

## EVALUATION OF NEW POLAR FUNCTIONALISED SOL-GEL HYBRID SORBENT FOR STIR BAR SORPTIVE EXTRACTION OF ORGANIC DYES

<sup>1</sup>NUR ATIQA AH ABU BAKAR, <sup>2\*</sup>WAN AINI WAN IBRAHIM,  
AND <sup>3</sup>MOHD. MARSIN SANAGI

<sup>1,2</sup>Separation Science and Technology Group (SepSTec),  
Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia,  
81310 UTM Johor Bahru, Johor, Malaysia

<sup>2,3</sup>Nanotechnology Research Alliance, Universiti Teknologi Malaysia,  
81310 UTM Johor Bahru, Johor, Malaysia

<sup>3</sup>Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia,  
81310 UTM Johor Bahru, Johor, Malaysia

<sup>1</sup>[atiqah0501@yahoo.com](mailto:atiqah0501@yahoo.com), <sup>2</sup>[waini@kimia.fs.utm.my](mailto:waini@kimia.fs.utm.my), [waini@utm.my](mailto:waini@utm.my),  
<sup>3</sup>[marsin@kimia.fs.utm.my](mailto:marsin@kimia.fs.utm.my)

\*Corresponding author

**Abstract.** Stir bar sorptive extraction is widely used in the extraction of analytes from aqueous samples. However, commercial stir bar is relatively expensive. The high cost of the stir bar has led to the development of new coatings mainly based on silica. In this study, a new organic-inorganic hybrid silica-based material based on 3-mercaptopropyltrimethoxysilane (MPTMOS) and methyltrimethoxysilane (MTMOS) was synthesized via sol-gel technology and use in the evaluation of its extraction performance of three organic dyes namely crystal violet, methylene blue and methyl orange as test analytes. The test analytes were analyzed simultaneously using UV-Vis spectroscopy at 422 nm for methyl orange, 592 nm for crystal violet and 653 nm for methylene blue. Several sol-gel preparation parameters were optimized to obtain the sorbent with optimum extraction efficiency for the three selected dyes. The organic-inorganic sol-gel hybrid sorbent with the composition 3:1 MPTMOS-MTMOS showed the highest extraction performance for the three selected dyes.

**Keywords** Sol-gel; hybrid sorbent; stir bar sorptive extraction; polar organic dyes; ultraviolet-visible spectroscopy

## 1.0 INTRODUCTION

Stir bar sorptive extraction (SBSE) is a preparation method for the extraction and enrichment of organic compounds from aqueous matrices. In SBSE technique, a stir bar coated with a sorbent is immersed in an aqueous solution to extract the analytes from the solution for a specified time to approach equilibrium. The movement (extraction) of the analytes from the aqueous phase into the extraction medium is controlled by the partitioning coefficient of the analytes between the silicone phase and the aqueous phase. Studies have correlated this partitioning coefficient with the octanol-water distribution coefficients ( $K_{o/w}$ ).

Polydimethylsiloxane (PDMS) and ethylene glycol (EG)-Silicone are two commercially available coating materials for SBSE known as Twister<sup>®</sup>. PDMS is a polymeric stationary phase having higher affinity for non-polar compounds, giving limitations for the extraction of polar compounds. Many studies have been done in order to overcome the limitation by combining (couple) the PDMS on the stir bar with other material via sol-gel technique to overcome the PDMS's non-polar property. On the other hand, the newer commercial stir bar namely EG-Silicone Twister<sup>®</sup> has polar property which enables it to extract polar compounds. However, the cost for each commercial stir bar is relatively expensive (around RM600 each).

Limitations of PDMS on extracting polar analytes and the high cost of commercial stir bar has led to the development of novel in house stir bars with better affinity for polar compounds to improve the flexibility and selectivity of SBSE. Nowadays, researchers have focused their attention on the synthesis of novel polar coatings using different approaches including sol-gel technology to develop new materials or to produce PDMS-modified coatings. Some examples of SBSE coatings successfully synthesized using sol-gel technique are PDMS-polythiophene [1], PDMS-tetraethoxysilane [2], PDMS-cyanopropyltriethoxysilane [3], PDMS- $\beta$ -cyclodextrin [4] and poly(ethylene)glycol-PDMS-poly(vinyl alcohol) [5].

In this study, the main focus is on the preparation of sol-gel hybrid coating for SBSE which can enhance the extraction of polar analytes with low production cost. In the current work, sol-gel organic-inorganic hybrid based on (3-mercaptopropyl)trimethoxysilane (MPTMOS) and methyltrimethoxysilane (MTMOS) was developed as SBSE coating material. To the best of our knowledge, no literature on MPTMOS-MTMOS as coating material has been reported. The focus was given in obtaining optimum MPTMOS-MTMOS-derived hybrid sol conditions by manipulating the mol ratio of precursors, types of solvent and acid catalyst. The synthesized MPTMOS-MTMOS was coated on the glass-encased stir bar and further used for SBSE of three organic dyes (crystal violet, methyl orange and methylene blue), followed by analysis using Ultraviolet-Visible spectroscopy.

## **2.0 EXPERIMENTAL**

### **2.1 Chemicals and Reagents**

The stir bar coating materials, 3-mercapto-propyltrimethoxysilane (MPMTOS), methyltrimethoxysilane (MTMOS), poly(methylhydroxysiloxane) (PMHS) and trifluoroacetic acid (TFA) were purchased from Sigma-Aldrich (Missouri, USA). HPLC grade methanol was obtained from Merck (Darmstadt, Germany). Sodium hydroxide pellet and hydrochloric acid were obtained from Fluka Chemica (Buchs, Switzerland).

All selected organic dyes standards, crystal violet, methylene blue and methyl orange were purchased from Fisher Chemicals (Loughborough, U.K). Individual stock solutions were prepared in methanol (MeOH) at concentration of  $1000 \mu\text{g mL}^{-1}$  and kept at  $4^\circ\text{C}$  prior to use and further dilution.

### **2.2 Experimental**

### **2.2.1 Preparation of mercaptopropyltrimethoxysilane-methyltrimethoxysilane (MPTMOS-MTMOS) and coating process of stir bar**

A glass tube (20 mm × 4 mm × 0.5 mm i.d) sealed with an iron wire cuttings (15 mm × 2 mm × 0.4 mm i.d) in it was used as the support of coating for the dumb bell-shaped stir bar. Before coating, the glass-encased dumb bell-shaped stir bar was sequentially cleaned with water and methylene chloride by ultrasonication for 30 min, followed by dipping in 1.0 mol/L NaOH solution for 24 h to expose the maximum number of silanol groups on the surface. The treated stir bar was sequentially cleaned with water, 0.1 mol L<sup>-1</sup> HCl solution and water to neutralize the excess NaOH, and dried at 60°C for 3 h.

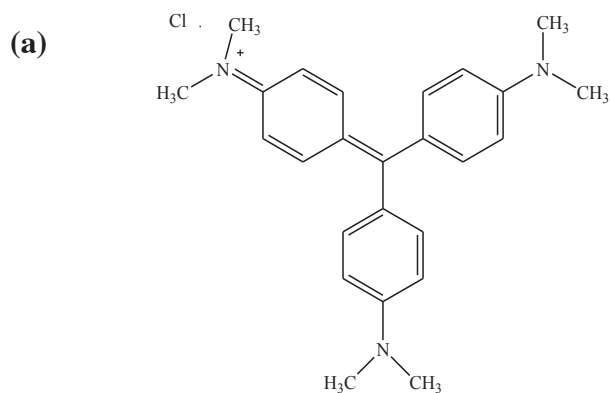
The sol solution of MPTMOS-MTMOS was prepared by mixing 186 µL MPTMOS, 143 µL MTMOS, 108 µL H<sub>2</sub>O, 246 µL MeOH, 200 µL TFA and 25 µL PMHS in a 2 mL polyethylene bullet-shape tube. The mixture was mixed and vortexed for 2 min before undergo centrifugation at 12,000 rpm for 5 min. The mixture was allowed to react at room temperature. The preparation steps were repeated using 372, 558 and 744 µL MPTMOS. A homogenous solution was obtained for all the sol-gel solution prepared.

The treated bare dumb-bell shaped stir bar was immersed vertically into the prepared sol solution for 30 min, then removed and placed in the desiccator for 1 h, before dried at 70°C for 24 h. Prior to use, the dumb-bell shaped stir bar was cleaned in methanol by ultrasonication for 10 min to get rid of the organic contaminants in the coating.

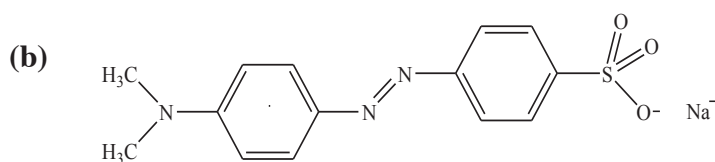
### **2.2.2 Stir bar sorptive extraction process**

A 6 mL aqueous solution spiked with 10 µg mL<sup>-1</sup> methyl orange and 5 µg mL<sup>-1</sup> of each crystal violet and methylene blue standard solution was introduced into a beaker. The structures and pK<sub>a</sub> values of crystal violet, methyl orange and methylene blue are shown in Figure 1. The stir bar coated with MPTMOS-MTMOS derived-hybrid was immersed into the solution for SBSE process. The extraction of the dyes was performed at room temperature for 60 min and the solution was stirred at 150 rpm (Figure 2). After extraction, the stir bar was

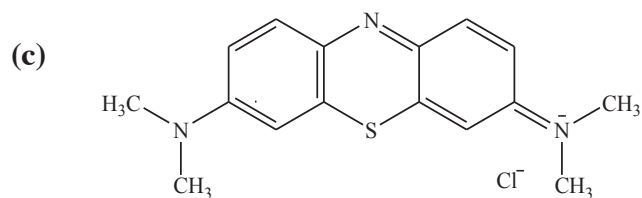
carefully removed from the solution, rinsed with deionized water and patted dried with lintless tissue. The stir bar was placed in an ultrasonic assisted system for 20 min using 3 mL MeOH as desorption solvent before UV-Vis analysis. The analysis was done using a Lambda 25 UV-Vis Spectrometer from Perkin Elmer (Massachusetts, USA) recorded in the range from 300-800 nm.



pKa value = 4.83

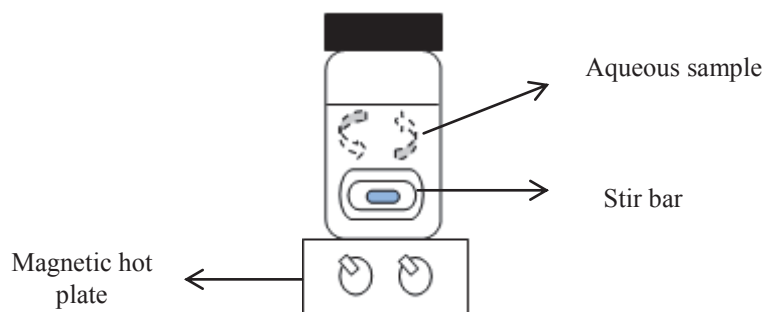


pKa value = 3.47



pKa value = 3.8

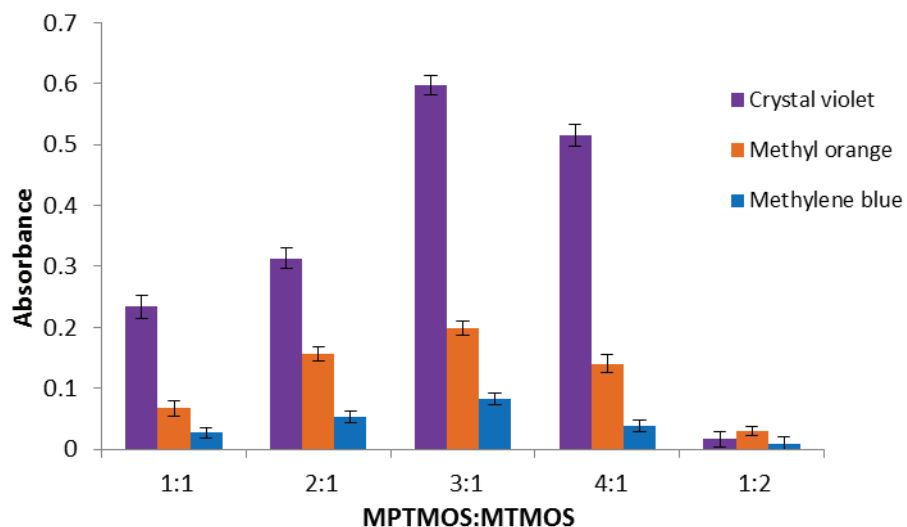
**Figure 1** The structures and pKa value of organic dyes (a) crystal violet, (b) methyl orange and (c) methylene blue



**Figure 2** Schematic of SBSE procedure

### 3.0 RESULTS AND DISCUSSIONS

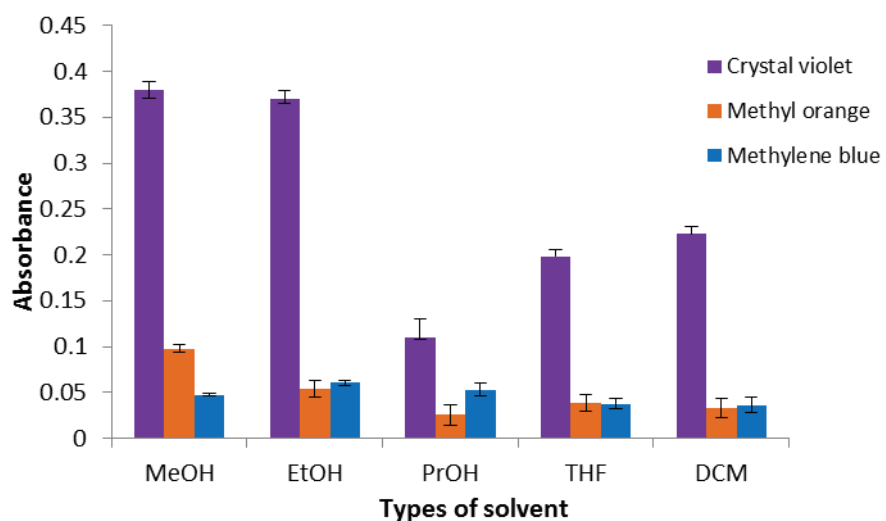
In sol-gel process, obtaining homogeneous MPTMOS-MTMOS-derived hybrid sol is very important as it ensures reaction and hybridization of sol components during the process. In this study, homogeneous MPTMOS-MTMOS sol was obtained for the sol-gel solution prepared. Investigation on the effect of no. of mol of MPTMOS:MTMOS on the sorbent coating's performance was carried out by using five different mol ratios of MPTMOS:MTMOS (1:1, 2:1, 3:1, 4:1 and 1:2). The mol ratios of other sol-gel ingredients (polydimethylhydroxy-siloxane as deactivating agent, 95% trifluoroacetic acid as acid catalyst, water and methanol) were kept constant at 25  $\mu$ L, 2.5 mmol, 6 mmol and 6 mmol respectively. The sol-gel solution of mol ratio 3:1 MPTMOS:MTMOS was chosen as the best composition for coating and was used in further analysis as it exhibited the highest ability to extract the selected dyes (Figure 3). The gelation time of the sol-gel produced was found to increase with increasing mol of MPTMOS (7 h for 1:1, 10 h for 2:1, 17 h for 3:1, 24 h for 4:1 and 6 h for 1:2 MPTMOS:MTMOS). Gelation time is the duration for the sol seized to move even when the tube is tilted or inverted after preparation.



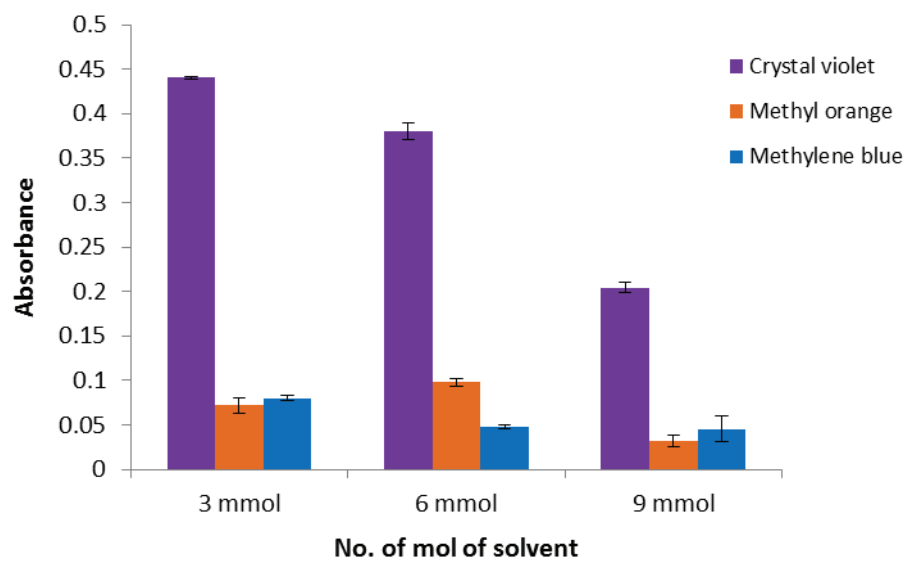
**Figure 3** Effect of different mol ratio of MPTMOS: MTMOS used in the extraction of selected dyes. Extraction conditions: 150 rpm stirring rate, 60 min extraction time, 20 min desorption time, desorption using 3 mL methanol.

In the optimization of solvent types, five solvents were used, namely methanol, ethanol, propanol, tetrahydrofuran and dichloromethane. A solvent functions in helping the sol-gel materials mix together to ensure a homogeneous sol-gel network formation. As molecules polymerize into sol, the solvent is needed to be able to keep the sol-gel materials dissolved so that they do not precipitate out of liquid [6]. Figure 4 shows the extraction efficiency of dyes by different types of solvent in the synthesis of MPTMOS-MTMOS sol-gel hybrid. The use of methanol yields the highest extraction efficiency for the selected dyes and was chosen for further analysis. The preparation of sol using ethanol and propanol was found to result in longer gelation time (slower evaporation) due to their higher boiling point (78°C and 97°C respectively).

In addition, the no. of mol of optimum solvent (MeOH) was also investigated to study the sufficient amount of MeOH needed in the sol-gel process. For the optimization of no. of mol of solvent, 3, 6 and 9 mmol were used. Figure 5 shows that 3 mmol of MeOH gives the best extraction efficiency for the selected dyes compared to the other two.



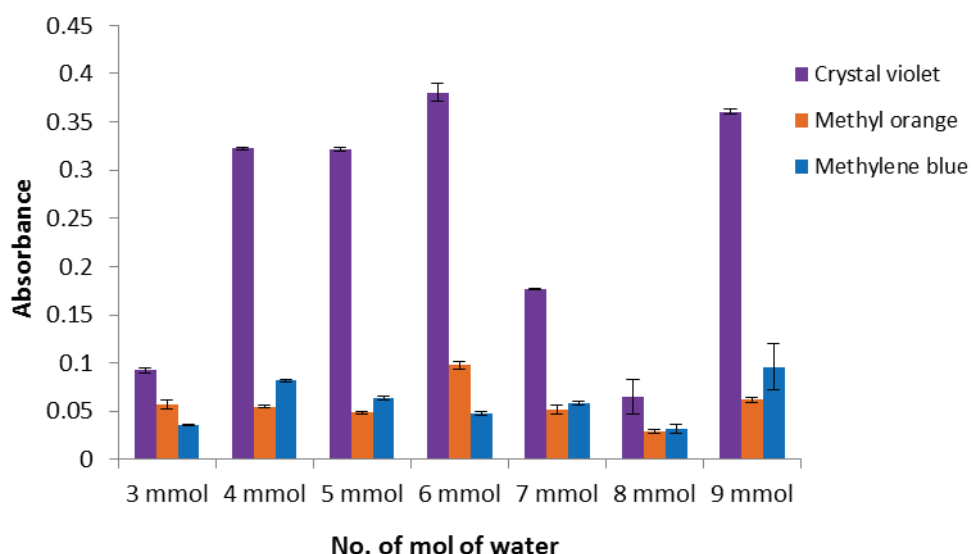
**Figure 4** Effect of different types of solvent used in preparation of MPTMOS-MTMOS sol-gel hybrid. Extraction conditions: 150 rpm stirring rate, 60 min extraction time, 20 min desorption time, desorption using 3 mL methanol.



**Figure 5** Effect of different no. of mol of solvent (MeOH) used in preparation of MPTMOS-MTMOS sol-gel hybrid. Extraction conditions: 150 rpm stirring rate, 60 min extraction time, 20 min desorption time, desorption using 3 mL methanol.



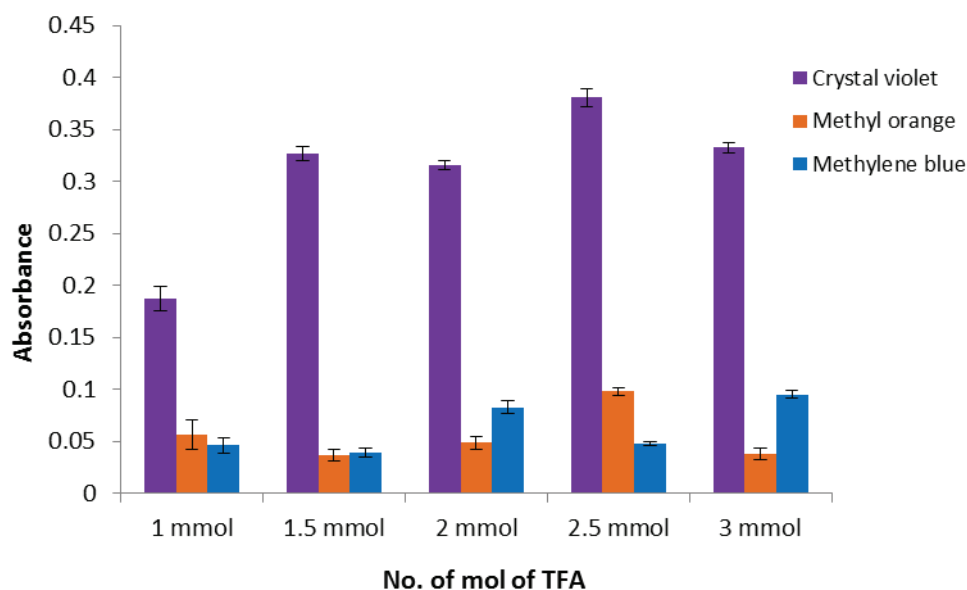
The effect of different no. mol of water in the preparation of MPTMOS-MTMOS sol-gel hybrid was evaluated and the absorbance obtained from UV-Vis is shown in Figure 6. In this study, water was used as a hydrolysis agent, therefore it is important to investigate the appropriate amount of water needed for the process. In this optimization step, no. of mol of water ranging from 1 mmol to 9 mmol was chosen. From the graph, 6 mmol of water gave the best extraction efficiency and further increment in the no. of mol of water resulted in lower amount of dyes being extracted. This explained that further increase in the number of water will increase the pore size, which in turn decreases the surface area of sol-gel hybrid coating available for extraction [7]. Thus, 6 mmol of water was selected as optimum condition and was used in further analysis.



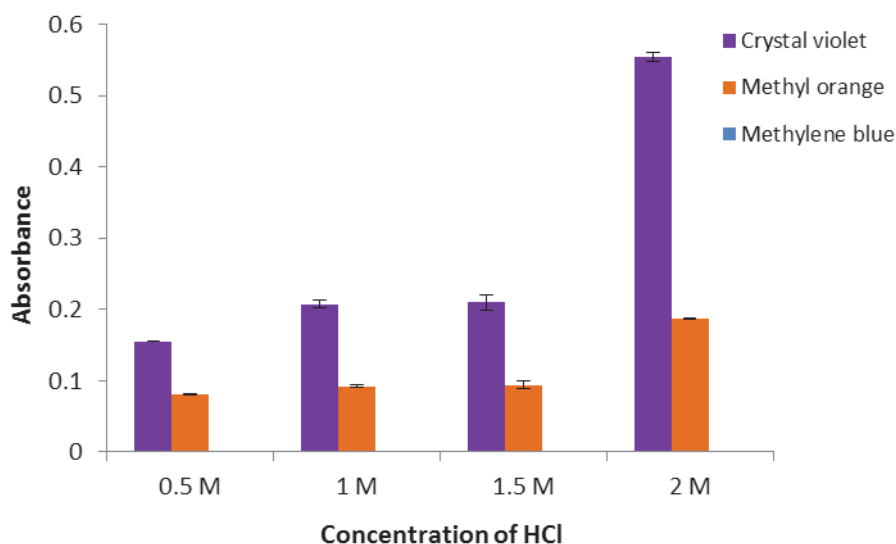
**Figure 6** Effect of different no. of mol of water used in preparation of MPTMOS-MTMOS sol-gel hybrid. Extraction conditions: 150 rpm stirring rate, 60 min extraction time, 20 min desorption time, desorption using 3 mL methanol.

Further improvement of the MPTMOS-MTMOS sol-gel hybrid produced was done by optimizing the types of acid catalyst used in the sol-gel process. The addition of acid catalyst speeds up the hydrolysis and condensation process, resulted in faster gelation time. In this study, two types of acid catalyst (trifluoroacetic acid, TFA and hydrochloric acid, HCl) were employed. The first

part involved the optimization of different no. of mol of TFA (1, 1.5, 2, 2.5 and 3 mmol of TFA) and the second part is the optimization of HCl concentration (0.5, 1, 1.5 and 2 M). TFA is a very common and widely used acid catalyst in the preparation of sol-gel material for coating, while HCl is usually used for the preparation of sol-gel particle. From Figure 7, 2.5 mmol of TFA shows the highest extraction efficiency for the selected dyes. Figure 8 shows that 2 M HCl was able to extract more crystal violet and methyl orange compared when using TFA. However, the preparation of sol-gel hybrid using HCl was unable to extract methylene blue at all concentrations. Therefore, the sol-gel prepared using 2.5 mmol TFA was selected and used in further analysis.

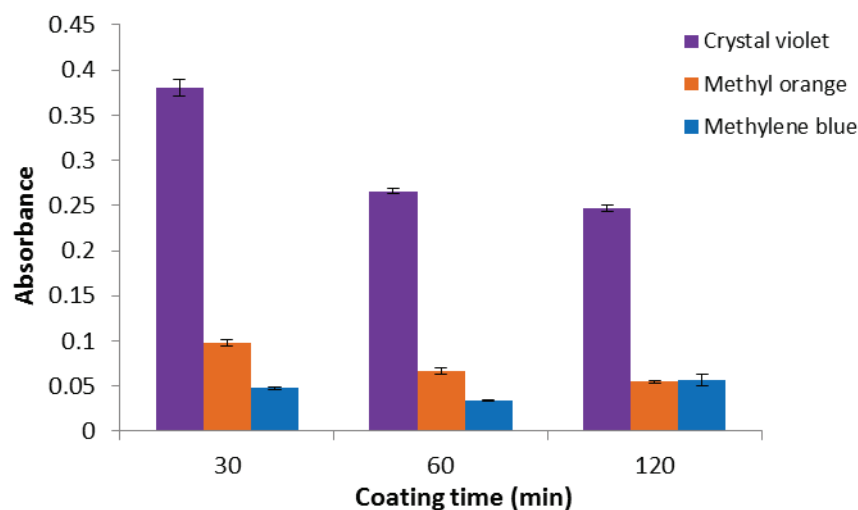


**Figure 7** Effect of different no. of mol of TFA used in preparation of MPTMOS-MTMOS sol-gel hybrid. Extraction conditions: 150 rpm stirring rate, 60 min extraction time, 20 min desorption time, desorption using 3 mL methanol.



**Figure 8** Effect of different concentration of HCl used in preparation of MPTMOS-MTMOS sol-gel hybrid. Extraction conditions: 150 rpm stirring rate, 60 min extraction time, 20 min desorption time, desorption using 3 mL methanol.

Three different time durations (30, 60 and 120 min) were evaluated for the optimization of coating time. Coating time is the duration for the bare stir bar dipped into the sol solution during coating process. In the process, the glass bar should be coated with a non-wetting layer. The coating process may need to be longer for the sol solution to attack the glass under the non-wetting layer. Insufficient wetting ability of glass substrate (insufficient hydroxyl group) for deposition of sol solution during coating process will result in non-chemically bonded of the material (MPTMOS-MTMOS) to the surface of the glass [8]. From Figure 9, 30 min was selected as the best coating time, as the increase in coating time resulted in lower extraction efficiency.



**Figure 9** Effect of different coating time in the preparation of MPTMOS-MTMOS sol-gel hybrid. Extraction conditions: 150 rpm stirring rate, 60 min extraction time, 20 min desorption time, desorption using 3 mL methanol.

#### 4.0 CONCLUSIONS

The MPTMOS-MTMOS sol-gel hybrid for use as stir bar sorptive extraction (SBSE) coating was successfully synthesized via sol-gel technique using MPTMOS and MTMOS as the precursors, and TFA as acid catalyst. The coating with composition 3:1 mol ratio MPTMOS:MTMOS showed highest extraction performance towards three selected organic dyes, crystal violet, methyl orange and methylene blue. The sol-gel parameters affecting the extraction performance of the coating material were optimized as follows: 3 mmol of MeOH (solvent), 6 mmol of water, 2.5 mmol of TFA and 30 min coating time. More work is in the progress to study the SBSE parameters such as stirring rate, extraction time, desorption solvent and salt addition affecting the extraction process to further improve the performance of the coating material.

#### 5.0 ACKNOWLEDGEMENT

The authors gratefully acknowledged Ministry of Higher Education, Malaysia (MOHE) under Research University Grant (GUP) (Vote number 04H22) and University Universiti Teknologi Malaysia (UTM) for funding the research.

## REFERENCES

- [1] Hu, C., He, M., Chen B., and Hu, B. (2013). A Sol–Gel Polydimethylsiloxane/ Polythiophene Coated Stir Bar Sorptive Extraction Combined with Gas Chromatography-Flame Photometric Detection for the Determination of Organophosphorus Pesticides in Environmental Water Samples. *J. Chromatogr. A.* **1275**:25-31.
- [2] Wan Ibrahim, W.A., Wan Ismail, W.F., Abdul Keyon, A.S., and Sanagi, M.M. (a) (2011) Preparation and Characterization of a New Sol-Gel Hybrid Based Tetraethoxysilane-Polydimethylsiloxane as a Stir Bar Extraction Sorbent Materials. *J. Sol-Gel Sci. Technol.* **58(3)**. 602-611.
- [3] Wan Ibrahim, W.A., Abdul Keyon, A.S., Prastomo, N., and Matsuda, A. (b) (2011). Synthesis and Characterization of Polydimethylsiloxane-Cyanopropyltriethoxysilane Derived Hybrid Coating for Stir-bar Sorptive Extraction. *J Sol-Gel Sci. Technol.* **59**:128–134.
- [4] Yu, B., and Hu, B. (2007). Novel Combined Stir Bar Sorptive Extraction Coupled with Ultrasonic Assisted Extraction for the Determination of Brominated Flame Retardants in Environmental Samples using High Performance Liquid Chromatography. *J. Chromatogr. A.* **1160**:71-80.
- [5] Yu, C., Li, X., and Hu, B. (2008). Preparation of Sol–Gel Polyethylene Glycol–Polydimethylsiloxane–Poly(vinylalcohol)-Coated Sorptive Bar for the Determination of Organic Sulfur Compounds in Water. *J. Chromatogr. A.* **1202**:102-106.
- [6] Kabir, A., Furton, K.G. and Malik, A. (2013). Innovations in Sol-Gel Microextraction Phases for Solvent-free Sample Preparation in Analytical Chemistry. *Trends Anal. Chem.* **45**:197-218.
- [7] Lopez, T., Ortiz, E., Alexander-Katz, R., Odriozola, Quintana, P., Gonzalez, R.D., Lottici, P.P. and Marino, I.G. (2010). The Effect of Water on Particle Size, Porosity and the Rate of Drug Release from Implanted Titania Reservoirs. *J. Biomed. Mater. Res. B.* **938**:401.
- [8] Jing, C., Hou, J., Zhang, Y. and Xu, X. (2007). Preparation of Thick, Crack-free Germanosilicate Glass Films by Polyvinylpyrrolidone and Study of the UV-Bleachable Absorption Band. *J. Non-Cryst Solids.* **353**:4128-4136.