

Application of Spherical Mesoporous Silica MCM-41 for Adsorption of Dibenzothiophene (A Sulfur Containing Compound) from Model Oil

Ahmadi Nasab, Navid; Hassani Kumleh, Hassan

Biotechnology Department, University of Guilan, University Campus 2, Guilan, I.R. IRAN

Kazemzad, Mahmood⁺; Ghavipankeh, Farideh*

Materials and Energy Research Center, Tehran, I.R. IRAN

ABSTRACT: Spherical mesoporous silica MCM-41 was synthesized for adsorptive removal of sulfur compounds from fossil fuels using 1mM solution of dibenzothiophene (DBT) in dodecane as model oil. The prepared silica adsorbent has been characterized by nitrogen adsorption-desorption analysis as well as Small Angle X-ray Scattering (SAXS), and transmission and Scanning Electron Microscopy (SEM) methods. Results showed that the prepared mesoporous adsorbent has ordered pore structures with surface area of 1106 m²/g and mean pore diameter of 3.54 nm. SEM micrographs indicated that prepared mesoporous silica (MCM-41) has spherical morphology with the narrow size distribution in the range of 200-300 nm. Hexagonal structure of pores has also been confirmed by high resolution transmission electron microscopy and SAXS pattern. High performance liquid chromatography analysis has also been utilized to study the kinetics of the DBT adsorption from dodecane solution by means of the synthesized silica. Results showed that 0.03 g/mL of mesoporous silica has capability to adsorb more than 42% of DBT (a sulfur containing compound) from dodecane solution. The improvement of mass transfer via adsorption DBT by the prepared nanosorbent is an efficient method for enhancement of biodesulfurization kinetic.

KEY WORDS: MCM-41, Mesoporous Silica, Dibenzothiophene, Nanosorbent, Sulfur Removal.

INTRODUCTION

Energy consumption of world has been tremendously increased due to growth of industrial activities; however, limited reservoirs of fossil fuels in addition to enormous extraction of them make their quality decrease [1]. Presence of undesired contaminants such as sulfur, nitrogen and heavy metals in remained reservoirs of fossil fuels reduces both the viscosity and molecular weight

enrichment of crude oil resulting in diminished fuel ignition index. Sulfur content is one of the most important obstacles causing damage of crude oil refinery systems and environmental pollution. Sulfur oxides in combination with water vapor can cause corrosive wear and premature engine failure [1,2].

Sulfur reduces catalyst efficiency in modern vehicles,

* To whom correspondence should be addressed.

+ E-mail: m-kazemzad@merc.ac.ir

1021-9986/14/3/

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and vehicles operating with higher sulfur gasoline have higher emissions than vehicles operating on lower sulfur gasoline. Frankly, sulfur is the third element of heavy oil after carbon and hydrogen with concentration more than 14% whereas crude oil contains 0.05-5% sulfur (organosulfur) depending on the source of crude oil [3-5].

In this regard, regulations are now put in place by states, regional and international agencies. According to Environmental Protection Agency (EPA) amount of sulfur in diesel oil should not be above 15 mg/L. By the same regulations no more than 15% of aromatic compounds are allowed in diesel oils [6-10].

Among the various methods applied for removal of sulfur, hydrodesulfurization is conventionally applied more than other techniques. However, this method requires high pressure which is either economically undesirable or makes fuel properties decay through degradation of special compounds. In addition, about 70% aromatic sulfur compounds such as 4- and 4, 6- alkyl substituted dibenzothiophene and also heterocyclic polyaromatic sulfur compounds could not be completely removed by this method. There are many attempts to find new benign and mild methods for sulfur removal beside to greenhouse emission reduction [3, 11-16].

Biological desulfurization is a new microbial method, capable of selective desulfurization without the fuel properties loss [1, 2, 16]. Biological oxidation of sulfur to sulfate takes place through a 4 step continuous process where dibenzothiophene (DBT) will change to 2-hydroxy biphenyl [17-20]. However, kinetics of microbial desulfurization is slow and its activity is affected by mass transfer rate of reactants us from organic phase to aqueous phase and then onto the surface of living cells [21-25]. The key point should be application of surfactants and/or nanoadsorbents to overcome mass transfer problem [26, 27]. So, the mass transfer and steric effect can be eliminated by stable, recoverable high surface area adsorbents which it is possible to control both their pore size and shape [28].

Mesoporous silica is a suitable choice for the above application because of its large surface area, structure stability and existence of a great number of ordered pores. The pore size distribution of mesoporous silica compounds are in the range of 2-50 nm making it suitable for such applications like drug releasing adsorption, catalysis, and waste treatment. The compound is an ideal

choice as a host for adsorption of guest molecules with different shape, size and properties e.g. sulfur [10, 29-33].

Herein, the synthesis of mesoporous silica (MCM-41) and optimizing condition of DBT adsorption onto its surface from dodecane solution as model oil is determined by application of High Performance Liquid Chromatography (HPLC) analysis.

EXPERIMENTAL SECTION

Materials

DBT (98%), 2-HBP (99%), n-dodecane, tetraethylorthosilicate (TEOS 99%), CTAB, solvents and all other chemicals has been purchased from Merck and utilized without further purification.

Synthesis of spherical mesoporous silica MCM-41

MCM-41 nanoadsorbent has been synthesized at room temperature in according to the procedure introduced by *Melendez-Ortiz et al.* [31]. In a typical procedure 0.5 g of Cetyl Trimethyl Ammonium Bromide (CTAB) was dissolved in 96mL of deionized water under mild stirring. After a clear solution has been obtained, 34ml of ethanol and 10mL of 25% ammonia solution have been added to the above transparent solution following by stirring for 5 min again. Finally, 2ml of TEOS was added to this mixture, and obtained solution stirred for 3 h at room temperature and solid product was filtered, washed and dried at room temperature for 24 hours. CTAB template was removed by heat treatment of dry powder in a furnace at 540°C for 9h [31].

Characterization of nanosorbent

The ordering and structure of the prepared silica's pores were studied by Small Angle X-ray Scattering (SAXS) method applying PANalytical X'Pert MPD instrument operating at 40V and 40 mA with Cu K α ($\lambda=1.5406\text{\AA}$) as X-ray source. The morphology and microstructure of the sample were also investigated by scanning electron microscopy (SEM) (Stroscon 360, Leica Cambridge) with an accelerating voltage of 20 kV. Transmission Electron Microscopy (TEM) analysis was also carried out by Philips electron microscope (model CM 200) with 200KV field emission gun.

Barrett-Joyner-Halenda (BJH) pore size and Brunauer-Emmett-Teller (BET) surface area measurement methods using N₂ adsorption-desorption

Table 1: Properties of the prepared MCM-41 samples.

Wall Thickness (nm)	Mean diameter of pores (nm)	Surface area (m ² /g)	Total pore volume (cm ³ /g)
0.87	3.54	1106	0.977

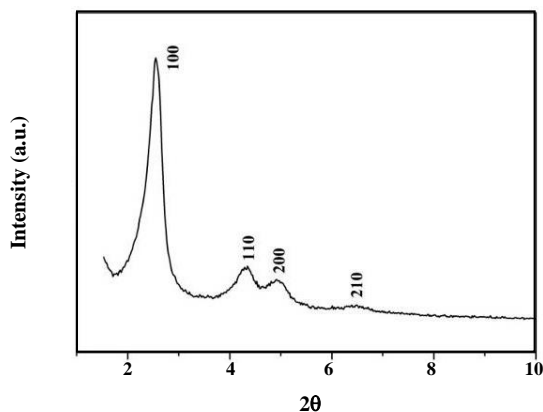


Fig. 1: SAXS pattern of synthesized MCM-41 sample.

isotherm have been performed by the Micromeritics Gemini III 2375 instrument. The sample was heated at 200 °C for 10 h before analysis in order to evacuate its pores before surface analysis.

Adsorption of DBT from model oil

Different amounts of MCM-41 nanosorbent was dispersed by sonication in 10 ml aliquots of dodecane for 10min. Samples containing 0.05, 0.1, 0.15, 0.2, 0.25, 0.35 and 0.5 g of adsorbent were deagglomerated by slight mixing with shaker at 30 °C for 4h before HPLC analyses.

HPLC Analysis

HPLC analyses of DBT have been performed by Gradient HPLC instrument equipped with UV detector ($\lambda=280$ nm), thermo stated ODS-3 column (250 mm \times 4.6 mm \times 5 μ m) and Eurochrom 2000 software. Flow rate of acetonitrile-water mixture solvents (ratio of 4:1) and column temperature has been set to 1mL/min and 25 °C, respectively.

RESULTS AND DISCUSSION

Nanosorbent Characterization

Fig. 1 shows SAXS pattern of the prepared MCM-41 sample. Peaks observed in $2\theta = 2.52, 4.30, 4.94$ and 6.47 are clearly in accordance with hexagonal structure of MCM-41.

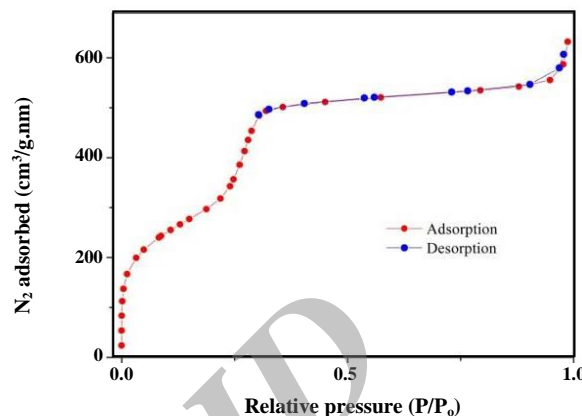


Fig. 2: Nitrogen adsorption-desorption isotherms of the prepared mesoporous silica sample (MCM-41).

The low intensity peaks of (110), (200) and (210) observed in this figure related to two dimensional hexagonal structure of sample.

Surface analysis of samples using BJH model are shown in Fig. 2 which are in good agreement with type (IV) isotherms of IUPAC classification [34]. Mean pore diameter calculated by BJH models for the sample is 3.54 nm. Table 1 lists the surface area as well as other data obtained by the BET-BJH models.

Fig. 3 shows the SEM image of the mesoporous silica powders. This figure indicates homogeneous and spherical morphology of adsorbent powder. It is observed that particle sizes are in the range of 200-300 nm. TEM studies confirmed the same morphology reported for MCM-41 as well as its hexagonal meso-structure [31,34] (Fig. 4). Pore diameter and wall thickness obtained from the HRTEM image (inset of Fig. 4) are also depicted in this image. Results are in good agreement with data obtained by BET-BJH surface analysis.

Adsorption properties of adsorbent from DBT- dodecane solution

Fig. 5 shows the DBT concentration curve vs. time of infiltration with various amounts of dispersed adsorbent. Fig. 6 on the other hands illustrate the percent of DBT adsorption against mass of adsorbent in different times. Referring to these results, the adsorption rate is very high

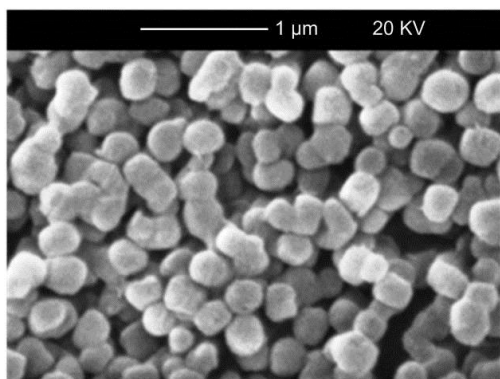


Fig. 3: SEM image of the prepared MCM-41 samples.

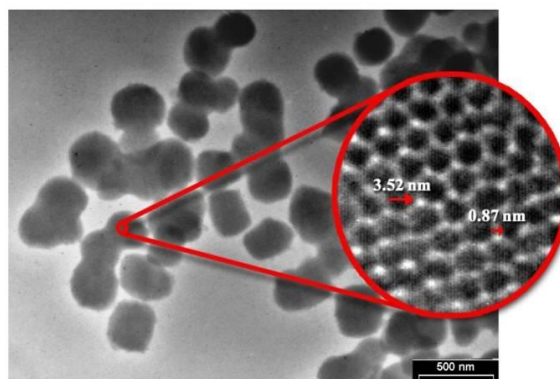


Fig. 4: TEM image of the prepared MCM-41 samples (estimation of wall thickness and pore diameter).

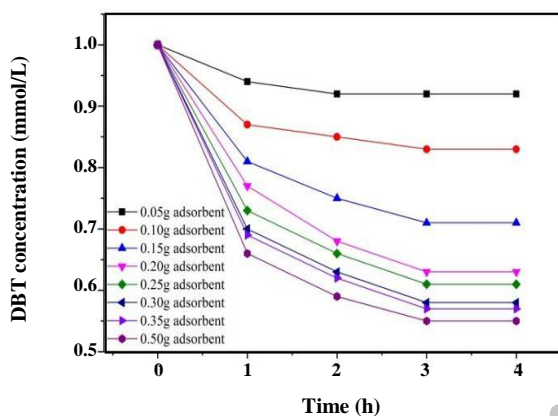


Fig. 5: Adsorption of DBT with different amount of the prepared MCM-41 samples.

at first hour, but the whole process is completed after 3h. According to adsorption experiments, 29, 37, 39, 42, 43 and 45 percent of DBT could be adsorbed after 3 h using 0.15, 0.2, 0.25, 0.3, 0.35 and 0.5 g of adsorbents. Results showed that saturation of DBT adsorption from the suspensions containing 0.05 and 0.1 g of adsorbent are occurred faster than other ones and their adsorption percent in the final solution have been determined to be 8% and 15%, respectively. Based on these data and considering the slope of curves, there is no direct relation between amount of adsorbent and that of adsorption rate. From the view of the kinetic and economic approach, the best results obtained while using 0.03 g/ml of adsorbent for 3 h. Considering Fig. 7, it seems that agglomeration of particles in higher amounts of adsorbent takes place which may consequently reduce the surface to volume ratio of the adsorbent resulting in lower efficiency of

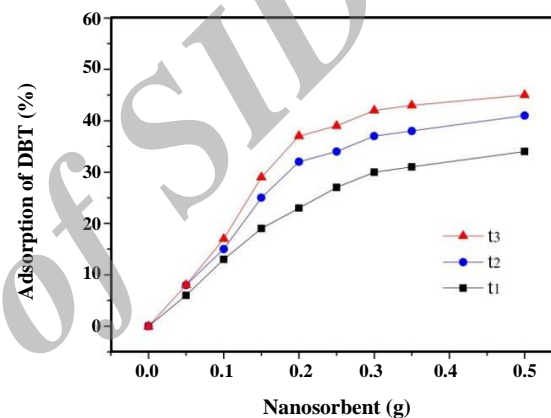


Fig. 6: Adsorption of DBT with different amount of the prepared MCM-41 samples at different time.

adsorption in comparison with that of theoretically predicted amount.

CONCLUSIONS

In this study, spherical mesoporous silica MCM-41 was synthesized as an eco-friendly nanosorbent using a quaternary ammonium template, CTAB in basic water-ethanol mixture. It has been applied for adsorptive removal of sulfur compounds from fossil fuels using 1mM solution of DBT in dodecane as model oil. This investigation shows that the synthesized MCM-41 mesoporous silica is an efficient adsorbent of DBT from model oil. The optimized condition determined in this research for DBT adsorption by the synthesized mesoporous silica (1mM solution of DBT in dodecane as model oil) is 0.03 g/ml of adsorbent for 3 h of treatment.

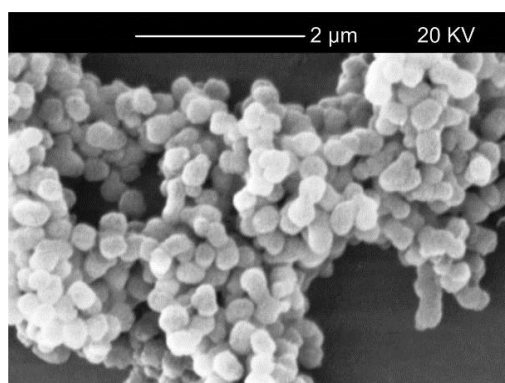


Fig. 7: SEM image of agglomerated MCM-41 particles in high concentration suspension (0.05 g/ml).

Acknowledgment

We would like to thank Mr. Yadolah Ganjkanlou at the University of Turin for his assistance in preparation of this paper.

Received : Mar. 3, 2013 ; Accepted : Jan. 10, 2014

REFERENCES

- [1] Nuhu A.A, Bio-catalytic Desulfurization of Fossil Fuels: a Mini Review, *Rev Environ Sci Biotechnol*, **12**: 9-23 (2012).
- [2] Soleimani M, Bassi A, Margaritis A, Biodesulfurization of Refractory Organic Sulfur Compounds in Fossil Fuels, *Biotechnology Advances*, **25**: 570-596 (2007).
- [3] Bahuguna A, Lily M.K, Munjal A, Singh R.N, Dangwal K, Desulfurization of Dibenzothiophene (DBT) by a Novel Strain *Lysinibacillus Sphaericus* DMT-7 Isolated from Diesel Contaminated Soil, *J. Environ. Sci. (China)*, **23**: 975-982 (2011).
- [4] Davoodi-Dehaghani F, Vosoughi M, Ziaee A.A, Biodesulfurization of Dibenzothiophene by a Newly Isolated *Rhodococcus Erythropolis* Strain, *Bioresource Technology*, **101**: 1102-1105 (2010).
- [5] Kayser K.J, Cleveland L, Park H.S, Kwak J.H, Kolhatkar A, Kilbane J.J, Isolation and Characterization of a Moderate Thermophile, *Mycobacterium phlei* GTIS10, Capable of Dibenzothiophene Desulfurization, *Appl Microbiol Biotechnol*, **59**: 737-745 (2002).
- [6] Alcon A, Santos V.E, Martin A.B, Yustos P, Garcia-Ochoa F, Biodesulfurization of DBT with *Pseudomonas Putida* CECT5279 by Resting cells: Influence of Cell Growth Time on Reducing Equivalent Concentration and HpaC Activity, *Biochemical Engineering Journal*, **26**: 168-175 (2005).
- [7] Calzada J, Alcon A, Santos V.E, Garcia-Ochoa F, Mixtures of *Pseudomonas Putida* CECT 5279 Cells of Different Ages: Optimization as Biodesulfurization Catalyst, *Process Biochemistry*, **46**: 1323-1328 (2011).
- [8] Caro A, Boltes K, Letón P, García-Calvo E, Dibenzothiophene Biodesulfurization in Resting cell Conditions by Aerobic Bacteria, *Biochemical Engineering Journal*, **35**: 191-197 (2007).
- [9] Kilbane J.J, Microbial Biocatalyst Developments to Upgrade Fossil Fuels, *Current Opinion in Biotechnology*, **17**: 305-314 (2006).
- [10] Dabaghi H.H, Kazemzad M, Ganjkanlou Y, Yuzbashi A.A, Electrochemical Preparation of New Organosilicone Compounds for Functionalizing of Mesoporous Silica, *Functional Materials Letters*, **6**: 1350031-1350034 (2013).
- [11] Caro A, Boltes K, Letón P, García-Calvo E, Biodesulfurization of Dibenzothiophene by Growing Cells of *Pseudomonas Putida* CECT 5279 in Biphasic Media, *Chemosphere*, **73**: 663-669 (2008).
- [12] Faghihian H, Naeemi Sh, Application of a Novel Nanocomposite for Desulfurization of a Typical Organo Sulfur Compound, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **32**: 9-15 (2013).
- [13] Mohebbi G, Ball A.S, Rasekh B, Kaytash A, Biodesulfurization Potential of a Newly Isolated Bacterium, *Gordonia Alkanivorans* RIPI90A, *Enzyme and Microbial Technology*, **40**: 578-584 (2007).
- [14] Tanaka Y, Matsui T, Konishi J, Maruhashi K, Kurane R, Biodesulfurization of Benzothiophene and Dibenzothiophene by a Newly Isolated *Rhodococcus* Strain, *Appl Microbiol Biotechnol*, **59**: 325-328 (2002).
- [15] Yang J, Marison I.W, Two-Stage Process Design for the Biodesulfurization of a Model Diesel by a Newly Isolated *Rhodococcus Globerulus* DAQ3, *Biochemical Engineering Journal*, **27**: 77-82 (2005).

- [16] Marcelis C.L.M, [Anaerobic Biodesulfurization of Thiophenes](#), *Wageningen University*, **90**, p.178 (2002).
- [17] Borgne S.L, Quintero R, [Biotechnological Processes for the Refining of Petroleum](#), *Fuel Processing Technology*, **81**: 155-169 (2003).
- [18] Holland H.L, Brown F.M, Kerridge A, Pienkos P, Arensdor J, [Biotransformation of Sulfides by Rhodococcus Erythropolis](#), *Journal of Molecular Catalysis B: Enzymatic*, **22**: 219-223 (2003).
- [19] Maghsoudi S, Kheirrolmoom A, Vossoughi M, Tanaka E, Katoh S, [Selective Desulfurization of Dibenzothiophene by Newly Isolated Corynebacterium sp. Strain P32C1](#), *Biochemical Engineering Journal*, **5**: 11-16 (2000).
- [20] Monticello D.J, [Biodesulfurization and the Upgrading of Petroleum Distillates](#), *Current Opinion in Biotechnology*, **11**: 540-546 (2000).
- [21] Ansari F, Grigoriev P, Libor S, Tothill I.E, Ramsden J.J, [DBT Degradation Enhancement by Decorating Rhodococcus Erythropolis IGST8 with Magnetic Fe₃O₄ Nanoparticles](#), *Biotechnol. Bioeng*, **102**: 1505-1512 (2009).
- [22] Guobin S, Huaiying Z, Weiquan C, Jianmin X, Huizhou L, [Improvement of Biodesulfurization Rate by Assembling Nanosorbents on the Surfaces of Microbial Cells](#), *Biophys. J.*, **89**: 58-60 (2005).
- [23] Shan G, Xing J, Zhang H, Liu H, [Biodesulfurization of Dibenzothiophene by Microbial Cells Coated with Magnetite Nanoparticles](#), *Applied and Environmental Microbiology*, **71**: 4497-4502 (2005).
- [24] Zhang H, Liu Q, Li Y, Li W, Xiong X, Xing J, Liu H, [Selection of Adsorbents for In-Situ Coupling Technology of Adsorptive Desulfurization and Biodesulfurization](#), *Sci. China Ser. B-Chem*, **51**: 69-77 (2008).
- [25] Zhang T, Li W.L, Chen X.X, Tang H, Li Q, Xing J.M, Liu H.Z, [Enhanced Biodesulfurization by Magnetic Immobilized Rhodococcus Erythropolis LSSE8-1-Vgb Assembled with Nano- \$\gamma\$ -Al₂O₃](#), *World J Microbiol Biotechnol*, **27**: 299-305 (2011).
- [26] Li W, Tang H, Liu Q, Xing J, Li Q, Wang D, Yang M, Li X, Liu H, [Deep Desulfurization of Diesel by Integrating Adsorption and Microbial Method](#), *Biochemical Engineering Journal*, **44**: 297-301 (2009).
- [27] Zhang H, Shan G, Liu H, Xing J, [Surface Modification of \$\gamma\$ -Al₂O₃ Nano-Particles with Gum Arabic and its Applications in Adsorption and Biodesulfurization](#), *Surface and Coatings Technology*, **201**: 6917-6921 (2007).
- [28] Dinamarca M.A, Ibacache-Quiroga C, Baeza P, Galvez S, Villarroel M, Olivero P, Ojeda J, [Biodesulfurization of Gas Oil Using Inorganic Supports Biomodified with Metabolically Active Cells Immobilized by Adsorption](#), *Bioresource Technology*, **101**: 2375-2378 (2010).
- [29] Chen Y, Shi X, Han B, Qin H, Li Z, Lu Y, Wang J, Kong Y, [The Complete Control for the Nanosize of Spherical MCM-41](#), *J. Nanosci. Nanotechnol*, **12**: 7239-7249 (2012).
- [30] Dai Q, He N, Weng K, Lin B, Lu Z, Yuan C, [Enhanced Photocatalytic Activity of Titanium Dioxide Supported on Hexagonal Mesoporous Silica at Lower Coverage](#), *Journal of Inclusion Phenomena*, **35**: 11-21 (1999).
- [31] Meléndez-Ortiz H.I, García-Cerda L.A, Olivares-Maldonado Y, Castruita G, Mercado-Silva J.A, Perera-Mercado Y.A, [Preparation of Spherical MCM-41 Molecular Sieve at Room Temperature: Influence of the Synthesis Conditions in the Structural Properties](#), *Ceramics International*, **38**: 6353-6358 (2012).
- [32] Qu L, Tie S, [Mesoporous Silica-Coated Superparamagnetic Magnetite Functionalized with CuO and Its Application as a Ddesulfurizer](#), *Microporous and Mesoporous Materials*, **117**: 402-405 (2009).
- [33] Kazemzad M, Yuzbashi A.A, Balalaie S, Bararjanian M, [Modified SBA-15 as an Efficient Environmentally Friendly Nanocatalyst for One-Pot Synthesis of Tetrahydrobenzo\[b\]pyrane Derivatives](#), *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, **41**: 1182-1187 (2011).
- [34] Mahmoudi M, Rahnemaie R, Es-haghi A, Malakouti M.J, [Kinetics of Degradation and Adsorption-Desorption Isotherms of Thiobencarb and Oxadiargyl in Calcareous Paddy Fields](#), *Chemosphere*, **91**, p. 1009-1017 (2013).