Encapsulation iron magnetic particles onto molecular sieve silica SBA-15 by the simple arc discharge method for ibuprofen adsorption

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Abstract. In this paper, molecular sieve silica SBA-15-encapsulated iron nanoparticles (Fe/SBA-15) have been synthesized by arc discharge method. Molecular sieve silica SBA-15 prepared by self-assembly route using block copolymer P123 as structure directing agent and tetraethoxysilane as the source of silica under acidic condition. The transformation of texture dan structure of Fe/SBA-15 sample after heat-treatment at 900 °C was investigated by X-ray diffraction, scanning electron microscopy and nitrogen adsorption-desorption techniques, FTIR and VSM. The result shows that magnetic properties in Fe/SBA-15 sample have been observed by VSM as the impact of encapsulation process. The adsorption performance using Fe/SBA-15 sample was investigated by ibuprofen molecule as the drug model. The ibuprofen adsorption trend using reach the optimum equilibrium condition at 60 min which was closely related to the mesoporous structure of the materials. The most important of all, magnetic character of Fe/SBA-15 sample make detection of ibuprofen easier than mesoporous silica without magnetic character. It is can make Fe/SBA-15 sample be the new generation carrier material in drug delivery system in the future.

1. Introduction
Iron nanomaterial have attracted attention due to the wide application such as protective shells, resonance imaging, separating of biocell, water purification adsorption, catalytic material and drug delivery system [1]. The major requirement of all application is high stability material. The supporting material act as iron coating which limiting iron aggregation process. The most supporting material such us silica, carbon, and metal. Silica have been developed by previous researcher as iron protection. However, the most kind of silica including SiO2 and polymer silica, have a number of micropore without specific structure that have a bad impact on stability and loading capacity of material [2]. The mesoporous silica is the best candidate for iron coating due to the unique character such as large pore diameter, ordered honeycomb structure, high stability on chemical enviroment and high surface area. Iron Coating have been prepared by previous research via combustion method, hydrothermal reaction detonation synthesis, chemical vapour condensation, electron beam irradiation, laser ablation, arc discharge, co-carbonization, and thermal decomposition [3-5]. From all of these method, arc discharge is the most effective method because can produce not only uniform iron coating but also act as carrier material stabilizer in one pot process [6-7].
The aquatic environment was filled by pharmaceutical drug as long pollutant effect for human. One of the most dangerous pharmaceutical product is ibuprofen as non-steroidal anti-inflammatory drug due to the large volume production every year which is have bad impact in disposal release [8]. Several methods to treat ibuprofen such as as sonicing, ozonating, heating and adsorbing process. Adsorption is the favourable method due to the low cost and high performance for ibuprofen degradation [9-11]. However, ibuprofen adsorption performance using microporous material needs to be improved by using mesoporous material.

In the best of our knowledge, ibuprofen adsorption using iron particle with mesoporous silica as supporting material never investigated before. In this paper, a modified mesoporous silica encapsulating iron particle by arc-discharge has been investigated. Encapsulation iron magnetic particles onto molecular sieve silica SBA-15 (Fe/SBA-15) were obtained using mesoporous silica as carrier material. The character of iron magnetic in SBA-15 were studied by XRD, FTIR, VSM and SEM. We have also studied the adsorption performance of Fe/SBA-15 using ibuprofen as molecule model.

2. Experimental Methods

2.1 Material

All reagents and solvents were of analytical grade including tetraethylorthosilicate (TEOS, Aldrich) ibuprofen, ethanol, hydrochloric acid and co-block polymer Pluronic P123 (Aldrich).

2.2 Synthesis Mesoporous Silica SBA-15

The mesoporous silica sample synthesized based on previous procedure with small part modification. The pluronic p123 was mixed in hydrochloric acid solution to obtain P123 solution. The tetraethyl orthosilicate drop slowly into P123 solution under stirring 150 rpm for two night. The ratio of pluronic p123: tetraethyl orthosilicate: hydrochloric acid solution is 0.2:1:6 (w/w/v). The mixture was transferred into steel container and aged at 373 K for a night as hydrothermal step. The white composite separating with vacuum apparatus, washing with distilled water and drying in oven at 373 K for a night. Then, for removing p123 part, the grey-white powder was calcined at 873 K in air for a night. The white resulting sample labelled as SBA-15

2.3 Synthesis silica SBA-15-encapsulated iron nanoparticles (Fe/SBA-15) by arc discharge method.

The fabrication of mesoporous silica SBA-15 modified with iron oxide material was performed using the submerged arc discharge method. This method used two electrodes as the cathode and anode. The anode was a carbon electrode filled with a mix of graphite carbon, iron oxide (synthesized via electrolysis) and silica SBA-15 binder with a mass ratio composition of 3:1:1. The mix was sonicated for 480 seconds and then moulded into a rod with dimension of Ø 10 mm x 50 mm. The electrode was then heated in furnace at 180°C for 6 hours. The cathode used was a graphite electrode that had a sharp pencil tip. The cathode and anode distance were set with a very close gap to procure stepping electrons. Both the cathode and anode were set up in a 600-mL glass beaker containing 300 mL of 50% ethanol. A current of 10 A (13.75 V) was passed through electrodes. After arcing, the nanoparticles were collected, and the remaining ethanol was evaporated and dried.

2.4 Characterization

The nanoparticles obtained from the arc discharge were characterized using an X-Ray Diffractometer (XRD-6000, Shimadzu) (Cu; 40.0 kV; 30.0 mA) to analyse the crystallinity and elements contained in the material. The magnetization of the material was measured using a vibrating sample magnetometer (VSM OXFORD type 1.2H). The change of band gap energy was determined using a diffuse reflectance spectrophotometer-ultra violet (UV 1700 PHARMASPEC). The structure, shape and size of the nanoparticle were studied using a transmission electron microscope (JEOL JEM-1400).
2.5 Ibuprofen Adsorption-Release

A 1 g of Fe/SBA-15 silica was suspended in an ibuprofen solution (66 mg/ml, at room temperature) in n-hexane and magnetically stirred for 24 h. Then it was filtered off, washed with small amount of pure n-hexane and dried for a night at room temperature. Release was carried out with SBF solution. Load ibuprofen at FE/SBA-15 mixed with SBD then at selected intervals the ibuprofen concentration was spectrophotometrically measured at 265 nm. The percentage of ibuprofen released was calculated from the absorbance readings at each time point.

3. Results and Discussion

Fig 1 showed the XRD pattern of the molecular sieve silica SBA-15-encapsulated iron oxide (Fe/SBA-15) was characterized by wide angle XRD in range 2θ 10-80°. The Fe/SBA-15 synthesized by arc discharge via electrolysis and calcined at 250°C. Three peaks in small angle was resulted by XRD then indexed as (100), (110) and (200) at 2θ = 25.5°, 33.5° and 55.3°. The indexing analysis in this research have good agreement with previous report [12]. These peak is the character of the honeycomb structure of Fe-/SBA-15 which has the unique hexagonally nanopipe with space group p6mm. Not only show the ordered structure of Fe-/SBA-15 but also indicate the stability of SBA-15 after arc discharge process to encapsulating iron particle. Based on the Joint Committee on Powder Diffraction Standards (JCPDS), the wide angle X-ray diffraction (XRD) pattern of the Fe/SBA-15 shown in Fig. 1 showed the character of magnetite (Fe3O4) at 2θ = 32,5296°; 35,9186°; 43,6172°; 53,9676°; 57,5602° and 64,6690° which indexed as (220), (311), (400), (422), (511), and (440), respectively. Sum of all, the diffraktigram of Fe/SBA-15 represent the successfully encapsulating iron particle without any significant destruction structure. Figure 2 showed the isotherms of nitrogen adsorption and desorption on mesoporous silicas SBA-15 before and after arc discharge process. Both of isotherm curve of SBA-15 and Fe/SBA-15 showed a character IV isotherm with a H1 hysteresis loop which is mesoporous material type. The narrow-pore size distribution of SBA-15 indicated by full standing posisition capillary condensation step at relative pressure 0.4-0.8. For comparing study, Fe/SBA-15 showed the oblique of capillary condensation at the same relative pressure which was indicating the small part of material destruction. It is can logically accepted by remembering that desorption branch of the Fe/SBA-15 isotherm is shifted to lower pressures due to the presence of iron particle after arc-discharge step. The open nanopipe of mesoporous SBA-15 was covered by iron during impregnation which is give a smooth effect on pore swelling. In contrast to a naked SBA-15, the arc-discharge of SBA-15 with a slightly iron precursor solution decrease the uptake of nitrogen but does not result in any significant changes in the shape of the nitrogen isotherm. In the other word, iron particle encapsulation by SBA-15 could be decreasing the surface area by iron calcination but over all not change the shape of SBA-15 pore.

![Figure 1](image_url)
Figure 2. Nitrogen adsorption-desorption of SBA-15 and Fe-SBA-15 after arc discharge process

Figure 3. Spectra of Fe-SBA-15 after arc discharge process

Figure 4. Hysteresis loop of Fe/SBA-15 material after arc discharge.

Figure 3 showed the spectra of Fe-SBA-15 after arc discharge process. Generally, the essential peak can be seen at 3600 - 3745 cm\(^{-1}\) as silanol functional group [13-14]. The resulting spectra showed the small peak of the Fe-O bond at 460 - 555 cm\(^{-1}\) [15] indicating that the iron particle successfully
embedded onto SBA-15. The peak at 1000-1680 cm$^{-1}$ represent vibrating of stretching Si-O-Si. The bonding of Si-OH also showed by the peak at 800 cm$^{-1}$ which is demonstrated that silica of SBA-15 still stable after iron particle encapsulation via arc discharge route. For small conclusion, functional group from spectra FTIR trend show that arc discharge could helping iron coating route without significant element disruption.

Figure 4 shows the magnetic properties curve of Fe/SBA-15 by using the VSM which is describe the irregularity of spin magnetization in the range -8 to 8 emu at applied field (H(T)) range from -15 to +15 Tesla. The magnetic hysteresis loops shows that Fe/SBA-15 have strong magnetism with insignificant remanence which is indicate the magnetic character as nature in Fe particle of the SBA-15 samples. The magnetic sample exhibited magnetic behavior at room temperature with no coercivity and remanence. The incorporating process of iron particle onto SBA-15 can be seen at the strong peak in Figure 4 which represent that arc discharge technique was succesfully help the iron encapsulated by silica SBA-15. These phenomenon not only was caused by iron ion and oxygen interaction but also high affinity between them among atom coordination in silica surface. Sum of all, the magnetic character of Fe/SBA-15 was significant constructed among the whole material surface. Moreover, the covering iron onto SBA-15 surface can be seen clearly via scanning electron microscopy (SEM) investigation.

![Figure 5](image1.png)

**Figure 5.** The Image of Fe/SBA-15 syntesized via arc-discharge by scanning electron microscopy (SEM)

![Figure 6](image2.png)

**Figure 6.** Ibuprofen % release using mesoporous silica Fe/SBA-15
Figure 5 shows the scanning electron microscopy (SEM) imaging of encapsulation of iron oxide onto silica SBA-15 sample. As shown in Figure 5, the mesoporous silica clearly observed as rigid stick-like which is had a length in the range 5-10µm and a diameter in the range 0.5-1.0 µm. We can be seen that nothing particle image or coated layer in silica SBA-15 surface. In the other word, the iron particles distribute completely in a whole of mesoporous without any significant iron particle aggregation. In addition, from all of characterization result we can conclude that mesoporous silica SBA-15 still stable after iron encapsulation by arc-discharge step which was probably affected by original character of SBS-15 and arc discharge method for iron coating preparation.

Figure 6 shows the percentage of ibuprofen released using mesoporous silica Fe/SBA-15 as adsorbent. From Figure 6 we can see that after 10 min, the ibuprofen release about 27%. The increasing ibuprofen release was obtained at the time in the range 20-30 min which demonstrated that the mesopore part of silica Fe/SBA-15 were remove the ibuprofen from multilayer in deep inner surface. As we know, mesopore part in mesoporous silica SBA-15 material was the most dominant part than micropore or macropore part. So, if the mesopore part start to releasing ibuprofen, the release percentage would be increase spontaneously. However, a interesting behavior is observed for ibuprofen release after 50 min which is the release rate was slower than in the first step. This phenomenon probably the effected by anchoring effect of meso and micropore in inner and uter surface of material. Ibuprofen could be trapped in inner surface not only by the overlap position between ibuprofen each other but also by the strong interaction between silanol or iron ion and ibuprofen molecule. Moreover, magnetic character of Fe/SBA-15 sample make ibuprofen release was conducted easier than conventional way due to the less by product obtaining. For sum up, mesoporous silica Fe/SBA-15 could be the potential material in the future drug delivery system due to the unique character and the highly release capacity.

4. Conclusion
Molecular sieve silica SBA-15-encapsulated iron nanoparticles (Fe/SBA-15) have been synthesized by arc discharge method. The result show that Fe/SBA-15 material have regular mesopore type, rigid stick-like structure (0.5x10.0 µm) and high magnetic character without iron aggregation. X-ray diffraction, scanning electron microscopy and nitrogen adsorption-desorption techniques, FTIR and VSM. The result shows that magnetic properties in Fe/SBA-15 sample have been observed by VSM as the impact of encapsulation process. The adsorption performance using Fe/SBA-15 sample was investigated by release ibuprofen obeservation. Ibuprofen release reach the optimum at 60 min in about 67% which was closely related to the covering part of mesoporous structure by iron particle.

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6. References
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