washed and sieved 25.0 g of Bagasse fly Ash was mixed with 100.0 mL 4.0 M NaOH solution and refluxed for 4 h. The hot liquor was collected by vacuum filtration and the residue was further treated similarly for multiple extractions. The combine liquor was analyzed by ICP-AES. The composition was 35157.3 ppm silicone 280.18 ppm aluminum and 1702.61 ppm sodium. The liquor was further used for MCM-41 synthesis.

**Synthesis of BFA-MCM-41**

In typical process, appropriate amount of CTAB was dissolved in 100.0 mL of distilled water at temperature of 80°C with 300 rpm stirring rate to obtain an aqueous solution. Then 50.0 mL cooled extracted liquor was added drop wise and stirred for 2 h. The temperature was maintained 80°C during addition process. Further, 5.0 mL ethyl acetate was rapidly added to resultant mixture which promotes the hydrolysis process of silicate species and condensation of silicates starts with formation of gel. To the gel, 5 N H$_2$SO$_4$ solutions was added drop wise with stirring till the solution is reaches at pH 10. The final volume of the mixture was adjusted such that the molar gel composition attained the ratio Si: CTAB: Water (1:0.09738: 408.3). The resultant mixture was stirred at 80°C for 12 h while maintain pH 10. Then resultant mix was cured overnight at room temperature. The solid was then vacuum filtered, flushed twice with deionized water. The solid was dried at 100°C for 2 h, and finally calcined at 550°C for 5 h with a heating rate of 5°C/min in air atmosphere. The material obtained accordingly was denoted as BFA-MCM-41.

**Characterization**

The chemical composition of Bagasse fly ash and the MCM-41 was determined by X-ray fluorescence spectrometer (Rigaku, Japan). Phase analysis by X-ray diffraction (XRD) (30 kV, 20mA - Rigaku Geiger-miniFlex, Japan) was carried out at room temperature with Cu K as the radiation source using a scan speed of 0.5°min$^{-1}$ and a step scan of 0.02°A scan angle of 20 = 10° to 80° was used for identifying the phases present in BFA. The Small angle X-ray diffraction carried out with a PAN analytical Empyrean X-ray diffractometer using Cu Kα radiation, operating at 40 kV and 40 mA, at a scanning velocity of 0.02°min$^{-1}$ in the range of 0.5° to 10°. The porosities of the material were measured by N$_2$ adsorption-desorption (BET and BJH) at 77 K using the Quanta chrome Autosorb 1C BET Surface Area & Pore Volume Analyzer. The sample was previously dehydrated at 323K for 12 h. The surface area was calculated from the linear part of the plot using the Brunauer-Emmett-Teller (BET) equation. The pore size distributions were calculated by using the Barrett-Joyner-
Halenda (BJH) model and by Density Function Theory. The surface functional groups of synthesized sample was analyzed by Fourier transform infrared (FT-IR) spectrooscope (FT-IR-2000, PerkinElmer, USA), where the spectra were performed in KBr pellets and recorded from 4000 to 400 cm$^{-1}$.

The morphological analysis was examined on a Hitachi S-3400N scanning electron microscope (SEM), operated at an accelerating voltage of 15kV. The sample was initially placed in a vacuum chamber for coating with a thin layer (a few nanometers) of gold (Au). The EDS was simultaneously carried out with SEM using attachment of Thermo Electron Corporation.

The pore network and long range of ordering of material where analyzed by Transmission electron microscope (TEM). The images were collected on a Philips CM 200 Transmission electron microscope with a field emission gun as the source of electrons operated at an acceleration voltage of 200kV. Samples were prepared by dispersing the particles in ethanol and placed on a copper coated carbon grid and dried before loading in the electron beam.

RESULTS AND DISCUSSION

Mechanism of synthesis of BFA-MCM-41

The silica framework can be formed around preformed liquid crystal mesophases but, in many cases, the organized architectures are obtained via a self-assembly cooperative process taking place in situ between the templates and the silica network precursors. The organic template is then removed by calcination or solvent extraction to give the resulting mesoporous open structure. Cationic surfactants (e.g., long chain quaternary ammonium) were used at the beginning and are still widely utilized because of their favourable electrostatic interactions with the silica surface.

![Interaction of silicates with CTAB micelles](image.png)

**Figure 1.** Interaction of silicates with CTAB micelles
As illustrated in Figure 1, CTAB molecules arrange themselves forming rod like micelle self-assembly to form liquid-crystalline phases so as to reach the concentration level where packing parameter ‘g’ is between 1/2 to 1/3 [46]. The temperature of a system is quiet important for preventing shape change of micelles. The negatively charged silicate species obtained from BFA by dissolution were electrostatically attracted toward the positive head group of surfactant. As pH shifted to lower value by addition of acid, condensation begins to form an inorganic network, with a hexagonal ordering dictated by the interaction between the surfactant and silicate species. After removal of the surfactant templates by calcination, mesoporosity is obtained with pore size of 2–10 nm.

In general, the overall LCT (Liquid Crystal Templating) mechanism is governed by two factors: (i) the dynamics of surfactant molecules to form assemblies, micelles, and ultimately crystalline structure, functioning as template; and (ii) the ability of the inorganic oxide to undergo hydrolysis and polycondensation reactions leading to a network surrounding the organic template.

**Chemical Composition**

**X-ray Fluorescence Spectrometry (XRF) Characterization of BFA**

The chemical compositions of BFA were determined by quantitative XRF analysis as the result shown in Table 1. The results indicated that it consist large amount of SiO₂ as well as some small amount of Fe₂O₃, K₂O, CaO, P₂O₅, MgO, Al₂O₃, TiO₂ and Na₂O. Thus BFA is best silica source for synthesis of MCM-41.

**Table 1.** Mineral oxides compositions (in wt. %) of BFA dried at 373K.

<table>
<thead>
<tr>
<th>Oxides</th>
<th>SiO₂</th>
<th>K₂O</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>P₂O₅</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>TiO₂</th>
<th>Other minute constituents</th>
</tr>
</thead>
<tbody>
<tr>
<td>% weight composition</td>
<td>75.96</td>
<td>5.24</td>
<td>6.08</td>
<td>3.85</td>
<td>2.68</td>
<td>2.53</td>
<td>2.24</td>
<td>1.06</td>
<td>1.36</td>
</tr>
</tbody>
</table>
Energy Dispersive Spectrum (EDS) Characterization of BFA-MCM-41

The energy dispersive spectrum (EDS) of MCM-41-BFA showed that the relative weight percent of Si, O, Na and Al are 58.35%, 39.45%, 0.80% and 1.39% respectively. A typical EDS spectrum of BFA-MCM-41 is shown in Figure 2. The EDS spectrum at different points of the image confirms that the material is almost free from impurities and it is similar to reagent grade.

FT-IR Spectral analysis of BFA-MCM-41.

The FTIR analysis of calcined BFA-MCM-41 was carried out by KBr pellet method. The results are shown in Table 2. IR bands are observed for stretching and bending of hydroxyl group attached to surface silicon atom and for interstitial water molecules. Symmetric and asymmetric bands for tetrahedral units are also observed. These bands are typically observed for mesophase silica.[23] There are no bands observed around 2850 to 3000 cm\(^{-1}\) corresponds to stretching of \(-\text{C} - \text{H}\) group, indicates complete removal of the surfactant molecules form the pores of the synthesised material.
Table 2. FTIR analysis of BFA-MCM-41.

<table>
<thead>
<tr>
<th>Rang of IR bands (cm(^{-1}))</th>
<th>Observed bands (cm(^{-1}))</th>
<th>Possible assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3200-3500</td>
<td>3417.98</td>
<td>Stretching vibration of (\text{–OH}), Surface silanols and the adsorbed water molecules. (Si-OH)</td>
</tr>
<tr>
<td>1580-1700</td>
<td>1629.9</td>
<td>(-\text{OH}) deformation and bending vibration of interstitial water</td>
</tr>
<tr>
<td>1030-1240</td>
<td>1232.55</td>
<td>Asymmetric stretching of internal tetrahedral (\text{TO}_4), Si-O-Si</td>
</tr>
<tr>
<td>(\approx 800)</td>
<td>796.63</td>
<td>Symmetric stretching of internal tetrahedral (\text{TO}_4) (T = Si, Al)</td>
</tr>
<tr>
<td>1250-950</td>
<td>1078.24</td>
<td>Internal and external asymmetric Si–O stretching vibrations.</td>
</tr>
<tr>
<td>1230-860 420–500</td>
<td>962.51 and 478</td>
<td>Stretching and bending vibration of surface Si–O-groups</td>
</tr>
</tbody>
</table>

X-ray Diffraction (XRD)

XRD of BFA and BFAAE

The mineralogical composition of bagasse fly ash (BFA) before silica extraction and after extraction (BFAAE) was shown in Figure 3.

![Figure 3. X-ray Diffraction Patterns of BFA and BFA after extraction (BFAAE)](image-url)
The broad hump in the XRD pattern was removed after alkali extraction which shows that large amount of amorphous silica present in the BFA was extracted in the aqueous alkali which produces sodium silicate for mesoporous MCM-41 synthesis. The diffraction of hematite remains intact after extraction which concludes that hematite phase is stable even though it partially dissolves in alkali extraction process. The diffraction of stilbite completely disappears in BFAAE as it gets dissolved during extraction process. There is no extra diffraction observed after extraction which confirms the efficiency of silicate extraction process.

**XRD of BFA-MCM-41**

![XRD of BFA-MCM-41](image)

*Figure 4. Low angle XRD of BFA-MCM-41.*

The Low-angle powder X-ray diffraction (LAXRD) pattern of BFA-MCM-41 is shown in Figure 4. It exhibits four characteristic peaks that can be indexed on a hexagonal lattice of a typical mesoporous MCM-41 material as (100), (110), (200) and (210) planes [47,48]. They indicate a long-range ordered hexagonal mesoporous structure. The hexagonal unit cell parameter (\(a_0\)) indicates the sum of the internal pore diameter and pore wall thickness, which was 43.02 Å for BFA-MCM-41.
Microscopic analysis by SEM and TEM

Scanning Electron Microscopy (SEM) Characterization of BFA

The microscopic structure is quite important for the silicate species which are formed by dissolution with aqueous alkali. The SEM images observed in Figure 5 are both for BFA and BFAAE. Bagasse fly ash (BFA) particles are not spherical in shape and exhibit irregularly fragmented particles also its morphology is more compact with fewer pores while BFAAE is fibrous. BFA particles become more fibrous and porous as the dissolution of amorphous silicate, stilbite and some of quartz content takes place. The dissolution is also confirmed by weight difference of the residue.

Scanning Electron Microscopy (SEM) Characterization of BFA-MCM-41

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Figure 5. SEM images of BFA and BFAAE.

Figure 6. SEM images of BFA-MCM-41.
The SEM image of BFA-MCM-41 in Figure 6 shows agglomeration of spherical particles. It also shows that these particles are formed through the aggregation of very fine homogeneous grains of nano size.

**Transmission Electron Microscopy of BFA-MCM-41**

The TEM images of the BFA-MCM-41 synthesized from bagasse fly ash is presented in Figure 7. These images confirm that the material exhibited highly ordered 2-D hexagonal mesostructure of and streak structural features of typical MCM-41. In addition, particles were also observed with agglomeration of 50-60 nm size with porous structure in the TEM. The obtained pore size is about 2.94 nm which is in close agreement with the value determined from XRD (3.37 nm) and N2-adsorption measurements values (3.21 nm), which confirm the formation of high quality MCM-41 form bagasse fly ash.

**Nitrogen Adsorption-Desorption Characterization**

The mesoporous structure of synthesised BFA-MCM-41 was also confirmed by N2 adsorption tests. Figure 8 shows the N2 adsorption - desorption isotherms for the sample. Sample show a typical type IV isotherm according to the IUPAC classification, which is a characteristic isotherm shape for mesoporous silica MCM-41[49,50].
Figure 8. N₂ adsorption - desorption isotherm of BFA-MCM-41.

The isotherm exhibits three defined stages, with the inflection points at $P/P₀=0.29$ and $P/P₀=0.43$. The first stage is due to monolayer and multilayer adsorption of nitrogen to the walls of the mesoporous at low relative pressures ($P/P₀<0.25$). The second stage is characterized by a sharp increase in adsorption ($0.25<P/P₀<0.43$). As the relative pressure increases, the isotherms show that adsorption amount increases abruptly because of the capillary condensation within the uniform pores which confirms the existence of mesoporous structure of synthesized silica [51]. Third stage in the adsorption isotherm gradually increases at high $P/P₀$ (0.43-0.99) values due to multilayer adsorption on the external surface of the particles. The isotherms of mesoporous materials with high pressure can be attributed to the condensation of nitrogen within voids formed by crystal aggregates. The BET equation was applied to the monolayer region of the isotherm to estimate the surface area. The average pore diameter was calculated by gas desorption measurements. Also DFT was applied for pore size determination. The surface areas and pore diameters obtained from BET, BJH, DFT and XRD were given in Table 3, which are in good agreement with values of reported materials [52-55].

<table>
<thead>
<tr>
<th>BET Surface area</th>
<th>Pore Volume</th>
<th>BJH pore size</th>
<th>DFT pore size</th>
<th>XRD pore size</th>
<th>Pore wall Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>901 m²/g</td>
<td>0.723 cc/g</td>
<td>3.21 nm</td>
<td>3.31 nm</td>
<td>3.37 nm</td>
<td>1.0993 nm</td>
</tr>
</tbody>
</table>
The synthesized BFA-MCM-41 has been structurally characterized and is in good agreement with the commercial grade MCM-41 mesoporous material [58].

CONCLUSIONS
Sugar industry siliceous detritus can be successfully utilized as raw material for the synthesis of mesoporous MCM-41. The multistep silicate extraction gives large silicon content about 35,157 ppm. The synthesis of BFA-MCM-41 is successfully carried out with relatively low molar surfactant concentration. The synthesized material has higher surface area, large pore diameter and pore volume. Low angle X-ray diffraction pattern and nitrogen adsorption desorption obtained for BFA-MCM-41 confirms the successful synthesis of MCM-41. The purity of BFA-MCM-41 confirmed by EDS analysis which is same to that of commercial grade MCM-41. The material is suitable for further processing into materials for advanced applications such as the storage of hydrogen and capturing of carbon dioxide.

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