

# Facile and Economic Method for the Preparation of Core-Shell Magnetic Mesoporous Silica

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**ABSTRACT:** *In this work core-shell structure  $Fe_3O_4@SiO_2@meso-SiO_2$  microsphere has been successfully prepared. An inorganic magnetic core has been coated with multi-shell structure, dense nonporous silica as an inner layer and mesoporous silica as an outer layer. The dense silica shell can enhance the stability and minimize the negative effect of acidic condition on the inner core and the porous outer shell can provide high surface area and enhance the loading of a functionalized group. Cetyltrimethylammonium bromide (CTAB) has been used as a pore-forming agent and a modified methodology was adopted to improve the extraction condition of this kind of surfactant. The as-prepared microspheres were characterized by Field Emission Scanning Electron Microscope (FESEM), X-Ray Diffraction (XRD), Fourier Transform InfraRed (FT-IR) spectroscopy, Vibration Sample Magnetometer (VSM),  $N_2$  adsorption-desorption, and Particle Size Analyzer (PSA). The resulted materials possessing uniform core-shell structure, and well preserved structural stability. Additionally, they can be collected readily by using an external magnetic field. The prepared material has considerable potential applications in various fields including catalysis, drug delivery, and water treatment.*

**KEYWORDS:** *Magnetic  $Fe_3O_4$ ; Core-shell structure; Mesoporous silica; Nanoparticles; Solvent extraction.*

## INTRODUCTION

Core-shell structure materials have recently received much attention due to their great potential applications in catalysis, drug/DNA/gene delivery, water treatment, and so on [1-3]. As a main member of the core-shell family, magnetic nanospheres consisting of a magnetic core and silica shell have been developed for two important

reasons. The magnetic character makes iron oxide nanoparticles removable and recyclable by the magnetic field easily. Meanwhile, the coated silica layer can not only prevent the aggregation of a magnetic core, also protect it against oxidization condition. Also, mesoporous silica material has several appealing features, such as

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1021-9986/2019/5/1-9

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stable structure, high surface area, low toxicity, controllable pore diameters, and easily incorporated bonding groups which help to improve the performance of this material in different applications [4-7]. Wang *et al.* prepared a novel amino-functionalized magnetic nanomaterial with a core-shell structure to remove heavy metal ions from aqueous media. The structural, surface and magnetic characteristics of the adsorbent were investigated in detail. Due to the complexation of the metal ions by surface amino groups, this adsorbent exhibited high adsorption affinity for aqueous Cu (II), Pb (II), and Cd (II) ions. The adsorbent could be recovered readily from aqueous solution by magnetic separation and regenerated easily by acid treatment [8]. Min *et al.* have synthesized core-shell-shell structured nanoparticles with magnetic and luminescent features. The obtained magnetic-luminescent composite nanoparticles are characterized by different methodologies to confirm the core-shell-shell structure [9]. Yang *et al.* have synthesized Fe<sub>3</sub>O<sub>4</sub> microspheres encapsulated with nonporous silica and a further layer of mesoporous silica. The surface of the outer silica shell was also functionalized by the deposition of YVO<sub>4</sub>: Eu<sup>3+</sup> phosphors. The material was used as a drug carrier to investigate the storage and release properties using ibuprofen (IBU) as a model drug by the surface modification [10]. Yaung *et al.* developed a novel multifunctional magnetic mesoporous silica *via* two step sol-gel method. This adsorbent had a large pore size and has shown high adsorption capacity for heavy metal ions such as Cu (II), Pb (II), and Cd (II). After adsorption process, the material has been separated from the solution by the magnet and regenerated by acid treatment. The adsorption capacity of the adsorbent remained almost unchanged after 4 cycles [11].

The core-shell magnetic-mesoporous silica can be prepared by different methodologies [12]. In this paper, it is aimed to adopt the effective, economic and facile method to prepare the mentioned structure. First, the nanoparticle is synthesized through the co-precipitation method and transferred to an ethanol/ammonia mixture. Then silica shell is formed on the surface of magnetic nanoparticle through hydrolysis and condensation of tetraethylorthosilicate (TEOS). Uniform mesoporous silica shell is also coated on the obtained structure through a surfactant-templating agent such as cetyltrimethylammonium bromide (CTAB) [13]. To achieve

a mesoporous structure, the surfactant needs to be removed effectively. There are several strategies to remove this template including calcination, supercritical CO<sub>2</sub> extraction and solvent extraction [14, 15]. Each methodology follows specific advantages and disadvantages, however, the solvent extraction can be selected as one of the most common strategies due to several reasons. Firstly, compared to the calcination at a high temperature, solvent extraction can guarantee the stability of the structure during the process. Secondly, in comparison to the supercritical CO<sub>2</sub> method which needs to be performed at high pressure or temperature, extraction by solvent can be performed in a safe condition. However, it should be mentioned that the solvent extraction needs to be carefully developed to avoid the degradation of the material and subsequently ensure long-term reusability [16]. For example, if the extraction takes too much time or the temperature is failed to be controlled during the extraction process, the physical and chemical properties of materials may be changed or deteriorated.

Acetone is highly recommended as an effective solvent in this respect since it is more economical, has low toxicity and is widely available, however, it poses some problems. In one hand, the significant amount of acetone is required to extract surfactant from the structure to reach mesoporous material. On the other hand, it takes too much time to complete the extraction process, (at least 48h) [17]. Minimization and selection of the solvent can be considered as an important sustainability aspect which has been taken into account by some scientists. For instance, the optimal design of solvent blends for environmental impact minimization has been investigated by Buxton *et al.* They proposed a systematic procedure based on the optimal solvent blends for nonreactive, multicomponent absorption processes accounting for plant-wide point source environmental interactions. This methodology involves the selection of an optimal solvent blend candidate based on the global plant-wide process and environmental constraints [18]. Slater *et al.* suggested the greener process that uses a continuous adsorption system, composed of a more efficient adsorbent, consuming less organic solvent and rinse water, which leads to less waste disposal. The approach is also more energy and cost-efficient from an operational perspective since the carbon footprint reduces to 94% compared with the latest method [19].

**Table 1: Needed time and solvents for the preparation of core-shell magnetic mesoporous silica in recent works.**

Methodology to remove the surfactant	Type of solvent	Required solvent (mL)	Required time (h)	Reference
Solvent extraction	Ethanol	180	36	[22]
Solvent extraction	Ethanol	180	36	[23]
Calcination at high temperature	-	-	6	[24]
Solvent extraction	Acetone	250	48	[25]
Solvent extraction	Acetone	-	48	[1]
Calcination at high temperature	-	-	6	[26]
Solvent extraction	Acetone	300	144	[17]

Interestingly, the solvent used in the extraction process can be also sustainably recovered through membranes which is so useful from an environment and economic point of view [20, 21].

Therefore, preparing material in a short time and via less amount of solvent can be highly beneficial from an economic and environmental perspective. It can pave the way to produce this kind of material on an industrial scale, effectively. Therefore, the main purpose of this paper is to offer a specific solvent for the solvent extraction which needs the lower required time and solvent than those reported in the latest works (see Table 1).

## EXPERIMENTAL SECTION

### Material used

Ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), ferrous chloride ( $\text{FeCl}_2 \cdot 7\text{H}_2\text{O}$ ), tetraethylorthosilicate (TEOS),  $\text{NH}_4\text{OH}$  (28% wt.), cetyltrimethylammonium bromide (CTAB), absolute alcohol (EtOH) and toluene from Merck company. All chemical reagents and solvents were of analytical grades and used without further purification.

### Methods

#### Preparation of $\text{Fe}_3\text{O}_4$

The chemical co-precipitation method was employed to synthesize the Magnetic NanoParticles (MNPs) with some modification [27] using  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (molar ratio, 1:2) in deionized water. At 75 °C, about 75 mL of  $\text{NH}_4\text{OH}$  solution was added under vigorous stirring (1000 rpm) in the presence of nitrogen. The resulted in dark-colored precipitate turned black by heating at 80 °C for 20 min and 70 °C for 5 h and pH solution  $\pm 12$ . The precipitation of  $\text{Fe}_3\text{O}_4$  was completed at pH between 8 and 14. Then the particles

were washed several times with water and aqueous ethanol (volume ratio 2:1). At last, the obtained MNPs were dried in a vacuum oven overnight at 60 °C.

#### Synthesis of $\text{Fe}_3\text{O}_4@ \text{SiO}_2$

The interlayer of  $\text{SiO}_2$  was prepared through a simple sol-gel process [28]. Briefly, 0.1 g  $\text{Fe}_3\text{O}_4$  microspheres were homogeneously dispersed in a mixture of ethanol (30 mL) and deionized water (10 mL) under ultrasonic vibration for 10 min, then the concentrated ammonia aqueous solution (2 mL, 28 wt%) was added to this solution with the help of ultra-sonication for 10 min under the frequency of 40 kHz and power of 150 W, and followed by the addition of tetraethoxysilane dropwise until the total amount of TEOS reached 0.05 mL. After stirring for 8 h, at room temperature and mild stirring (500 rpm), the product was collected with the help of a magnet and washed with ethanol and water (volume ratio 2:1) for 3 times, and then vacuum dried at 80 °C for 12 h.

#### Synthesis of $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{meso-SiO}_2$ microspheres

The core-shell magnetic mesoporous  $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{meso-SiO}_2$  was prepared by adopting the mentioned method in the literature [29] with some modification. The suspension of the as-prepared core-shell magnetic  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  nanosphere (0.1 g) was diluted by a mixture of absolute alcohol (30 mL) and deionized water (20 mL) with the aid of sonication for 15 min. Subsequently, 1.5 mL of  $\text{NH}_4\text{OH}$  (28 wt%, A. R.), 0.4 g CTAB and 0.4 mL TEOS were added and the suspension was stirred (500 rpm) at room temperature for 7 h. Finally, the resultant product was collected by an external magnetic field and washed several times with ethanol and deionized water (volume ratio 1:2).



**Fig. 1:** Experimental set-up for the preparation of magnetic core-mesoporous shell.

The product was dried in a vacuum oven for 9 h. Finally, the obtained sample was re-dispersed in 100 ml ethanol solution containing 2%  $\text{NH}_4\text{NO}_3$  and stirred at 70 °C for 15 min to remove the surfactant. The resulted powder was washed with water and dried overnight at 60 °C. The synthesis reactor can be seen in Fig.1. It consists of a three-neck glass reactor with 250 ml capacity which is equipped with a thermometer, inlet pipe of nitrogen gas and a magnetic stirrer and this reactor should be placed in an oil, bath to achieve constant temperature during sample preparation.

### Characterization

The size and morphology of the core-shell magnetic mesoporous structure were characterized by field emission scanning electron microscope (FESEM, Hitachi 1460, Japan). The surface modification and pectinase binding were confirmed by FT-IR spectroscopy (Perkin Elmer spectrum) using the potassium bromide (KBr) pellet method in the range of 400–2400  $\text{cm}^{-1}$ . The crystalline structures of the sample would be assessed by XRD analysis on a Bruker AXS D8-Advance X-ray diffractometer with  $\text{CuK}\alpha$  radiation. Magnetization measurement was performed on a Superconducting Quantum Interference Device (SQUID) magnetometer at 300 K (VSM; Kavir Magnet Company, Iran). The average particle size was determined by Mettler-Toledo thermal instrument. The specific surface area and pore diameter of the magnetic microspheres was measured at 77 K on a PHS-1020 (PHS, China) analyzer by the

Brunauer–Emmett–Teller (BET) method. The ThermoGravimetric Analysis (TGA) curve was conducted using a Perkin–Elmer Pyris 1 TGA instrument (Perkin–Elmer, USA) from 25 °C to 700 °C under  $\text{N}_2$  at a heating rate of 15 °C /min.

## RESULTS AND DISCUSSIONS

### Characterization of magnetic mesoporous silica

#### Morphology analysis

Morphology of the  $\text{Fe}_3\text{O}_4$  @ $\text{SiO}_2$  and  $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$ @*meso*- $\text{SiO}_2$  samples were investigated by FE-SEM. The spherical morphology and solid  $\text{Fe}_3\text{O}_4$  @ $\text{SiO}_2$  nanoparticles with an average diameter of 34 nm were illustrated in Fig. 2a. Interestingly, the magnetic core-silica shell nanoparticles seem to be aggregated due to dipole-dipole interaction, but as it is shown in Fig. 2b,  $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$ @*meso*- $\text{SiO}_2$  looks good dispersal due to the repulsion of MNPs. It should also be mentioned that the proposed extraction process has not any adverse effect on the  $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$  and the morphological properties of this structure was kept unchanged after adopting this methodology. Furthermore, the mean diameter of  $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$ @*meso*- $\text{SiO}_2$  was reported to be about 684 nm.

#### Particle size analyzer

The PSA images of  $\text{Fe}_3\text{O}_4$  @ $\text{SiO}_2$  and  $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$ @*meso*- $\text{SiO}_2$  samples are shown in Fig. 3. It is seen that  $\text{Fe}_3\text{O}_4$  @ $\text{SiO}_2$  and  $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$  @*meso*- $\text{SiO}_2$  have a narrow size distribution and their mean diameters were obtained to be 36.7, 682 nm, which are in good agreement with the FESEM results.

#### FT-IR spectra

The FT-IR spectra of  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$ , and  $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$ @*meso*- $\text{SiO}_2$  are given in Fig. 4. For  $\text{Fe}_3\text{O}_4$  the peak at 578  $\text{cm}^{-1}$  corresponds to FeO stretching vibration and it can be proved that MNP has been successfully synthesized. The new peaks at 1087 and 786  $\text{cm}^{-1}$  can be ascribed to the antisymmetric and symmetric stretching vibration of Si-O-Si bond in oxygen-silica tetrahedron, respectively. It can confirm that  $\text{SiO}_2$  is successfully coated on the surface of the superparamagnetic  $\text{Fe}_3\text{O}_4$  nanoparticle [30]. The absorption peak of 3448  $\text{cm}^{-1}$  corresponding to the stretching vibration of OH group of water respectively [31].

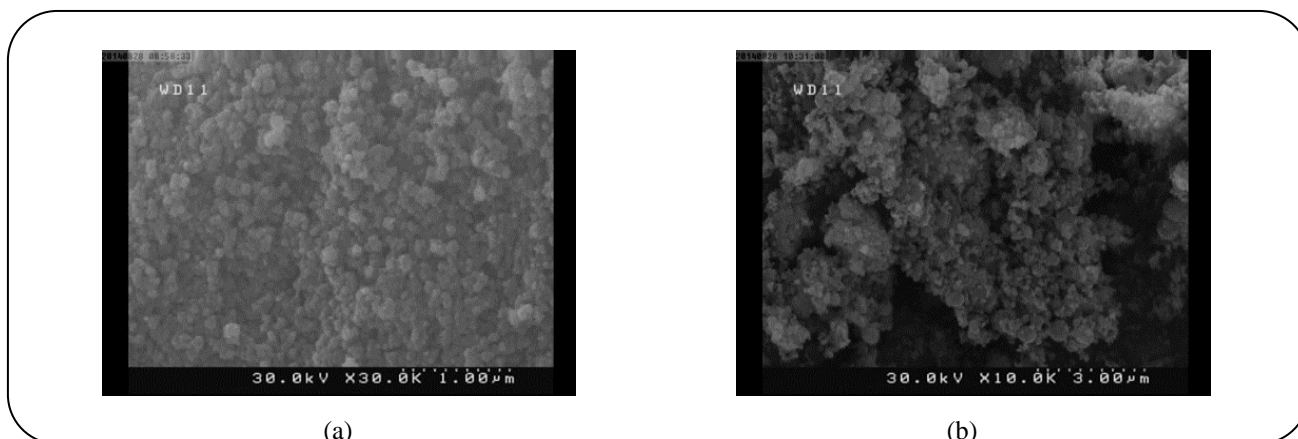


Fig. 2: FE-SEM images of (a)  $Fe_3O_4@SiO_2$  and (b)  $Fe_3O_4@SiO_2@meso-SiO_2$ .

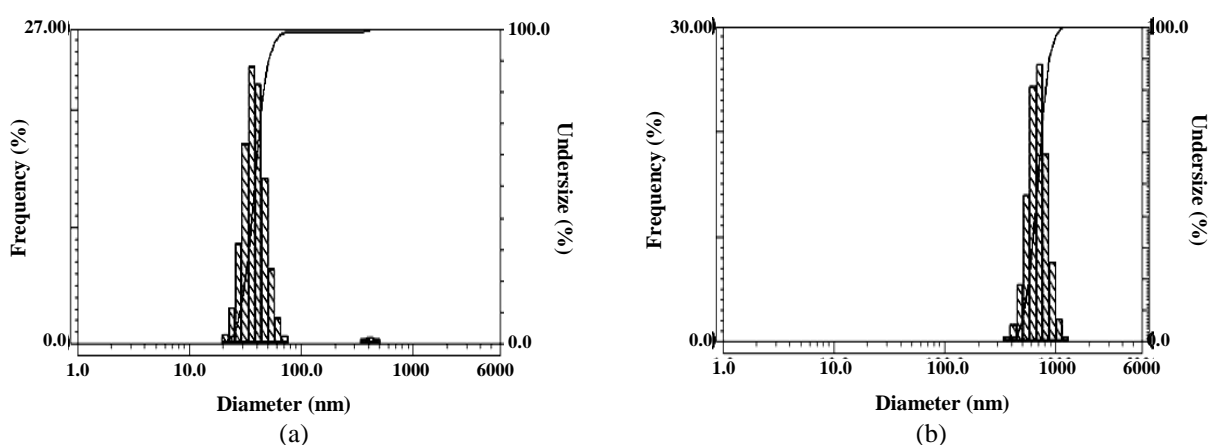


Fig. 3: PSA images of the  $Fe_3O_4@SiO_2$  (a) and  $Fe_3O_4@SiO_2@meso-SiO_2$  (b).

### XRD

The XRD patterns of  $Fe_3O_4$  and  $Fe_3O_4@SiO_2@meso-SiO_2$  samples shown in Fig. 5. The characteristic diffraction peaks at  $30.1^\circ$ ,  $35.4^\circ$ ,  $43.1^\circ$ ,  $53.4^\circ$ ,  $56.9^\circ$ , and  $62.5^\circ$  could be the index to the cubic structure of  $Fe_3O_4$  powder diffraction data, which indicates that the crystalline structure of  $Fe_3O_4$  was pure and there was no phase change in MNPs before and after surface coating and modification [32].

### TGA analysis

TGA analyses of the  $Fe_3O_4@SiO_2@meso-SiO_2$  were used to determine the heat endurance of the sample (Fig. 6).  $Fe_3O_4@SiO_2@meso-SiO_2$  microsphere indicated three distinct weight loss stages: the first region is characterized by rather a small weight loss below  $180^\circ C$  as a result of the evaporation of surface adsorbed alcohol and water. In the second region, a large weight loss in the range of  $200-600^\circ C$  can be attributed to the decomposition of organic substances. Whereas

in the third region, a minor weight loss above  $550^\circ C$  is associated with the release of structured water [8].

### Vibrating sample magnetization

The hysteresis loop for  $Fe_3O_4@SiO_2@meso-SiO_2$  microspheres is shown in Fig. 7. The magnetic saturation value of this sample is  $24 \text{ emu/g}$ . Due to the high magnetization, the  $Fe_3O_4@SiO_2@meso-SiO_2$  microspheres show a fast response to the external magnet and can be separated from the dispersion within the 50s (Fig. 8), which makes them favorable in diverse applications and its suitability for magnetic separation and targeting [33]. These particles can be also redispersed quickly with a slight shake when the magnetic field is removed.

### $N_2$ adsorption-desorption isotherm

$N_2$  adsorption-desorption isotherm of  $Fe_3O_4@SiO_2@meso-SiO_2$  microsphere is presented

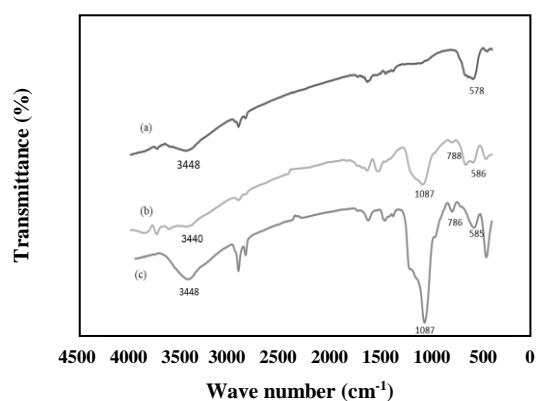


Fig. 4: FT-IR spectra of  $Fe_3O_4$  (a),  $Fe_3O_4@SiO_2$  (b) and  $Fe_3O_4@SiO_2@meso-SiO_2$  (c).

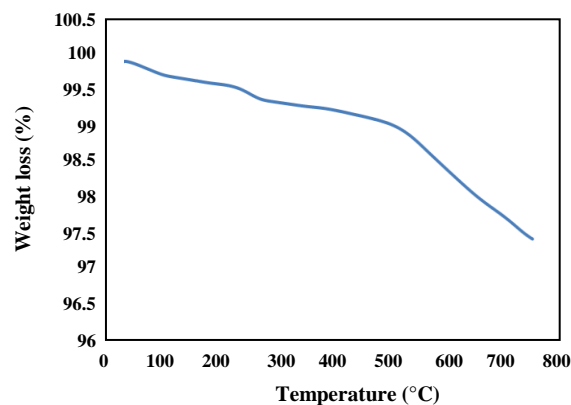


Fig. 6: TGA curve of  $Fe_3O_4@SiO_2@meso-SiO_2$  microsphere.

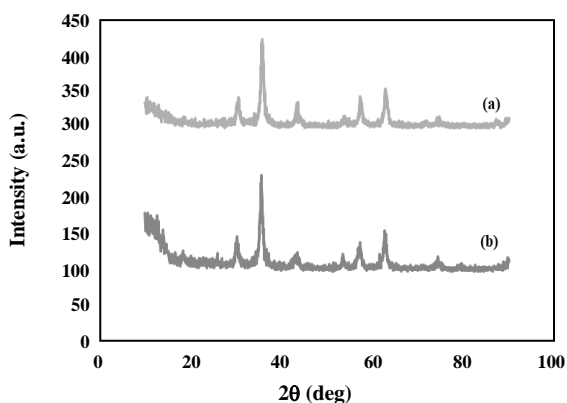


Fig. 5: XRD patterns of  $Fe_3O_4$  NPs (a) and  $Fe_3O_4@SiO_2@meso-SiO_2$  (b).

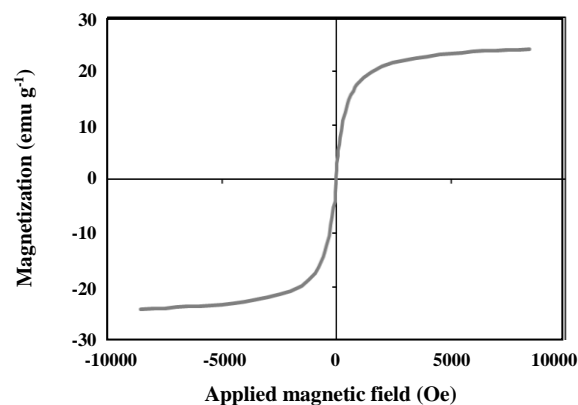


Fig. 7: Magnetization curve of  $Fe_3O_4@SiO_2@meso-SiO_2$  at room temperature.

in Fig.9 (a). This test also proves that  $Fe_3O_4@SiO_2@meso-SiO_2$  microsphere has a porous framework. The isotherm of  $Fe_3O_4@SiO_2@meso-SiO_2$  microsphere is identified as type IV curves with H1-type hysteresis loops, which reveals the formation of well-uniform mesoporous structure. The BET surface area and BJH pore volume of  $Fe_3O_4@SiO_2@meso-SiO_2$  are calculated to be  $230 \text{ m}^2/\text{g}$  and  $0.547 \text{ cm}^3/\text{g}$ , respectively. The average mesopore size of  $Fe_3O_4@SiO_2@meso-SiO_2$  is also reported to be 2.85 nm (Fig.9 (b)).

## CONCLUSION

In this study, magnetic nanoparticle coated with a dense nonporous silica layer and a mesoporous silica shell was prepared successfully by applying the facile, economic and prompt methodology. The required time and solvent for extraction of surfactant have decreased

significantly which can offer a unique synthesis approach for the large-scale production. The as-prepared core-shell structured material was characterized by FT-IR spectroscopy, XRD analysis, electron microscopy, TGA and nitrogen adsorption and desorption, which confirmed the successful formation of core-shell-shell structure. The resulted materials possessing uniform core-shell structure ( $\sim 648 \text{ nm}$ ), (BET) surface area of  $230 \text{ m}^2/\text{g}$ , the pore volume of  $0.547 \text{ cm}^3/\text{g}$  and well preserved structural stability. This multifunctional structure also shows good sustained properties and possesses a magnetization saturation of  $24 \text{ emu/g}$ . The prepared particles have great potential applications in various processes such as drug delivery, water purification, and catalysis. Therefore by adopting the proposed methodology, this kind of material can be easily provided on a large scale.



Fig. 8: Separation of  $Fe_3O_4@SiO_2@meso-SiO_2$  from water by a magnetic field

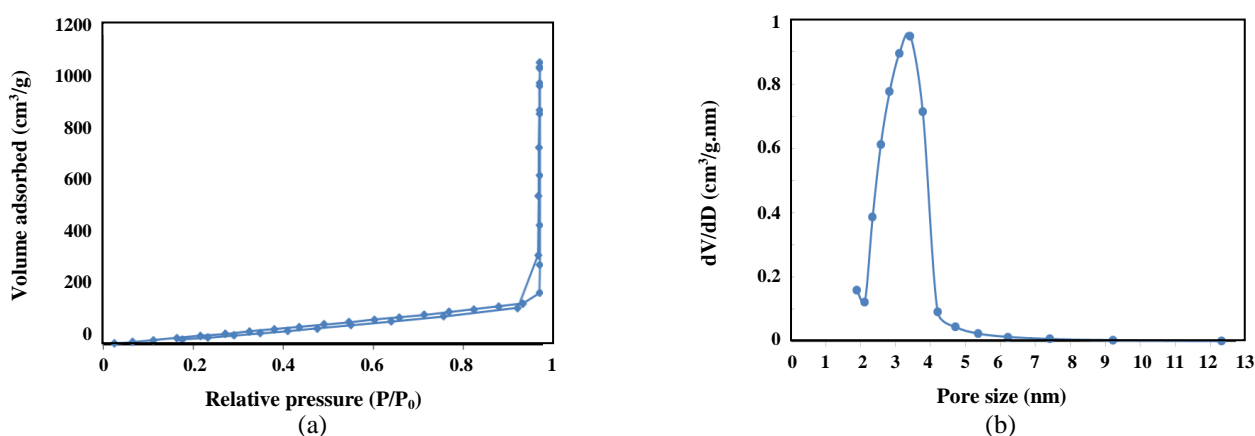


Fig. 9: (a) Nitrogen adsorption-desorption of  $Fe_3O_4@SiO_2@meso-SiO_2$ , (b) Pore size distribution of  $Fe_3O_4@SiO_2@meso-SiO_2$ .

### Acknowledgment

The authors are grateful to Dr. Ghodrattollah Absalan, Professor Masoumi Laboratory, Department of Chemistry, College of Science, Shiraz University, for his great assistance.

Received : Jul. 5, 2018 ; Accepted : Aug. 28, 2018

### REFERENCES

- [1] Wang W., Liu S., Li C., Wang Y., Yan C. Dual-Target Recognition Sandwich Assay Based on Core-Shell Magnetic Mesoporous Silica Nanoparticles for Sensitive Detection of Breast Cancer Cells, *Talanta.*, **182**: 306-313 (2018).
- [2] Lin F., Wang K., Tang Y., Lai J., Lou M., Huang M., Guo S. Enhanced Bifunctional Fuel Cell Catalysis via Pd/PtCu Core/Shell Nanoplates, *Chemical Communications*, **54**(11): 1315-1318 (2018).
- [3] Zhang X., Wang J., Preparation of Carbon Coated  $Fe_3O_4$  Nanoparticles for Magnetic Separation of Uranium, *Solid State Sciences.* **75**: 14-20 (2018).
- [4] Nasrallah G.K., Zhang Y., Zagho M.M., Ismail H.M., Al-Khalaf A A., Prieto R M., Albinali K E., Elzatahry A A., Deng Y., A Systematic Investigation of the Bio-Toxicity of Core-Shell Magnetic Mesoporous Silica Microspheres Using Zebrafish Model, *Microporous and Mesoporous Materials.* **265**: 195-201 (2018).
- [5] Mohammadi Ziarani G., Saidian F., Gholamzadeh P., Badiie A., Abolhasani Soorki A. Green Synthesis of Pyrazol-chromeno[2,3-d]pyrimidinones Using SBA-Pr-SO<sub>3</sub>H as an Efficient Nanocatalyst, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE).* **36**(6): 39-48 (2017).

- [6] Dolatyari L., Yaftian M. R., Rostamnia S. Th(IV)/U(VI) Sorption on Modified SBA-15 Mesoporous Materials in Fixed-Bed Column, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **36**(6): 115-125 (2017).
- [7] Ahmadi S. H., Davar P., Manbohi A. Adsorptive Removal of Reactive Orange 122 from Aqueous Solutions by Ionic Liquid Coated Fe<sub>3</sub>O<sub>4</sub> Magnetic Nanoparticles as an Efficient Adsorbent, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **35**(1): 63-73 (2016).
8. Wang J., Zheng S., Shao Y., Liu J., Xu Z., Zhu D. Amino-Functionalized Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub> Core-Shell Magnetic Nanomaterial as a Novel Adsorbent for Aqueous Heavy Metals Removal, *Journal of Colloid and Interface Science*, **349**(1): 293-299 (2010).
- [9] Min B., Wenzhong M., Study on Core-Shell-Shell Structured Nanoparticles with Magnetic and Luminescent Features: Construction, Characterization and Oxygen-Sensing Behavior, *Journal of Luminescence*, **141**: 80-86 (2013).
- [10] Yang P., Quan Z., Hou Z., Li C., Kang X., Cheng Z., Lin J., A Magnetic, Luminescent and Mesoporous Core-Shell Structured Composite Material as Drug Carrier, *Biomaterials*, **30**(27): 4786-4795 (2009).
- [11] Yuan Q., Li N., Chi Y., Geng W., Yan W., Zhao Y., Li X., Dong B., Effect of Large Pore Size of Multifunctional Mesoporous Microsphere on Removal of Heavy Metal Ions, *Journal of Hazardous Materials*, **254**: 157-165 (2013).
- [12] Adamski J., Qadir M. I., Serna J. P., Bernardi F., Baptista D. L., Salles B. R., Novak M. A., Machado G., Dupont J. Core-Shell Fe-Pt Nanoparticles in Ionic Liquids: Magnetic and Catalytic Properties, *The Journal of Physical Chemistry C*, **122**(8): 4641-4650 (2018).
- [13] Sağ Y. Biosorption of Heavy Metals by Fungal Biomass and Modeling of Fungal Biosorption: A Review, *Separation & Purification Reviews*, **30**(1): 1-48 (2001).
- [14] Liu H., Ji S., Yang H., Zhang H., Tang M. Ultrasonic-Assisted Ultra-Rapid Synthesis of Monodisperse Meso-SiO<sub>2</sub>@ Fe<sub>3</sub>O<sub>4</sub> Microspheres with Enhanced Mesoporous Structure, *Ultrasonics Sonochemistry*, **21**(2): 505-512 (2014).
- [15] Kheshti Z., Hassanajili S. Surfactant Removal from Mesoporous Silica Shell of Core-Shell Magnetic Microspheres by Modified Supercritical CO<sub>2</sub>, *International Journal of Nanoscience and Nanotechnology*, **13**(2): 119-127 (2017).
- [16] Kupai J., Razali M., Buyuktiryaki S., Kecili R., Szekely G. Long-Term Stability and Reusability of Molecularly Imprinted Polymers, *Polymer chemistry*, **8**(4): 666-673 (2017).
- [17] Yuan Q., Chi Y., Yu N., Zhao Y., Yan W., Li X., Dong B., Amino-functionalized Magnetic Mesoporous Microspheres with Good Adsorption properties, *Materials Research Bulletin*, **49**: 279-284 (2014).
- [18] Buxton A., Livingston A. G., Pistikopoulos E.N., Optimal Design of Solvent Blends for Environmental Impact Minimization, *AIChE Journal*, **45**(4): 817-843 (1999).
- [19] Slater C.S., Savelski M.J., Ruiz-Felix M.N., Life Cycle Analysis of Solvent Reduction in Pharmaceutical Synthesis Using Continuous Adsorption for Palladium Removal, *Journal of Environmental Science and Health, Part A*, **48**(13): 1602-1608 (2013).
- [20] Schaeperstoens M., Didaskalou C., Kim J. F., Livingston A. G., Szekely G., Solvent Recycle with Imperfect Membranes: A Semi-Continuous Workaround for Diafiltration, *Journal of Membrane Science*, **514**: 646-658 (2016).
- [21] Didaskalou C., Buyuktiryaki S., Kecili R., Fonte C. P., Szekely G., Valorisation of Agricultural Waste with an Adsorption/Nanofiltration Hybrid Process: from Materials to Sustainable Process Design, *Green Chemistry*, **19**(13): 3116-3125 (2017).
- [22] Yue Q., Zhang Y., Jiang Y., Li J., Zhang H., Yu C., Elzatahry A. A., Alghamdi A., Deng Y., Zhao D. Nanoengineering of Core-Shell Magnetic Mesoporous Microspheres with Tunable Surface Roughness, *Journal of the American Chemical Society*, **139**(13): 4954-4961 (2017).
- [23] Yue Q., Li J., Zhang Y., Cheng X., Chen X., Pan P., Su J., Elzatahry A. A., Alghamdi A., Deng Y. Plasmolysis-Inspired Nanoengineering of Functional Yolk-Shell Microspheres with Magnetic Core and Mesoporous Silica Shell, *Journal of the American Chemical Society*, **139**(43): 15486-15493 (2017).



- [24] Tai Z., Isaacs M.A., Parlett C M., Lee A.F., Wilson K., High Activity Magnetic Core-Mesoporous Shell Sulfonic Acid Silica Nanoparticles for Carboxylic Acid Esterification, *Catalysis Communications*. **92**: 56-60 (2017).
- [25] Gao J., Kong W., Zhou L., He Y., Ma L., Wang Y., Yin L., Jiang Y. Monodisperse Core-Shell Magnetic Organosilica Nanoflowers with Radial Wrinkle for Lipase Immobilization, *Chemical Engineering Journal*. **309**: 70-79 (2017).
- [26] Hou S., Li X., Wang H., Wang M., Zhang Y., Chi Y., Zhao Z., Synthesis of Core-Shell Structured Magnetic Mesoporous Silica Microspheres with Accessible Carboxyl Functionalized Surfaces and Radially Oriented Large Mesopores as Adsorbents for the Removal of Heavy Metal Ions, *RSC Advances*. **7**(82): 51993-52000 (2017).
- [27] Koneracká M., Kopčanský P., Antalík M., Timko M., Ramchand C.N., Lobo D., Mehta R.V., Upadhyay R.V., Immobilization of Proteins and Enzymes to Fine Magnetic Particles, *Journal of Magnetism and Magnetic Materials*. **201**(1-3): 427-430 (1999).
- [28] Luo B., Song X-J., Zhang F., Xia A., Yang W-L., Hu J-H., Wang C-C. Multi-Functional Thermosensitive Composite Microspheres with High Magnetic Susceptibility Based on Magnetite Colloidal Nanoparticle Clusters, *Langmuir*, **26**(3): 1674-1679 (2010).
- [29] Deng Y., Qi D., Deng C., Zhang X., Zhao D. Superparamagnetic High-Magnetization Microspheres with an Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> Core and Perpendicularly Aligned Mesoporous SiO<sub>2</sub> Shell for Removal of Microcystins, *Journal of the American Chemical Society*, **130**(1): 28-29 (2008).
- [30] Ou Q., Zhou L., Zhao S., Geng H., Hao J., Xu Y., Chen H., Chen X. Self-Templated Synthesis of Bifunctional Fe<sub>3</sub>O<sub>4</sub>@MgSiO<sub>3</sub> Magnetic Sub-Microspheres for Toxic Metal Ions Removal, *Chemical Engineering Journal*, **180**: 121-127 (2012).
- [31] Zhao L., Chi Y., Yuan Q., Li N., Yan W., Li X. Phosphotungstic Acid Anchored to Amino-Functionalized Core-Shell Magnetic Mesoporous Silica Microspheres: A Magnetically Recoverable Nanocomposite with Enhanced Photocatalytic Activity, *Journal of Colloid and Interface Science*, **390**(1): 70-77 (2013).
- [32] Ren Y., Abbood H.A., He F., Peng H., Huang K., Magnetic EDTA-Modified Chitosan/SiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> Adsorbent: Preparation, Characterization, and Application in Heavy Metal Adsorption, *Chemical Engineering Journal*, **226**: 300-311 (2013).
- [33] Wang X., Wang L., He X., Zhang Y., Chen L. A Molecularly Imprinted Polymer-Coated Nanocomposite of Magnetic Nanoparticles for Estrone Recognition, *Talanta*., **78**(2): 327-332 (2009).