

## Synthesis and characterization of rhodamine immobilized on mesoporous silica SBA-15 as metal ions chemosensor

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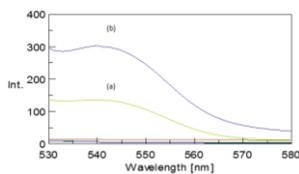
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### GRAPHICAL ABSTRACT



Fluorescence emission spectrum of (a) and (b) indicate rhodamine hydrazine and rhodamine immobilized SBA-15 respectively

### ABSTRACT

Development of chemosensor is essential for detection metals ions in the environment qualitatively and quantitatively. This study focuses on the synthesis and characterization of chemosensor based SBA-15 which is rhodamine immobilized SBA-15. SBA-15 is mesoporous silica that having excellent support for constructing fluorescent surface sensor with uniform hexagonal pore was first synthesized followed functionalize by (3-aminopropyl)triethoxysilane (APTES). Before attaching rhodamine onto SBA-15, rhodamine hydrazine was prepare and with the help of glutaraldehyde (GLU) as bridging agent, rhodamine was immobilized with SBA-15 silica. The synthesis of SBA-15 silica was successfully synthesized that prove by analysis of small angle X-ray scattering (SAXS) that showed it has uniform hexagonal pore and supported by high surface area from nitrogen adsorption-desorption analysis showed the highest BET surface area with pore size of 5.25 nm. The attachment of APTES, GLU, rhodamine hydrazine and rhodamine hydrazine onto SBA-15 were proven by using Fourier transform infrared (FTIR) spectroscopy. Fluorescence spectroscopy showed that there is fluorescence properties for rhodamine immobilized SBA-15 by the result of emission wavelength at 540nm which is same with rhodamine hydrazine emission wavelength alone. Thus, from the results it showed that the rhodamine immobilized SBA-15 has potential solid chemosensor for detecting metal ion.

*Keywords: mesoporous silica, chemosensor, rhodamine, SBA-15, metal ions.*

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## 1. INTRODUCTION

Nowadays, chemosensors have become more important because of their implications in various fields such as chemistry, biology, medicine, industries and environment studies [1]. Chemosensors is the compound that can detect analyte such as metal ion by invoking a change in one or more properties of the system by adsorption, emission, or even redox potential characteristic [1]. Chemosensors also can be defined as a supramolecule that are able to give electrical signal that has been converted from the chemical quantity [2]. Fluorescence detection considered the most effective tool for sensing applications owing to the high sensitivity, easy visualization, and short response time for detection [1]. Among all compounds used as fluorescent chemosensors, the heavy-metal complexes with phosphorescent emission are particularly attractive due to their rich chemicals structures, ease of chemical modification and high photoluminescence quantum yield [1].

Metal ions play an important role in wide range of chemical reactions including biological metabolisms as well as many other processes. Generally, metal ions can be classified into essential and nonessential ions. Nonessential heavy metals such as Cd, Hg, As and Pb, even at trace amount exposure they are vey toxic and carcinogenic. In the other side, essential metal like Cu, Fe, and Zn are required to support biological activities, these essential metals are toxic when in excess.  $Fe^{3+}$  and  $Cu^{2+}$  are the example of metal ions that should be given the highest concern of environment because they are essential trace elements in biological systems especially  $Fe^{3+}$  [3]. This is due to the  $Fe^{3+}$  ion is an essential transition metal ion in our body that involved in oxygen-transport mechanism and it also acts as a cofactor in many enzymatic electron transfer and oxidation reactions [3,4]. Besides, it also plays on important role as essential element for the formation of hemoglobin of red cells [5]. Recent research suggest that  $Fe^{3+}$  could be cause of various disorders such as could lead to anemia as well as the liver and kidney damage that known as *haemochromatosis* which might cause liver cancer, liver cirrhosis, arthritis, diabetes or heart failure[5].  $Fe^{3+}$  ion also highly related to the neurodegenerative disorders such as Parkinson's disease and Alzheimer's disease [6].

## 2. EXPERIMENTAL

### 2.1 Chemicals and Reagent

The synthesis of chemosensor rhodamine immobilized SBA-15 in this study was done by using Hydrazine hydrate, Pluronic 123, tetraethyl orthosilicate (TEOS) were purchased from Aldrich. Rhodamine 6G and glutaraldehyde were obtained from Acros Organic and Merck respectively. Distilled water was used throughout this work.

## 2.2 Synthesis of SBA-15

SBA-15 was synthesized by dissolving Pluronic P123 (4.0 g) in mixture of water (30 mL) and HCl (120 mL, 2M) solution with stirring at temperature range of 35 to 60°C. Tetraethyl orthosilicate, TEOS (8.5 g) was added to the mixture with stirring at the 35°C for 20 hours. After that, the mixture was aged at 80°C overnight in static condition. The solid product was recovered, washed with distilled water and dried at 50°C for 24 hours [7]. The mixture was soxhleted for 18 hours to remove the surfactant by mixing ethanol (200 mL) and distilled water (200 mL) as solvent. After that, the resulting solid product was dried at 50°C for 2 days.

## 2.3 Functionalization of SBA-15

The synthesized of SBA-15 was functionalized with 3-aminopropyltriethoxysilane (APTES) by mixing SBA-15 (2.0 g) and APTES (1.8 g) with toluene (30 mL) in a round bottom flask and reflux for 3 hours at 100°C. The mixture then was filter and dried at 50°C for 24 hours. To remove the unreacted APTES, soxhlet extraction was carried out for 18 hours by using toluene (400 mL) as a solvent. The functionalized SBA-15 was dried at 50°C for 24 hours.

## 2.4 Attachment of Glutaraldehyde

Prepare potassium buffer solution by mixing dipotassium phosphate,  $K_2HPO_4$  (4.335 g) and monopotassium phosphate,  $KH_2PO_4$  (3.4022 g) in volumetric flask (500 mL) and dilute with distilled water to the mark. Buffer solution was transferred into conical flask and the pH was adjusted into pH 7 by adding sodium hydroxide, NaOH (0.1 M) or phosphoric acid until the pH 7 reached. Next, functionalized SBA-15 (1.5 g) was added into the mixture of 25% glutaraldehyde solution (15mL) and pH 7 potassium phosphate buffer (150mL). The mixture was covered with aluminium foil followed by 24 hours stirring and product was filtered, washed with pH 7 potassium phosphate buffer solution followed by drying at 50°C for 2 days. The resulting solid product obtained was denoted as GLU-SBA-15.

## 2.5 Preparation of Rhodamine Hydrazine

Rhodamine 6G (2.0 g) was dissolved in methanol (40 mL) and add hydrazine hydrate (2.5 mL) then reflux until the red color disappeared and cooled it to room temperature followed by poured the solution into distilled water (800 mL) and left for 24 hours. Then, the solid product was filtered and dried in oven for 24 hours.

## 2.6 Immobilization of Rhodamine 6G on GLU-SBA-15

The resulted solids in synthesizing mesoporous SBA-15 were characterised by using Small Angle X-Ray Scattering (SAXS) for determination of the fingerprint characterization of crystalline materials and structure. The sample of SBA-15 was scanned for 100 seconds by using Bruker AXS Nanostart diffractometer with 1.5418Å nm Cu K $\alpha$  radiation operated at 35 kV and 40 mA and it was interpreted in the  $2\theta$  range within 1° to 6°. In addition, Perkin Elmer Fourier-Transform Infrared Spectroscopy (FTIR) to characterize mesoporous SBA-15 silica. The Potassium bromide (KBr) pellet method was used in FTIR and the spectrum was obtained by 16 scans with the absorption range of 4000-400  $cm^{-1}$  resolution. For the Nitrogen Adsorption Analysis was used Micromeritics 3Flex Surface characterization Analyzer was used in order to determine the BET Surface Area, t-plot Surface Area, BET Adsorption Isotherm, and BJH pore size distribution. The nitrogen gas was used as adsorbate at 77K and Fluorescence Spectroscopy of FP-8500 Jasco Spectrofluorometer was used to analyzed fluorescent properties of the rhodamine immobilized SBA-15. The spectrum obtained is in the emission measurement mode over the emission wavelength range of 530-580 nm with the excitation wavelength at 518 nm.

# 3. RESULTS AND DISCUSSION

## 3.1 Synthesis of SBA-15

From the FTIR absorption wavenumbers obtained, as-synthesized SBA-15 has the absorption bands at 2971, 2931, and 1458  $cm^{-1}$  indicates that the vibrations of C-H bonds such as -CH<sub>2</sub>- of polymer surfactant molecule. However, after undergoes soxhlet extraction to remove the surfactant template, the peaks were disappeared that indicates the surfactant was completely removed from mesoporous SBA-15 silica as illustrated in Figure 1. The SBA-15 shows the intense peak, which indicates it has the regular hexagonal phase showed by SAXS analysis as illustrated in Figure 2. From the nitrogen adsorption-desorption analysis, SBA-15 has type IV isotherm with hysteresis loop as shown in Figure 3. The hysteresis loop is associated with capillary condensation in mesopores and this isotherm can be used for pore size distribution calculations. The BET surface area obtained was 722.58  $m^2 g^{-1}$  with pore distribution of 5.25nm.

### 3.2 Rhodamine immobilized SBA-15 silica

From the FTIR, it shows the absorption bands of GLU-SBA-15 and rhodamine immobilized SBA-15. The absorption band of C=N at  $1647.60\text{ cm}^{-1}$  indicates that the reaction between GLU-SBA-15 and rhodamine hydrazine is occurred. From the Figure 4, it shows the spectrum of GLU-SBA-15 and rhodamine immobilized SBA-15. It can be said that, the absorption band of C=N bond that prove the attachment between GLU-SBA-15 and rhodamine hydrazine is overlapped at the  $1647.60\text{ cm}^{-1}$  with the C=O bond.

From the nitrogen adsorption-desorption analysis, the isotherm shows the low-pressure hysteresis isotherm that proposed by Arnell and McDermott. Hysteresis phenomena usually observed in the characterization of porous solid by using gas adsorption. Low-pressure hysteresis occurs due to some adsorbate is still remain even after prolonged out gassing. Low-pressure hysteresis occurs in SBA-15 because of the attachment of some molecules on the surface of SBA-15 such as APTES, GLU and rhodamine hydrazine and lead to the clogging of the silica's pore. The swelling of the molecules which accompanies adsorption distorts the structure of SBA-15. Due to the distortion is not perfectly elastic, some of the molecules become trapped in the pores that lead to very slow escape process or possibly not at all during the desorption unless the temperature is raised. From the Figure 5, the adsorption of the nitrogen gas is at the high pressure and the desorption of the gas is very slow. In the other word, the nitrogen gas could not released from the pores due to the pore is clogged by the molecules such as APTES, GLU and hydrazine hydrate that lead to the desorption of the gas from the pores is very slow.

The surface of BET was decrease from  $722.58\text{ m}^2\text{g}^{-1}$  to  $7.80\text{ m}^2\text{g}^{-1}$ . The decreasing of the BET surface area is because of the surface of the SBA-15 silica was modified by several molecules and created the few layers. The BET surface area of the rhodamine immobilized SBA-15 shows a very small surface area due to the surface of silica has been functionalized with several molecules such as APTES, GLU and rhodamine hydrazine and make the surface become smaller from the BET surface are of SBA-15 alone. The pore size distribution of rhodamine immobilized SBA-15 based on BJH desorption method shows that at the  $15.01\text{ nm}$  pore width. This method shows that the sample was shifted to the larger pore sizes due to the larger molecules grafted on the surface of SBA-15 and block the nitrogen gas from leaving the pores and remain in the pores of SBA-15. Hence, the desorption of the nitrogen gas from the SBA-15 occurs at a very high pressure.

Fluorescence spectroscopy was used in this characterization in order to determine the fluorescence properties of the samples. From the Figure 6, the emission of the rhodamine hydrazine and rhodamine immobilized SBA-15 show the same maximum emission at  $540\text{ nm}$  wavelength with the intensity of  $136.25$  and  $302.86$  respectively. From the Figure 6 also, the result obtained shows the intensity of GLU-SBA-15 is very low which is  $14.40$ . The intensity of rhodamine hydrazine is increased 2 fold from  $136.25$  to  $302.86$  after immobilized to the GLU-SBA-15 shows that the sample was more sensitive than the rhodamine hydrazine itself. The result obtained from the fluorescence spectroscopy shows that there is no emission wavelength for the SBA-15 and functionalized SBA-15 shows that the both samples have no fluorescence properties. From the result obtained, it can be suggested that the rhodamine immobilized SBA-15 has potential solid chemosensor to detect metal ion.

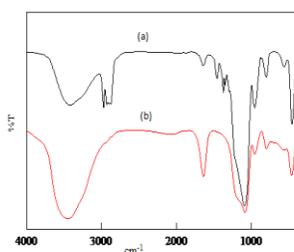


Fig. 1 FTIR spectra of (a) and (b), as-synthesized SBA-15 and SBA-15 after undergoes soxhlet extraction process respectively.

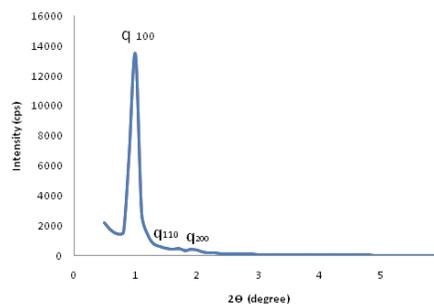


Fig. 2 Diffractogram of SBA-15

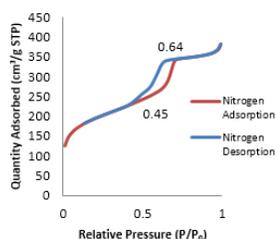


Fig. 3 Isotherm of SBA-15 silica

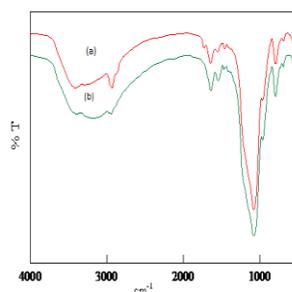


Fig. 4 FTIR spectra (a) and (b) of GLU-SBA-15 and rhodamine immobilized SBA-15 respectively.

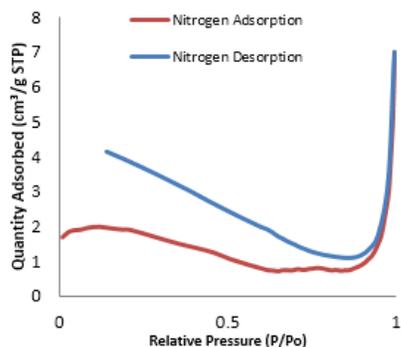


Fig. 5 Isotherm of rhodamine immobilized SBA-15

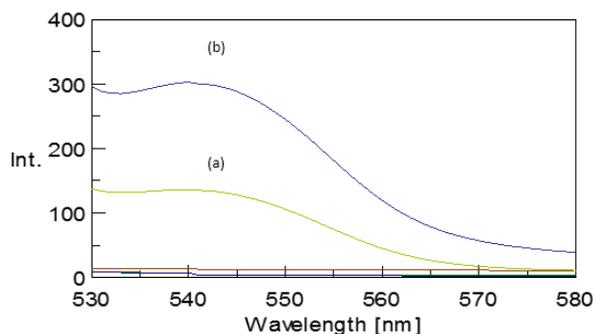


Fig. 6 Fluorescence emission spectrum of (a) and (b) indicate rhodamine hydrazine and rhodamine immobilized SBA-15 respectively

#### 4. CONCLUSION

In this study, rhodamine immobilized SBA-15 chemosensor was successfully synthesized. The surfactant of triblock copolymer Pluronic, P123 was completely removed from the surface of SBA-15 silica by undergoing soxhlet extraction process for 18 hours and has been confirmed by Fourier Transform Infrared (FTIR) Spectroscopy. The surface of SBA-15 was modified by attachment with APTES and followed by functionalization by glutaraldehyde (GLU) and immobilization of rhodamine hydrazine.

The sample of SBA-15 silica was characterized by using FTIR, Small Angle X-ray Scattering, Nitrogen Adsorption-desorption Measurement and Fluorescence Spectroscopy. The attachment of APTES, GLU and rhodamine hydrazine on the SBA-15 surface was confirmed by FTIR and supported by a decrease in BET surface area from  $722.68 \text{ m}^2\text{g}^{-1}$  to  $7.64 \text{ m}^2\text{g}^{-1}$ . It indicates that the molecules of rhodamine hydrazine were grafted on the surface of SBA-15.

The brown solid of rhodamine immobilized SBA-15 was characterized using Fluorescence Spectroscopy and shows the maximum emission wavelength at 540 nm. From the emission wavelength, it shows that rhodamine immobilized SBA-15 has potential as a solid chemosensor for detecting metal ions.

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