# Catalytic Oxidation of Toluene Using Co-MCM-48 and CoMn-MCM-48 Mesoporous Material

Sana Ahmad*, Khushnood Yasin and Asma Tufail Shah
*Department of Chemistry, Lahore College For Women University, Lahore. Pakistan,*
drsanaahmad@yahoo.com*

(Received on 30th January 2017, accepted in revised form 26th September 2017)

**Summary:** Mesoporous materials are widely used as catalysts, adsorbents and supports due to their advantages such as narrow pore size distribution, large surface area and long-range order. In the present study, MCM-48 mesoporous material was synthesized at room temperature by using cetyltrimethylammoniumbromide as a structure directing agent. The catalytic activity of MCM-48 was improved by the incorporation of either single metal (Co) or two metal atoms (Co and Mn). Techniques such as SEM, TGA, BET and FTIR were used to characterize the as synthesized catalysts. The catalytic activity of the as prepared catalyst was investigated for the oxidation of toluene using hydrogen peroxide as an oxidizing agent and the reaction products were analyzed by gas chromatography and mass spectrometry. The results revealed that only benzaldehyde was obtained over Co-MCM-48 while a mixture of benzaldehyde and benzyl alcohol was obtained over CoMn-MCM-48. These results confirmed that both catalysts have high stability and activity for the oxidation of toluene.

Keywords: Mesoporous Materials; Toluene; Co-MCM-48; CoMn-MCM-48; MCM-48

## Introduction

Porous materials have various applications in human life whether they are manufactured synthetically or naturally. In 1992 the scientist of “Mobil Corporation Laboratories” discovered the highly ordered mesoporous materials. They are member of M41S family and were called as “*Mobil Composition of Matters*” (“MCM”). $SiO_2$ (silica) is one of the most significant unit of M41S family.[1]

MCM-50, MCM-41 and MCM-48 are the key representative of this family. These mesoporous members own numerous structures, e.g., MCM-50 exhibits a lamellar framework, MCM-48 has a cubic and three-dimensional formation while MCM-41 exhibits hexagonal arrangement of one dimensional pores.[2, 3]

MCM-48 has many attractive properties such as great thermal strength, adjustable pore volume, uniform pore sizes and great surface area in the range of 1000-2500 $m^2g^{-1}$ which permits the excessive distribution of active catalytic sites. It is more resistant to pore blockage and provides an undisturbed way for products and reactants to pass through its three-dimensional framework.[4, 5].

The deficiency of active sites in MCM-48 is considered as one of its main limitation. Its mesoporous framework is neutral. Hence in various chemical reactions it exhibits a very little number of catalytic applications. These limitations are the main cause of slight ion-exchange ability, reduced hydrothermal strength, small number of catalytic active sites and fragile acidity of surface in MCM-48. Several researchers attempted to incorporate various metal atoms such as Ni, Ti, Au, Fe, etc. into the mesoporous framework to increase its active centers. These metal atoms are helpful to develop the unique catalytic properties of MCM-48. [5-7] The isomorphous swap of Si atoms in the frame of mesoporous substance with different heteroatoms is one of the finest planned approach to incorporate metal atoms. By this procedure active sites are developed on the extremely accessible inner sides of the pore [8].

Generally catalytic systems involve elevated temperatures so the catalysts are frequently subjected to critical reaction conditions. Bimetallic mesoporous materials usually increase the adsorption, strength, reduction properties, catalytic activity, structural characteristics and selectivity of single metal doping catalysts [9]. Therefore, two metal atoms doped MCM-48 is extremely demanded as one metal would improve the structural and redox properties of second metal atom. In addition, both metals would contribute their own unique properties to the catalyst. In this work, MCM-48 material incorporated with one (Co) and two (Co and Mn) metal atoms were prepared and characterized by FTIR, SEM, TGA and nitrogen

---

[*] **To whom all correspondence should be addressed.**

adsorption/desorption method. As per our knowledge, so far this combination of metals has not been used together in a catalyst. The catalytic activity of metal doped catalyst was tested for the oxidation of toluene with hydrogen peroxide as an oxidizing agent [10].

## Results and Discussion

### *FTIR*

FTIR spectra of as prepared catalysts are given in Fig 1. MCM-48 displays Si-O symmetric vibrations (1087 cm$^{-1}$), asymmetric stretching vibrations (802 cm$^{-1}$) and Si-O-Si bond peak (466 cm$^{-1}$) [9]. The stretching vibrations of Si-OH corresponds to vibrational band at 960 cm$^{-1}$ [12]. A small peak at 1631 cm$^{-1}$ is due to deformation vibrations of adsorbed water molecules [13]. The presence of these bands indicates the formation of our required Si-O-Si network in the synthesized sample. In case of Co-MCM-48, same peaks were obtained as in the MCM-48. This indicates that the structure of the material has not changed due to the incorporation of Co metal Bimetallic catalyst correspondingly exhibits typical stretching bands of MCM-48 at 962 cm$^{-1}$ and 1095 cm$^{-1}$. A decline in wavelength is detected at 1095 cm$^{-1}$ band in case of CoMn-MCM-48. This blue shift confirms the incorporation of metal ions [9]. The band at 962 cm$^{-1}$ represents the Si-O-M linkage (M = Mn and Co) [16].

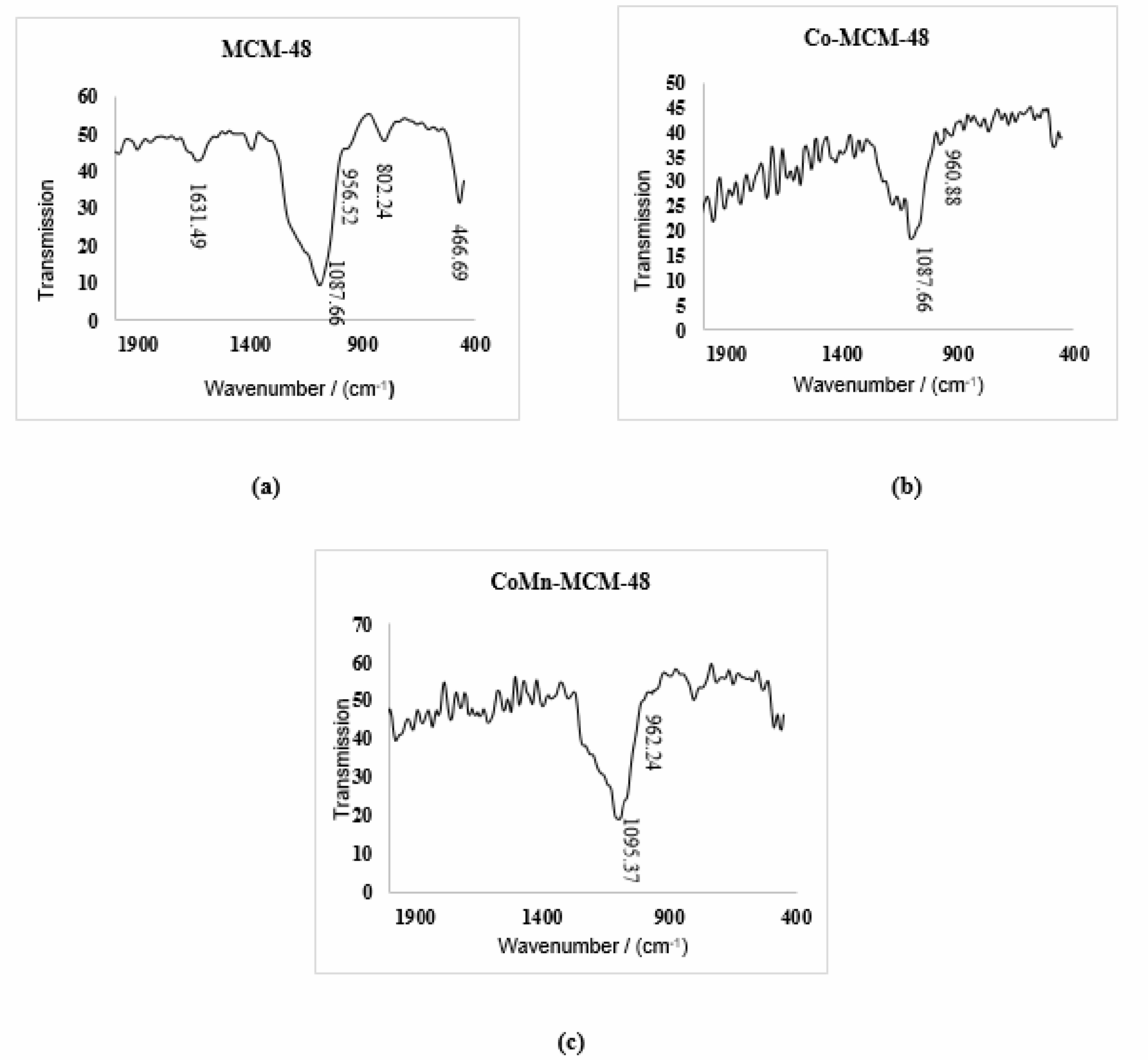


Fig. 1: FT-IR spectrum of (a) MCM-48, (b) Co-MCM-48 (c) CoMn-MCM-48.

*Thermogravimetric Analysis (TGA)*

TGA graphs of prepared catalysts are given in Fig 2. A typical weight loss pattern is seen in case of MCM-48, Co-MCM-48 and CoMn-MCM-48 mesoporous materials. In TGA analysis, the weight loss mainly occurs in two stages. 1) In the first stage between temperature range of 25-150°C, weight reduction corresponds to the desorption of physically adsorbed water molecule and ethanol from the exterior surface of the mesoporous material. 2) The next weight loss between 150-700°C occurs due to the thermal degradation and elimination of residual surfactant molecules[14].

The overall weight loss of MCM-48 is 10%. After 550°C, the surfactant was completely removed and hence this temperature was selected as calcination temperature for the preparation of catalysts. In Co-MCM-48 and CoMn-MCM-48, the entire weight loss is almost 10% and 12% respectively. The result shows that nature of the samples and its mesoporous structure is not destroyed with the incorporation of metal atoms. The metal doped MCM-48 shows good thermal stabilities.

.

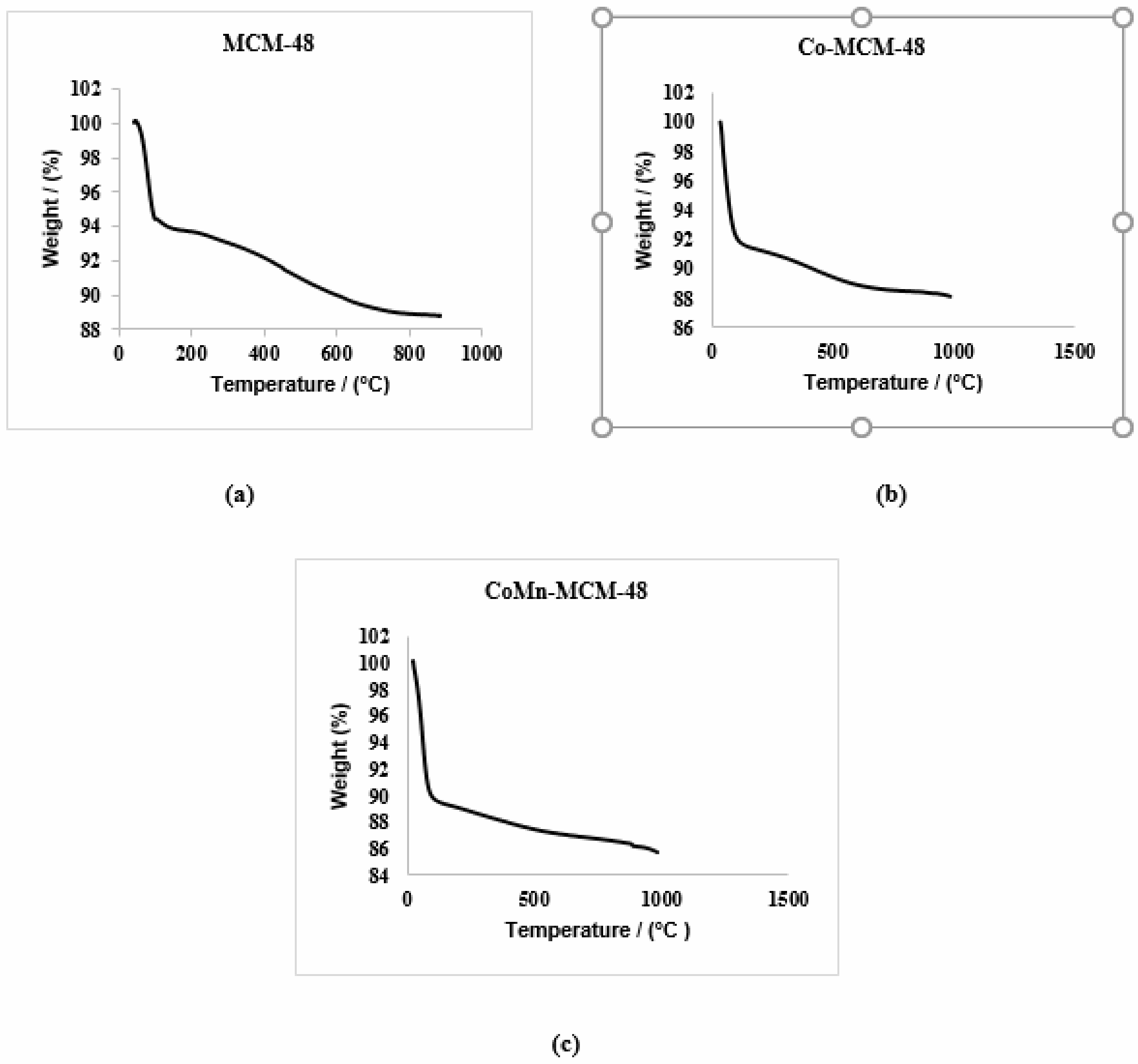


Fig. 2: TGA Graph of (a) MCM-48, (b) Co-MCM-48 (c) CoMn-MCM-48.

Table 1: Nitrogen Absorption/Desorption Data

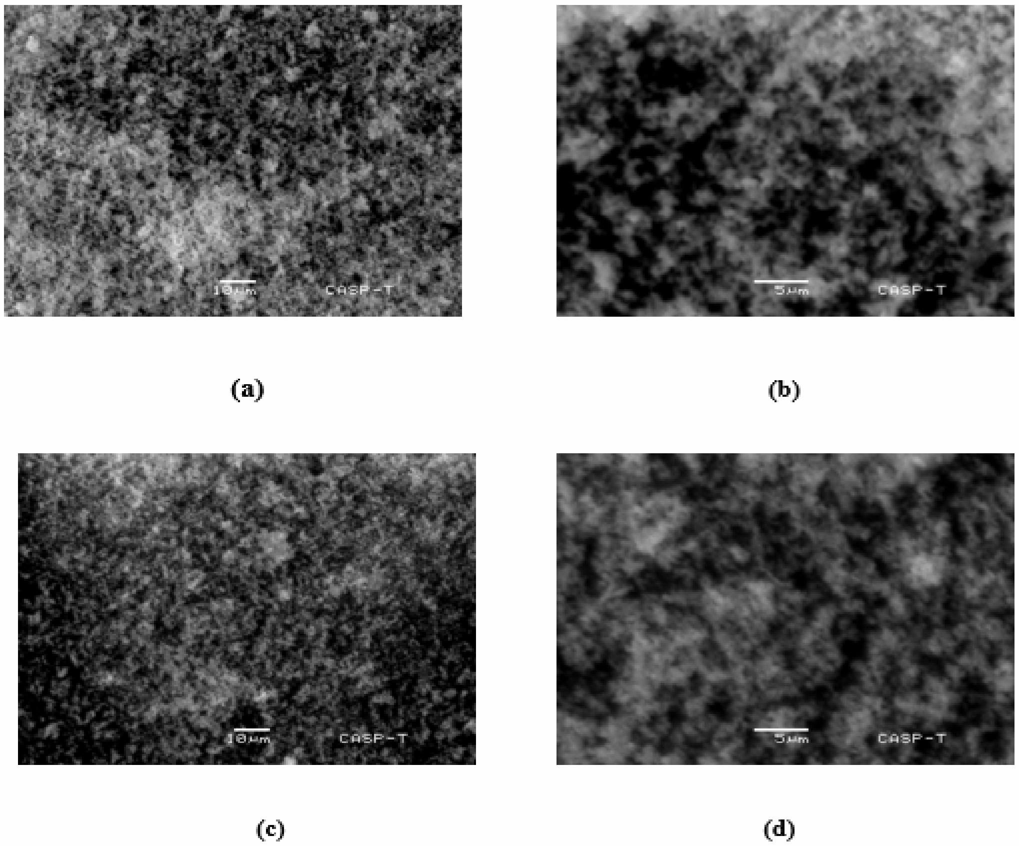
| Sr no | Catalyst | BET Surface Area (m²/g) | Pore Volume (cm³/g) | Pore Size (A°) |
|---|---|---|---|---|
| 1 | Co-MCM-48 | 185.9252 | 0.34 | 73.83 |
| 2 | CoMn-MCM-48 | 231.2435 | 0.35 | 60.93 |

### *Nitrogen Adsorption/Desorption Method*

This process includes the study of pore volume, specific surface area and pore size of synthesized metal comprising catalysts. The pore diameter was calculated by BJH method whereas surface area was studied via BET method. The results are presented in table 1. The BET surface area of CoMn-MCM-48 and Co-MCM-48 is 231.24 m²/g, and 185.92 m²/g respectively. These values are lower than the expectation and can be attributed to the incorporation of metal atoms in the framework of MCM-48[5]. A little pore blockage could result due to the incorporation of metal atoms and can result in reduced surface area. The pore size and pore volume of both samples are almost equal.

### *Scanning Electron Microscopy (SEM)*

The JEOLJSM-6480LV microscope was used to take SEM pictures of synthesized samples. The SEM pictures of prepared catalysts are given in Fig 3. Homogenous and good dispersion of particle with no big clusters formation was observed. Particle size is approximately 400 nm. The SEM images of CoMn-MCM-48 are given in Fig. 3 (c) and (d). These pictures display the same particle size and morphology as MCM-48 without the introduction of metal atom. Highly-ordered and dispersed particles of mesoporous material were detected with homogenous particle size. SEM images show that incorporation of metals do not affect the textural properties of MCM-48 as no cluster development is detected.



(a) (b)

(c) (d)

**Fig. 3: SEM image of MCM-48 (a) and (b), CoMn-MCM-48 (C) and (d).**

### *Catalytic Activity*

The Co-MCM-48 and CoMn-MCM-48 catalysts were used for the oxidation of toluene with $H_2O_2$ at 80°C for 12 h in the absence of solvent to examine the result of metal atom incorporation on activity and selectivity of MCM-48. The GC/MS technique was used to study the reaction products attained from both catalysts.

Following products were obtained.

| S. No. | Reactants | Catalyst | Products |
|---|---|---|---|
| 1. | Toluene+$H_2O_2$ | Co-MCM-48 | Benzaldehyde (100%) |
| 2. | Toluene+$H_2O_2$ | CoMn-MCM-48 | Benzaldehyde (82%)+<br>Benzyl Alcohol (18%) |

The GC/MS results confirmed that the oxidation product obtained after reaction of toluene and hydrogen peroxide in the presence of Co-MCM-48 and CoMn-MCM-48 are benzaldehyde and benzyl alcohol. The bimetallic catalyst gives two products due to the presence of two metals. Both metals perform independently and gave different reaction products.

Hence, these catalysts are highly suitable for the manufacturing of benzaldehyde or a mixture of benzaldehyde and benzyl alcohol. A great stability and activity is also shown by these catalysts for the oxidation of toluene. The metal containing MCM-48 has several benefits over simple metal salts like homogenous spreading of metal atoms, catalyst can be recovered with much ease and reaction products are easily separated.

## Conclusion

Mesoporous MCM-48 material with three-dimensional pore structure was prepared by a simple method at room temperature and all the synthesis steps do not involve extreme conditions. It was further used as a support for incorporation of two different metal atoms by direct method. Monometallic (Co-MCM-48) and bimetallic (CoMn-MCM-48) catalysts were synthesized and characterized. The characterization exhibited that the as prepared catalysts have high thermal stability, non-agglomerated particles and uniform particle sizes. The MCM-48 mesoporous structure is not altered by the incorporation of metal atoms. To study the catalytic activity of mono and bimetallic catalyst, the oxidation of toluene was carried out with hydrogen-peroxide. Excellent results were obtained with both the catalysts with 100% conversion of toluene to oxidation products. Benzaldehyde was obtained with Co-MCM-48 and a mixture of benzaldehyde and benzyl alcohol was obtained with CoMn-MCM-48. Both metals independently carried out the oxidation reaction leading to two independent products. Hence incorporation of two metal atoms not only enhances its thermal stability but also increases the activity of mesoporous MCM-48 material.

## References

1. F. Kleitz, *Ruhr University Bochum, Ordered Mesoporous Materials: Template Removal, Frameworks and Morphology.* **(2002)**.
2. H. Maneesuwan, R. Longloilert, T. Chaisuwan, S. Wongkasemjit, Synthesis and characterization of Fe-Ce-MCM-48 from silatrane precursor via sol-gel process, *Mater. Lett*., **94**, 65 (2013).
3. J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, J. L. Schlenker, A new family of mesoporous molecular-sieves prepared with liquid-crystal templates *J. Am. Chem. Soc.*, **114**, 10834 (1992).
4. S. Gunduz, *Middle East Technical University, Sorption Enhanced Ethanol Reforming over Cobalt, Nickel Incorporated MCM-41 for Hydrogen Production*. (2011).
5. S. Banerjee, H. Khatri, V. Balasanthiran, R. T. Koodali, G. Sereda, Synthesis of substituted acetylenes, aryl-alkyl ethers, 2-alkene-4-ynoates and nitriles using heterogeneous mesoporous Pd-MCM-48 as reusable catalyst *Tetrahedron,* **67**, 5717 (2011).
6. Q. Zhaoa, X. Zhou, M. Ji, H. Ding, T. Jiang, C. Li, H. Yin, Stability and textural properties of cobalt incorporated MCM-48 mesoporous molecular sieve, *App. Surf. Sci*., **257**, 2436 (2011).
7. D. Marczewska, W. Gac, N. Popivnyak, G. Zukocinski, S. Pasieczna, The influence of preparation method on the structure and redox properties of mesoporous Mn-MCM-41 materials, *Catal. Today*, **114**, 293 (2006).
8. Fechete, B. Donnio, O. Ersen, T. Dintzer, A. Djeddi, F. Garin, F. Single crystals of mesoporous tungstenosilicate W-MCM-48 molecular sieves for the conversion of methylcyclopentane (MCP) *App. Surf. Sci.*, **2011**, *257*, 2791.
9. L.F.F.P.G. Braganc, R. R. Avilez, M. I. P. D. Silva, Synthesis of cobalt-iron bimetallic nanocrystals supported on mesoporous silica using different templates, *Colloids Surf. A*, **358**, 79 (2010).

10. X. Li, B. Lu, J. Sun, X. Wang, J. Zhao, Q. Cai, Selective solvent-free oxidation of toluene to benzaldehyde over zeolite supported iron*, Catal. Commun*, **39**, 115 (2013).
11. R. J. Kalbasi, N. Mosaddegh, Synthesis and characterization of poly(4-vinylpyridine)/MCM-48 catalyst for one-pot synthesis of substituted 4H-chromenes*, Catal. Commun.*, **12**, 1231 (2011).
12. S. Endud, K. L. Wong, Mesoporous silica MCM-48 molecular sieve modified with SnCl2 in alkaline medium for selective oxidation of alcohol, *Micropor. Mesopor. Mater*., 2007, **101**, 256.
13. V. Parvulescu, C. Anastasescu, C. Constantin, B. L. Su, Mono (V, Nb) or bimetallic (V-Ti, Nb-Ti) ions modified MCM-41 catalysts: synthesis, characterization and catalysis in oxidation of hydrocarbons (aromatics and alcohols), *Catal. Today*., **78**, 477 (2003).
14. F. Raji, M. Pakizeh, Study of Hg(II) species removal from aqueous solution using hybrid ZnCl2-MCM-41 adsorbent *App. Surf. Sci*., **282**, 415 (2013).
15. S. S Lapari, S. Parham, *Int. J. Eng. Sci. Invent.,* **5***,* 2013 (2013).