

# *Synthesis, Characterization and Environmental application of Al and Zr doped MCM-41*

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**NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA**

By

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ROURKELA-769008

May 2015

# CERTIFICATE

*This is to certify that the dissertation entitled “Synthesis, Characterization and Environmental application of Al and Zr doped MCM-41” by Suchismita Mehena (Roll no: 413CY2010) to the department of chemistry, National Institute of Technology, Rourkela for the degree of Master of Science in Chemistry is based on the result obtained in the bonafide project work carried out by her under my guidance and supervision. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.*

*I further certify that to the best of my knowledge Suchismita Mehena bears a good moral character.*

**Place: Rourkela**

Supervisor

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Rourkela-769008**

## DECLARATION

I, Suchismita Mehena hereby declare that this project report entitled “*Synthesis, Characterization and Environmental application of Al and Zr doped MCM-41*” is the original work carried out by us under supervision of **Prof. Garudadhvaj Hota**, Department of chemistry, National Institute of Technology Rourkela (NIT), Rourkela and the present work or any other part thereof has not been presented to any other University or Institution for the award of any other degree regarding to our belief.

Suchismita Mehena  
Roll No.: 412CY2010

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Suchismita Mehena

## ABSTRACT

Arising out of their high surface area, tunable pore sizes, large pore volumes and ordered morphology, mesoporous silica materials exhibit wide applications in the field of adsorption, catalysis, membrane separation, pharmaceutical, fixing agent for biomolecule and semiconductor cluster, functional electronics and photonics applications etc. Ordered mesoporous silica with hexagonal structure, type Mobil Composite Material number 41 (MCM-41) is one of the most important class of mesoporous material. In the present work, we have prepared MCM-41 using cetyltrimethylammonium bromide, tetraethyl orthosilicate, ammonia and water by wet chemical method. Then Al and Zr doped MCM-41 have been prepared by introducing aluminium nitrate and zirconyl chloride salts respectively. All the samples are characterized by using XRD, FTIR, FESEM, BET Surface area measurement techniques. To study the environmental implication of the prepared adsorbents, we have carried out batch experiments for removal of fluoride ions from aqueous solution. By studying the effect of pH, effect of dose and effect of time it is observed that, Zr-MCM-41 shows highest percentage of removal of fluoride ion as compared to Al-MCM-41 and MCM-41.

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**Keywords:** Mesoporous materials; MCM-41; Wet chemical method; Adsorption; Fluoride ion removal.

# CHAPTER-1

## INTRODUCTION

### 1.1 Mesoporous material

Mesoporous materials are defined as natural or synthetic materials having a pore diameter of 2-50 nm, halfway between the pore sizes that define micro- and macroporous materials. They have a large surface area and are particularly useful for applications in catalysis, separation, and absorption. This particular pore architecture makes them suitable candidates for hosting and further delivering under appropriate conditions of a variety of molecules of pharmaceutical interest. Due to combination of porous structure and high surface area the materials expected to having unique properties for applications in the field of adsorption, catalysis, membrane separation, fixing agent for biomolecule and semiconductor cluster, functional electronics and photonics applications [1].

### 1.2 MCM-41

Mobil Composition of Matter (MCM) is the initial name given for a series of mesoporous material that were first synthesized by Mobil's researchers in 1992[2, 3]. MCM-41 (Mobil Composition of Matter No. 41) and MCM-48 (Mobil Composition of Matter No. 48) are two of the most popular mesoporous molecular sieves that are keenly studied by researchers. The most striking fact about the MCM-41 and MCM-48 is that, although composed of amorphous silica wall, they possess long range ordered framework with uniform mesopores. These materials also possess large surface area, which can be up to more than  $1000 \text{ m}^2\text{g}^{-1}$ . Moreover, the pore diameter of these materials can be nicely controlled within mesoporous range between 1.5 to 20 nm by adjusting the synthesis conditions and/or by employing surfactants with different chain lengths in their preparation. It is a member of M41S family, contains of a hexagonal array of tubular pores possessing a high surface area i.e. more than  $1000\text{m}^2/\text{g}$  and uniform pore size distribution. MCM-41 material exhibits a regular, hexagonal arrangement of pores with one-dimensional parallel channels, formed a liquid crystal templating. Typically, these materials are synthesized by self-assembly [4] of silica-surfactant in which inorganic species simultaneously condense, giving rise to mesoscopically ordered composites formation. The presence of large internal surface area and favourable uniformity with easily controlled size of the pore enables the material (MCM-41) for applications of

various fields in physics, chemistry, materials science and other relevant areas such as: shape/size selective adsorbents in waste water treatment, hosts for quantum structures, catalysts, and catalyst supports for drug delivery system [5].

### **1.3 Method of preparation of MCM-41**

There are a number of synthetic techniques used for the synthesis of mesoporous MCM-41. The synthetic technique is classified into two categories, namely physical and chemical method. The different types of chemical methods are:

- Post synthesis and co-condensation
- Ion exchange
- Wet impregnation
- Template isolation

### **1.4 Object of the study:**

- Preparation of mesoporous MCM-41, Al doped MCM-41 and Zr doped MCM-41 by a facile surfactant based wet chemical method.
- Characterization of the above prepared mesoporous materials by XRD, FE-SEM, FTIR and BET analytical techniques.
- Environmental application of the synthesized mesoporous materials (MCM-41, Al-MCM-41 and Zr-MCM-41) towards adsorptive removal of fluoride ion from aqueous media.

## **CHAPTER-2**

### **MATERIALS AND METHODS**

#### **2.1 Synthesis**

2.4 g of CTAB was dissolved in 120 ml double distilled water. Then 8 ml of  $\text{NH}_4\text{OH}$  and 10 ml of TEOS was added slowly with continuous and constant stirring and then the stirring was continued for 12h. Then the solid product was filtered, washed repeatedly with water, and then dried for some hours and then calcined at 823K for 5h. 2.4 g of CTAB was dissolved in 120 ml double distilled water. 8 ml of ammonia solution (28.30 %) was added to the CTAB solution with constant stirring. 1.613 g of aluminium nitrate was dissolved in methanol.

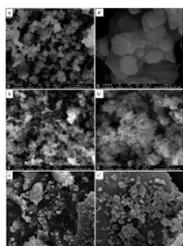
Amount of methanol used depends until the aluminium nitrate was properly dissolved. The prepared aluminium nitrate solution was added to 10 ml of TEOS and then the mixture was added the CTAB solution drop wise with constant stirring. The stirring was continued for 12 hours. Then the solid product was filtered and washed repeatedly with water. The product was then dried and calcined at 823K for 5h to obtain aluminium doped MCM-41. 2.4 g of CTAB was dissolved in 120 ml double distilled water. 8 ml of ammonia solution (28.30 %) was added to the CTAB solution with constant stirring. 1.67 g of zirconyl chloride was mixed with methanol. The prepared zirconium solution was added to 10 ml TEOS and then the mixture was added to CTAB solution with stirring. The stirring was continued for 12 hours. Then the solid product was filtered and washed repeatedly with water. Then the product was dried and calcined at 823K for 5 h to obtain zirconium doped MCM-41.

## CHAPTER-3

### RESULTS AND DISCUSSION

#### 3.1 FESEM Analysis

The shape, size and surface morphology of the prepared MCM-41, Al-MCM-41 and Zr-MCM-41 were investigated by Field Emission Scanning Electron Microscope. Figure 3.1 represents the surface structure of (a) MCM-41 (b) Al-MCM-41 and (c) Zr-MCM-41 both in low and high magnification. The FESEM images suggest that the morphologies of all the samples are spherical in nature. MCM-41 has average diameter nearly 300 nm, Al-MCM-41 has diameter 200 nm and Zr-MCM-41 has approximate diameter nearly 250 nm. The mesoporous structures are observed in the magnified images.



**Figure 3.1 High and low magnification FESEM images of (a, a') MCM-41, (b, b') Al-MCM-41 and (c, c') Zr-MCM-41.**

#### 3.2 EDAX analysis

Figure 3.2 shows EDAX of the synthesized mesoporous materials. From figure 3.2a, it is observed that the MCM-41 contains Si and O without any impurities. The spectrum of Al-

MCM-41 contains Al, Si and O elements (figure 3.2b). Similarly, the spectrum of Zr-MCM-41 contains Al, Si and O elements (figure 3.2a). As we have used carbon tape and gold coating for all the materials, additional peaks of C and Au are present in the spectra.

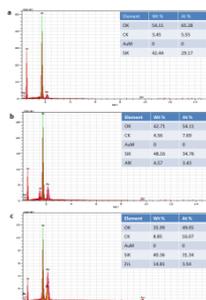


Figure 3.2 EDAX of (a) MCM-41, (b) Al-MCM-41 and (c) Zr-MCM-41.

### 3.3 XRD analysis

The formation and phase evolution of the as prepared MCM-41, Al-MCM-41 and Zr-MCM-41 were studied by XRD analysis in a Philip's PAN analytical X-ray diffractometer and the patterns are shown in figure 3.3. From the figure it is observed that each pattern consists of a broad peak at  $2\theta=23^\circ$ . These results indicated that MCM-41 structure was retained after the direct introduction of aluminium and zirconium into its framework. No characteristic peaks of Al and Zr species were observed for in the doped MCM-41 materials, which suggested that metallic or metal oxide species might be present as finely dispersed nano dimensional particles below the detection limits of x-ray and/or as amorphous particles in the framework of MCM-41.

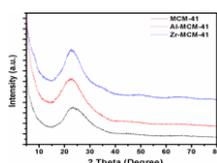
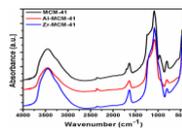


Figure 3.3 XRD patterns of MCM-41, Al-MCM-41 and Zr-MCM-41

### 3.4 FTIR analysis

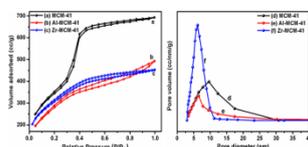
FTIR spectra of MCM-41, Al-MCM-41 and Zr-MCM-41 are shown in figure 3.4. In the spectra of MCM-41, the absorption peak at  $3,400\text{ cm}^{-1}$  is due to hydroxyl group (OH). Peaks at  $1600\text{-}1700\text{ cm}^{-1}$  shows that C=O groups are present. Peaks in the range of  $1000\text{-}1300\text{ cm}^{-1}$  are due to the presence of C-O group. FTIR spectra of MCM-41, Al-MCM-41 and Zr-MCM-41 are shown in figure 6. Peak in the region of  $1200\text{-}1000\text{ cm}^{-1}$  is assigned to Si-O-Si asymmetric stretching mode. Peaks near  $800\text{ cm}^{-1}$  are attributed to symmetric stretching vibration Si-O-Si [6]. No additional peak is observed in case of Al and Zr doped MCM-41.



**Figure 3.4 FTIR spectra of MCM-41, Al-MCM-41 and Zr-MCM-41**

### 3.5 BET surface area and Pore size distribution

The characterization of the textural features of the prepared MCM-41, Al-MCM-41 and Zn-MCM-41 was done by measuring their nitrogen adsorption/desorption isotherms. The N<sub>2</sub> adsorption–desorption isotherms and pore size distributions are shown in figure 3.5. For MCM-41 Three well-defined stages may be identified: (1) A slow increase in nitrogen uptake at low relative pressure, corresponding to monolayer-multilayer adsorption on the pore walls; (2) a sharp step at intermediate relative pressures indicative of capillary condensation within mesopores; and (3) a plateau with a slight inclination at high relative pressures associated with multilayer adsorption on the external surface of the crystals [7]. The sample exhibit pronounced steep condensation step for relative pressures 0.2 to 0.4 arising from condensation of nitrogen inside the primary mesopores which is a characteristic of typical type IV adsorption/desorption isotherm. In case of Al and Zr-doped MCM-41 the step condensation step is slightly disappeared, but still the materials possess type IV adsorption/desorption isotherm curve. Hence it is observed that, the incorporation of Al and Zr atoms to into the framework of MCM-41 causes a slightly disorder in the mesoporous hexagonal arrays of MCM-41. The surface area of MCM-41, Al-MCM-41 and Zr-MCM-41 were found to be 1248, 1029 and 1067 m<sup>2</sup>/g, respectively. Similarly, the pore diameter of MCM-41, Al-MCM-41 and Zr-MCM-41 were found to be 9.6, 6.54 and 6.21 nm, respectively. From the results it is observed that incorporation of Al and Zr on MCM-41 causes decreased in its surface area, and pore diameter.



**Figure 3.5 N<sub>2</sub> adsorption/desorption isotherms of (a) MCM-41, (b) Al-MCM-41 and (c) Zr-MCM-41 and the relevant pore size distribution curves of (d) MCM-41, (e) Al-MCM-41 and (f) Zr-MCM-41**

### 3.6 Application of doped MCM-41 in removal of fluoride ion

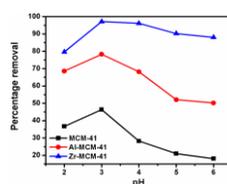
Fluoride in drinking water above permissible levels is responsible for human dental and skeletal fluorosis.

## Adsorption experiment

Stock solutions of 1000 ppm, 100 ppm and 10 ppm were prepared by dissolving 0.221 gm of sodium fluoride by adding required amount of water to it. Now to study effect of various adsorbents, 0.05 gm of each adsorbents (MCM-41, Al-MCM-41 and Zr-MCM-41) were taken along with 20ml of 10 ppm stock solution and the solution is stirred for 1 hour; filtered and the filtrate is collected for further study.

### 3.6.1 Effect of pH

To study effect of pH, previously prepared solutions are maintained at pH of 2-6 and solution is stirred for 1 hour; filtered and the concentration of filtrate are measured by fluoride ion selective electrode using TISAB-III.

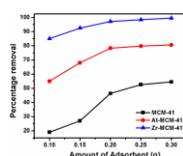


**Figure 3.6 Effect of pH on percentage removal of fluoride ion**

From graph it is found that, maximum percentage of removal of fluoride occurs for fluoride solution with pH 3 for all the adsorbents. Thus, further studies were carried out with pH 3 of fluoride solution.

### 3.6.2 Effect of dose

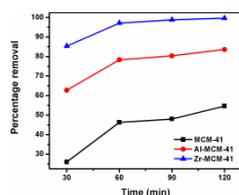
The effect of adsorbent doses on the adsorption of fluoride onto MCM-41, Al-MCM-41 and Zr-MCM-41 surface was studied at pH=3 using 20 ml of 10 mg/L fluoride solution for 1 h contact time. The result obtained is represented in figure 3.7. From the figure it is observed that, with an increase in adsorption dose from 0.01 to 0.2 g, the percentage of removal of fluoride increases up to a maximum value of 97.1 % for Zr-MCM-41, 78.3 % for Al-MCM-41 and 46.3 % for MCM-41, respectively. After that further increase in the amount of the adsorbent, no considerable change in the adsorption was observed. Hence, 0.2 g of each adsorbent was chosen as the optimum amount in future studies.



**Figure 3.7 Effect of amount of adsorbent on percentage removal of fluoride ion**

### 3.6.3 Effect of time

The effect of contact time on the adsorption of fluoride by MCM-41, Al-MCM-41 and Zr-MCM-41 was studied for initial concentration of 10 mg/L of 20 ml fluoride solution by using 0.2 g adsorbent at pH 3. The contact time was varied from 0.5 to 1 h and the result obtained is shown in figure 3.8. From the figure, it is observed that maximum adsorption occurred within 1 h of contact time; thereafter the rate of removal became rather slow i.e. the adsorption reaches steady state after 1 h for all the adsorbents.



**Figure 3.8 Effect of time on percentage removal of fluoride ion**

## CONCLUSIONS AND SCOPE OF FUTURE WORK

### Conclusions

We have synthesized mesoporous material MCM-41 by a facile surfactant based two-step wet chemical method using  $\text{NH}_4\text{OH}$ , TEOS and CTAB as surfactant. Then we have prepared doped MCM-41 such as Al-MCM-41 and Zr-MCM-41 by introducing Aluminium nitrate and Zirconyl chloride, respectively following the similar procedure for MCM-41 synthesis. Then all the prepared mesoporous materials are characterized by XRD, FESEM, FTIR and BET-Surface area measurement techniques. In application part we studied removal of fluoride ion from water by observing the effect of pH, effect of dose and effect of time. It is observed that, the Zr-MCM-41 showed highest percentage (97 %) of removal of fluoride as compared to Al-MCM-41 and MCM-41. Hence the prepared doped mesoporous Zr-MCM-41 is regarded as an excellent adsorbent for removal of fluoride ions from aqueous media.

### Scope of future work

- Synthesis of different transition metal doped MCM-41.
- TEM/HRTEM and XPS studies of the prepared particles needed to study, in order to obtain the exact particle size and morphology.
- Small angle XRD (SAXS) study of the prepared samples to confirm the exact phase.
- Removal of other water contaminants by using the adsorbents.

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