Jurnal Teknologi

Full Paper

SOL-GEL (3-MERCAPTOPROPYL)TRIMETHOXYSILANE-METHYLTRIMETHOXYSILANE AS ADSORBENT FOR STIR BAR SORPTIVE EXTRACTION OF SELECTED ORGANIC DYES

Article history
Received
10 February 2015
Received in revised form
28 December 2015
Accepted
28 December 2015

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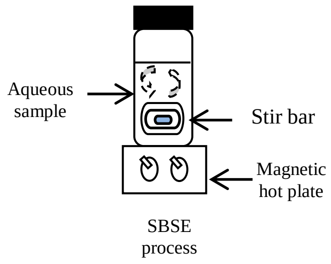
Graphical abstract



Abstract

A new sol-gel hybrid silica-based (3-mercaptopropyl)trimethoxysilane-methyltrimethoxysilane (MPTMOS-MTMOS) in the ratio of 3:1 was synthesized and applied as an adsorbent in stir bar sorptive extraction (SBSE) of three selected polar organic dyes from water sample. Three organic dyes were used as test analytes namely crystal violet, methyl orange and methylene blue. Analysis of the organic dyes was performed using ultraviolet-visible spectroscopy. Optimum extraction conditions was achieved using 50 min extraction time, 240 rpm stirring rate, ultrasonic aided desorption for 15 min using 3 mL methanol and sample solution at pH 4 with addition of 5% (w/v) NaCl. The sol-gel hybrid MPTMOS-MTMOS showed better extraction efficiency (based on absorbance) for the selected organic dyes compared to commercial ethylene-glycol/silicone Twister™ stir bar. Limit of detection obtained was in the range 0.34 -0.75 µg mL^{-1} (S/N = 3) and linear range achieved was 10 order of magnitude (1.0-10 µg mL^{-1}). The developed sol-gel hybrid material showed high potential as an alternative adsorbent for SBSE of organic dyes. MPTMOS-MTMOS SBSE was successfully applied for simultaneous analysis of three organic dyes from river water with good recovery.

Keywords: Sol-gel hybrid; MPTMOS-MTMOS; stir bar sorptive extraction; organic dyes; ultraviolet-visible spectroscopy

Abstrak

Satu bahan baharu hibrid sol-gel berasaskan silika (3-merkaptopropil)trimetoksisilana-metiltrimetoksisilana (MPTMOS-MTMOS) dengan nisbah 3:1 telah disintesis dan diaplikasikan sebagai bahan penjerap dalam pengekstrakan jerapan bar berputar untuk tiga pewarna organik berkutub terpilih daripada sampel air. Tiga pewarna organik telah digunakan sebagai analit uji iaitu kristal ungu, metil jingga dan metilena biru. Analisis pewarna dilakukan menggunakan spektroskopi ultralembayung-nampak. Keadaan pengekstrakan optimum telah dicapai menggunakan 50 min masa pengekstrakan, 240 rpm kelajuan putaran, nyahjerapan berbantukan ultrasonik selama 15 min menggunakan metanol dan larutan sampel pada pH 4 dengan penambahan 5% (w/v) NaCl. Hibrid sol-gel MPTMOS-MTMOS menunjukkan kecekapan pengekstrakan yang lebih baik (berdasarkan keserapan) untuk pewarna organik terpilih berbanding bar berputar komersial etilena-glikol/silikon

Twister™. Had pengesanan diperoleh dalam julat 0.34 -0.75 µg mL^{-1} (S/N = 3) dan julat linear dicapai ialah 10 tertib magnitud (1.0-10 µg mL^{-1}). Bahan hibrid sol-gel yang dibangunkan ini menunjukkan potensi tinggi sebagai bahan penjerap alternatif untuk SBSE pewarna organik. MPTMOS-MPTMOS SBSE telah digunakan dengan jayanya untuk analisis serentak tiga pewarna organik daripada sampel air sungai dengan pengembalian semula yang baik.

Kata kunci: Hibrid sol-gel; MPTMOS-MTMOS; pengekstrakan jerapan bar berputar, pewarna organik; spektroskopi ultralembayung-nampak

1.0 INTRODUCTION

Dye is a type of colorant which is widely used in many industrial applications including food, textiles, paper and plastic industries. The massive used of synthetic dyes in industries which involves the discharge of colored effluents into natural waters leads to environmental pollution and health problems[1]. These are due to the low biodegradability of synthetic dyes and their cytotoxic and carcinogenic properties to human[2]. Therefore, there is an increasing concern on the determination of dyes in various water samples. In an analysis, sample preparation step is carried out to provide a sample free of matrices and interfering analytes. From previous studies, the extraction methods which are commonly used in the determination of dyes in various types of samples were liquid-liquid extraction (LLE) and solid phase extraction (SPE)[3-6]. The analysis was mostly performed using high performance liquid chromatography-ultraviolet detector (HPLC-UV) and ultraviolet-visible spectroscopy (UV-Vis)[5-8] Recently stir bar sorptive extraction (SBSE) has gained popularity as one of the sample preparation techniques.

SBSE is an equilibrium technique, similar to solid phase microextraction (SPME). In SBSE, a stir bar coated with sorbent material is immersed into a sample solution to extract analytes for a specified time until equilibrium is reached[9]. This technique was developed to overcome the limitation of SPME, which allowed a very limited amount of extraction medium on the SPME fiber.

The types of stir bar (coating material) commercially available for SBSE include polydimethylsiloxane (PDMS) and ethylene-glycol (EG)-silicone, which known as Twister™. PDMS showed high affinity for non-polar compounds, giving limitation to the extraction of polar compounds. Many studies have been done to overcome the limitation by combining PDMS with materials having polar property using different approaches including sol-gel technology[9-14]. The new commercial stir bar, EG-silicone was designed for the extraction of polar compounds as an alternative to PDMS. However, the cost of each commercial stir bar is relatively expensive. There is an increasing number of works reported on the synthesis of SBSE coatings using sol-gel technology. Sol-gel technique is suitable for the preparation of film as it provides direct chemical binding of the coating and the surface of glass. This result in higher solvent stability and longer lifetime compared to physical deposition technique[15]. Previous successful work[9,10] on the use of sol-gel hybrid adsorbent for SBSE has prompted us to produce a sol-gel hybrid SBSE adsorbent for application of dyes. In the present work, a new silica-based sol-gel hybrid based on (3-mercaptopropyl)trimethoxysilane (MPTMOS) and methyltrimethoxysilane (MTMOS) was successfully synthesized as an adsorbent/coating for SBSE. MTMOS was selected as a co-precursor because it gives more open structure and may effectively relieve stress during drying process in sol-gel method, thus reduce shrinkage and cracks on the coating surface. Meanwhile, MPTMS has thiol functional group which is reactive and hydrophilic, thus may be highly effective in the extraction of polar dyes from aqueous sample. The modification of hybrid MPTMOS-MTMOS with dual properties can also be used in the extraction of other polar and non-polar analytes. In this study, the sol-gel hybrid adsorbent was able to successfully extract the three polar dyes; crystal violet, methyl orange and methylene blue (log $k_{o/w}$ = 1.40, 2.61 and 0.75 respectively) with higher extraction efficiency compared to commercial EG-silicone Twister™.

2.0 EXPERIMENTAL

2.1 Chemicals and Reagents

The two sol-gel materials, (3-mercaptopropyl) trimethoxysilane (MPTMOS), methyltrimethoxysilane (MTMOS), poly(methyl-hydroxysiloxane) (PMHS) and trifluoroacetic acid (TFA) were purchased from Sigma-Aldrich (Missouri, USA). Standard dyes of crystal violet (CV), methylene blue (MB) and methyl orange (MO) were obtained from Fisher Chemicals (Loughborough, U.K.). Stock solutions of 1000 µg mL^{-1} of each dye was prepared using HPLC grade methanol (MeOH) from Merck (Darmstadt, Germany). Stock solution was stored at 4°C prior to use.

2.2 Preparation of Stir Bar and Sol-gel Hybrid MPTMOS-MTMOS

A dumb bell-shaped stir bar was prepared by sealing iron wire cuttings (15 mm × 2 mm × 0.4 mm i.d) into a glass tube with a dimension of 20 mm × 4 mm × 0.5 mm i.d. The glass-encased stir bar was sequentially cleaned with water and methylene chloride with aid of ultrasonication for 30 min. The stir bar was then dipped in 1.0 M sodium hydroxide (NaOH) solution for 24 h to expose maximum number of silanol groups on the glass surface. The treated stir bar was then cleaned with water, 0.1 M hydrochloric acid solution followed with water to neutralize excess NaOH, before drying in the oven at 60°C for 3 h.

The MPTMOS-MTMOS sol solution was synthesized by mixing 186 µL MPTMOS, 143 µL MTMOS, 108 µL H_2O, 246 µL MeOH, 200 µL TFA and 25 µL PMHS in a 2 mL polyethylene bullet-shaped tube. The mixture was vortexed for 2 min, followed by centrifugation at 12000 rpm for 5 min and was allowed to react at room temperature. The pretreated stir bar was immersed vertically in the sol solution for 30 min, and dried at 70°C for 24 h. The coated stir bar was cleaned with methanol with aid of ultrasonication for 10 min prior to extraction process.

2.3 Stir Bar Sorptive Extraction Process

In SBSE process, the MPTMOS-MTMOS coated stir bar was immersed in 10 mL of sample solution containing 5 µg mL^{-1} of each CV and MB, and 10 µg mL^{-1} of MO. Extraction was performed at room temperature for 60 min with stirring at 150 rpm. Then, the stir bar was carefully removed from the solution, rinsed with deionized water and patted dry with lintless tissue. The stir bar was placed in an ultrasonic assisted system for 20 min (ultrasonic assisted liquid desorption, UALD) using 3 mL of MeOH as desorption solvent. The extracted solution was finally analyzed using a Lambda 25 UV-Vis Spectrometer from Perkin Elmer (Massachusetts, USA) in the range of 300-800 nm.

2.4 Characterization of Sol-gel Hybrid MPTMOS-MTMOS

The raw MTMOS, MPTMOS and sol-gel hybrid MPTMOS-MTMOS were characterized using Fourier transform infrared spectroscopy (FTIR) using ATR method on a Perkin Elmer FTIR spectrum 100 (MA, USA) fitted with ATR (Ge/Ge) accessory in the range of 600-4000 cm^{-1}.

2.5 Real Sample Analysis

Calibration graph of analyte absorbance versus its concentration was constructed to validate the SBSE-UV-Vis method towards the three selected organic dyes using optimum SBSE conditions (50 min extraction time, 240 rpm stirring rate, ultrasonic assisted desorption for 15 min using 3 mL methanol and sample solution at pH 4 with addition of 5% (w/v) NaCl). Linearity range, coefficient of determination (R^2) and limit of detection (LOD at 3 S/N) was determined from the graph. For real sample analysis, river water sample was collected from Sungai Skudai, Johor, Malaysia. The water sample was filtered using 0.45 µm nylon membrane filter from Whatmann (NJ, USA). For recovery analysis, the sample was spiked with 2 µg mL^{-1} of each CV and MB and 4 µg mL^{-1} of MO.

3.0 RESULTS AND DISCUSSION

3.1 Optimization of Extraction Conditions

To obtain an optimum condition of SBSE, several factors influencing the extraction including extraction time, desorption time, desorption solvent, stirring rate, salt addition and pH of sample solution were considered. Optimization was carried out using one-at-a-time optimization strategy.

3.1.1 Extraction Time

SBSE involves equilibrium process and is significantly influenced by extraction time. The extraction time is determined by the duration required for the analyte in the sample and the coating stationary phase to reach equilibrium. The equilibrium can be affected by various factors, such as the nature of the sorbent and the identity of the analyte. Therefore, extraction time was optimized to determine the best conditions between time and efficiency. Five different extraction times between 20 to 80 min were evaluated. Figure 1 shows the effect of extraction time on the extraction efficiency of dyes using MPTMOS-MTMOS coated stir bar.

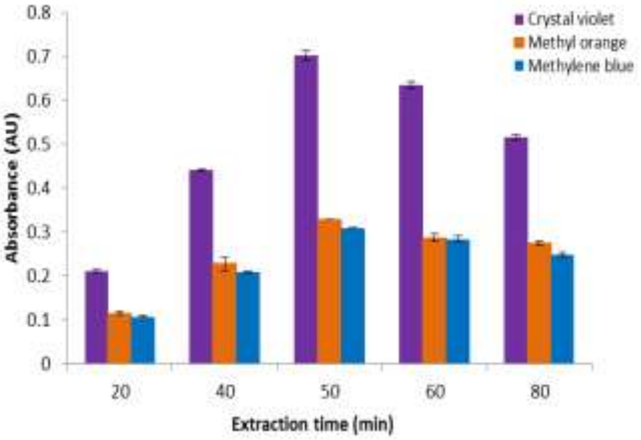


Figure 1 Effect of extraction time on the extraction of three selected organic dyes using sol-gel hybrid MPTMOS-MTMOS stir bar. SBSE conditions: 150 rpm stirring rate, UASL for 20 min desorption time using 3 mL methanol as desorption solvent.

The equilibrium of each dye extracted was achieved at 50 min as it gives the highest extraction efficiency. The slight decrease in the extraction efficiency after 50 min extraction time might be due to the back extraction of dyes from the extracting phase to the aqueous phase after equilibrium is reached, resulting in lower extraction performance. The time required for extraction was faster compared to the optimum extraction time using EG-silicone Twister™ stir bar which was achieved at 80 min (data not shown). This might be attributed to the thinner coating of the MPTMOS-MTMOS sol-gel hybrid (~822 µm) compared to EG-silicone Twister™ coating (1 mm), which allows faster partitioning of dyes from the aqueous sample to extracting phase. The micron size coating thickness gave reasonable sample capacity to extract high amount of dyes at a faster extraction time.

3.1.2 Desorption Time

It is important to study the effect of desorption time to achieve highest sensitivity and to avoid carry over in SBSE. In this work, ultrasonic assisted liquid desorption (UA-LD) was used to accelerate analyte removal from the stir bar. Desorption time used for the organic dyes using MPTMOS-MTMOS stir bar was varied between 10 to 20 min (Figure 2).

The highest extraction efficiency for the organic dyes was achieved at 15 min desorption time and was applied in the next optimization process. Further increase in desorption time resulted in an almost constant extraction efficiency.

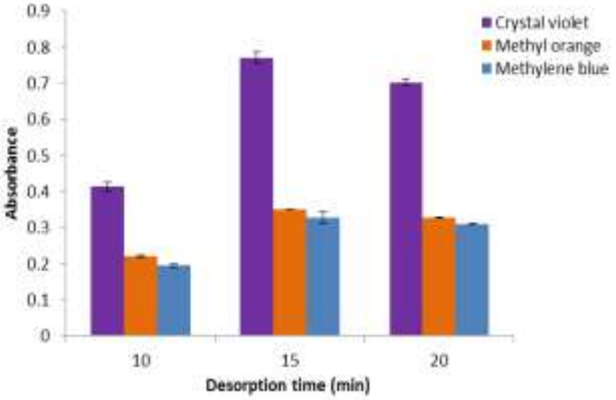


Figure 2 Effect of desorption time on the extraction of three selected organic dyes using sol-gel hybrid MPTMOS-MTMOS stir bar. Extraction conditions: 50 min extraction time, 150 rpm stirring rate, UA-LD using 3 mL methanol as desorption solvent.

3.1.3 Desorption Solvent

It is crucial to select a suitable desorption solvent to ensure that the adsorbed organic dyes can be stripped off from the sol-gel hybrid MPTMS-MTMOS stir bar effectively for quantitative recovery. Based on the basic principle of extraction where 'like dissolve like', four solvents with different polarity were chosen to study their effect on the UA-LD) of the selected dyes (Figure 3). Acetonitrile is the most polar solvent followed by methanol, ethanol and 1-propanol. It was observed that desorption using methanol shows the highest extraction efficiency. This is due to its higher polarity compared to ethanol and 1-propanol, thus allowing more desorption of the extracted dyes from the MPTMOS-MTMOS coating. However, acetonitrile shows relatively low extraction performance. This may due to its high solvent strength which possibly strips off the MPTMOS-MTMOS coating, resulting in less extracting phase available for extraction of dyes. Considering the highest extraction efficiency for the dyes and mild toxicity of methanol, it was chosen as the suitable desorption solvent for further experiment.

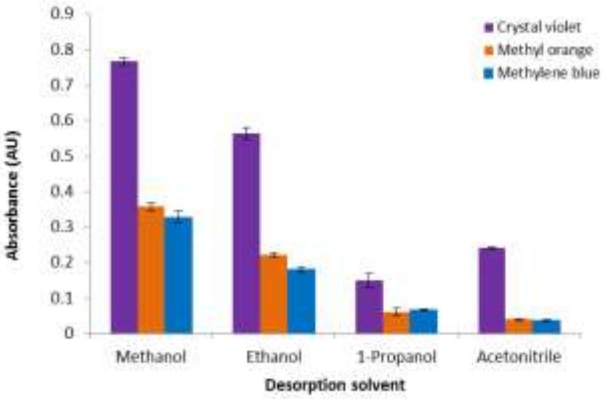


Figure 3 Effect of different desorption solvent (3 mL) on the extraction of three selected organic dyes using sol-gel hybrid MPTMOS-MTMOS stir bar. Extraction conditions: 50 min

extraction time, 150 rpm stirring rate, UA-LD for 20 min desorption time.

3.1.4 Stirring Rate

During equilibrium process, the mass transfer of analytes from the sample matrix towards the stationary phase is controlled by stirring rate[16]. Therefore, it is essential to optimize the stirring rate parameter. The sol-gel hybrid MPTMOS-MTMOS stir bar utilized laboratory magnetic stirrer with stirring rate between 150 to 300 rpm (Figure 4). Higher stirring rate was not used as it cannot maintain the stability (peeling of coating) of the sol-gel coating on the stir bar, thus affecting the extraction process.

Figure 4 shows that the highest extraction efficiency of organic dyes was achieved at 240 rpm stirring rate. The extraction efficiency significantly decreased as faster stirring rate was used. Although efficient stirring can enhance the extraction process, a faster stirring however may affect the mass transfer or the movement of dyes into the MPTMS-MTMOS coating during extraction process, resulting in lower extraction efficiency. Therefore, 240 rpm was chosen as the optimum stirring rate for the next optimization.

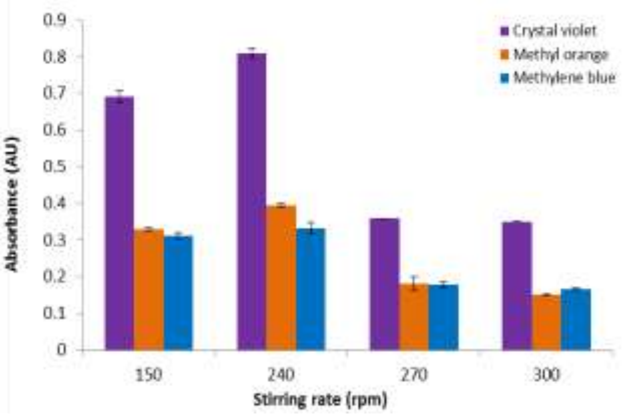


Figure 4 Effect of stirring rate on the extraction of three selected organic dyes using sol-gel hybrid MPTMOS-MTMOS stir bar. Extraction conditions: 50 min extraction time, 150 rpm stirring rate, 15 min UA-LD using 3 mL methanol as desorption solvent.

3.1.5 Salt Addition

The addition of salt to a sample solution can decrease the affinity of analytes to aqueous sample matrix, thus enhancing their affinity towards the extracting phase[17]. To study the effect of ionic strength on the extraction process, four different amounts of sodium chloride (NaCl) ranges from 0 to 10% (w/v) was applied into the sample solution. Figure 5 shows the extraction efficiency for selected dyes extracted at different salt concentrations. As expected from Figure 5, the dyes extracted shows significant increment when the amount of NaCl introduced into the sample was increased up to 5% w/v. However, further addition of NaCl (10% w/v) resulted in a drastic decrease in the extraction efficiency. This could probably be attributed to a production of a more viscous solution which reduced the movement of dyes into the extracting phase during extraction process. Therefore, lessdyes were extracted resulting in low extraction efficiency. For further optimization, 5% w/v of NaCl was selected as the optimum condition for salt addition.

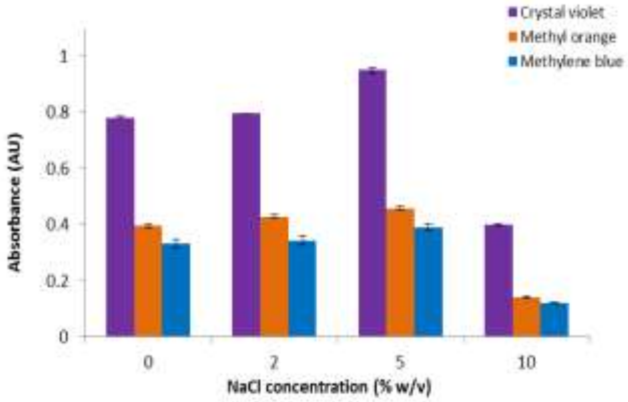


Figure 5 Effect of salt addition on the extraction of three selected organic dyes using MPTMOS-MTMOS stir bar. Extraction conditions: 50 min extraction time, 240 rpm stirring rate, 15 min UA-LD desorption using 3 mL methanol as desorption solvent.

3.1.6 pH of Sample Solution

The pH of sample solution was optimized at four different in order to study its effect on the extraction efficiency of organic dyes using MPTMOS-MTMOS coated stir bar (Figure 6). Highest extraction efficiency was achieved at pH 4 for the three organic dyes. At pH 4, the dyes are partially ionized (protonated). They present in molecule and also ionic forms. The high extraction efficiency of dyes is mainly contributed by two types of interactions; the dipole-dipole interaction and molecule-ion interaction between the dyes and extracting phase. Meanwhile, at pH 5.8 (no pH alteration), the dyes and extracting phase are in molecule form. The slight decrease in the extraction efficiency may be due to only dipole-dipole interaction present between dyes and extracting phase, resulting in lower extraction performance. Further increase in sample pH (pH 8) showed a drastic decrease in the extraction efficiency for all dyes. At basic condition, the reactive thiol group is ionized. Therefore, the interaction will only occur between the dyes and the backbone of the MPTMOS-MTMOS extracting phase (no interaction with thiol group), which resulted in the lower extraction efficiency. The optimum sample solution pH of pH 4 was selected for subsequent experiments. Similar condition for sample solution pH was also obtained from study by Ahmad *et al.*[18] for the removal of dyes from waste water.

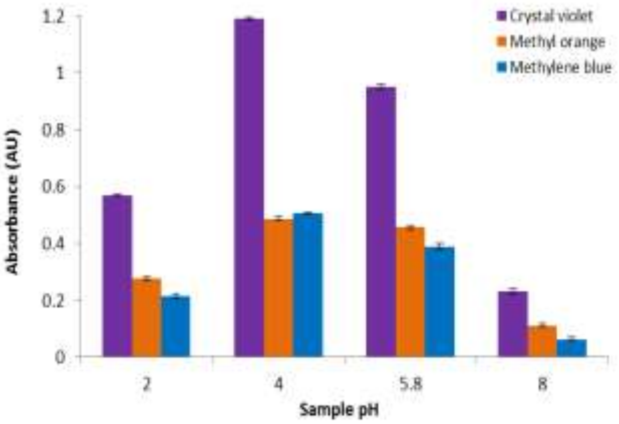


Figure 6 Effect of sample solution pH on the extraction of three selected organic dyes using sol-gel hybrid MPTMOS-MTMOS stir bar. Extraction conditions: 50 min extraction time, 240 rpm stirring rate, 5% w/v NaCl, 15 min UA-LD desorption using 3 mL methanol as desorption solvent.

3.2 Characterization of Sol-gel Hybrid MPTMOS-MTMOS

Physical characterization of sol-gel hybrid MPTMOS-MTMOS was carried out using Fourier transform infrared spectroscopy (FTIR) to observe the functional groups absorption and to confirm the formation of siloxane (Si-O-Si) linkages.

Figure 7 shows the spectra of raw MTMOS, MPTMOS and sol-gel hybrid MPTMOS-MTMOS. The spectrum of raw MTMOS shows the presence of absorption band of C-H stretching at 2945.84 cm^{-1} and Si-O-Si absorption bands at 1050.72 cm^{-1} and 847.04 cm^{-1}. Meanwhile, the spectrum of raw MPTMOS shows absorption bands of C-H stretching at 2941.96 cm^{-1} and strong Si-O-Si at 1074.80 cm^{-1} and 801.78 cm^{-1}. The spectrum also shows a weak absorption band of S-H stretching at 2564.91 cm^{-1}. For the spectrum of sol-gel hybrid MPTMOS-MTMOS, it shows absorption bands of Si-O-Si at 1004.36 cm^{-1} and 895.92 cm^{-1} and C-H stretching at 2930.51 cm^{-1}. The most significant feature of successful MPTMOS-MTMOS hybridization is the existence of weak S-H absorption band at 2555.40 cm^{-1}, which is the important characteristic of MPTMOS that can possibly aid the extraction of polar dyes due to its hydrophilic and reactive nature (thiol group, -SH).

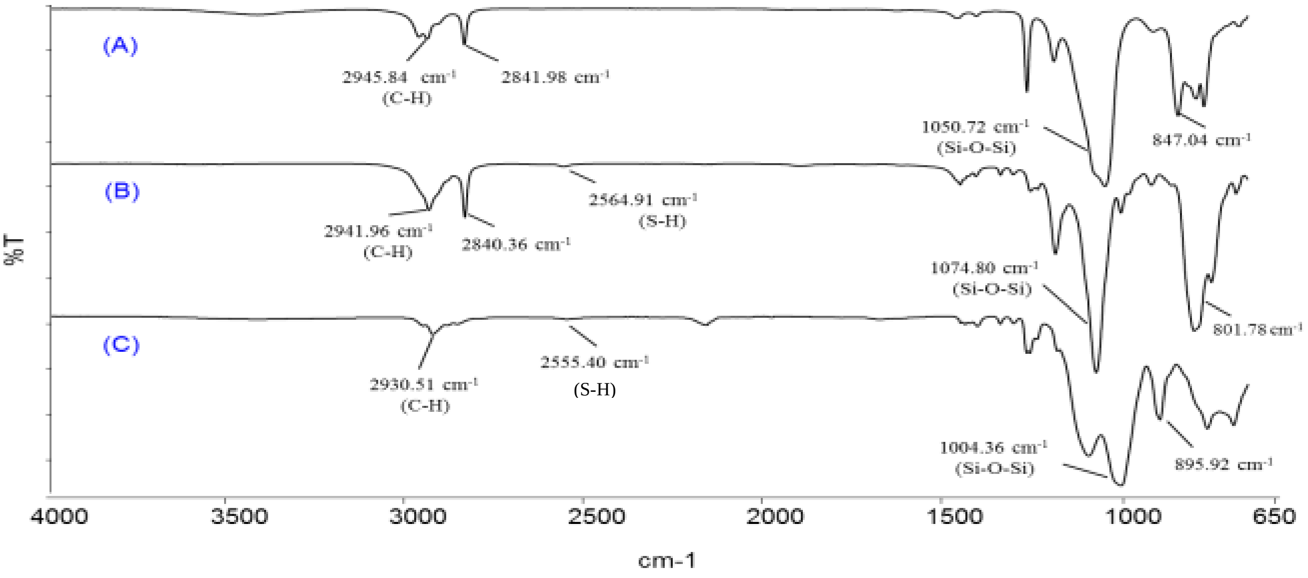


Figure 7 FTIR spectra of (A) raw MTMOS, (B) raw MPTMOS and (C) sol-gel hybrid MPTMOS-MTMOS

3.3 Comparison of Extraction Efficiency of Sol-gel Hybrid MPTMOS-MTMOS with Commercial Stir Bar

The extraction efficiency of sol-gel hybrid MPTMOS-MTMOS coating for the extraction of three selected organic dyes was compared (based on the absorbance of the dyes extracted) with commercial EG-silicone Twister™ coating (Figure 8). It was observed that the MPTMOS-MTMOS stir bar showed higher extraction efficiency compared to commercial EG-silicone Twister™ for all three organic selected dyes. The EG-silicone is a combination of ethylene glycol and PDMS. It gives moderate extraction performance of the selected dyes, which may due to the smaller size of stir bar. The sol-gel hybrid MPTMS-MTMOS stir bar is longer in size (20 mm) compared to EG-silicone Twister™ stir bar (10 mm). Thus, the in-house stir bar provides more extracting phase available for the extraction of dyes, and showed better extraction performance. The sol-gel hybrid MPTMOS-MPTMOS showed excellent selectivity for CV and good performance for MB and MO. This shows the potential of the sol-gel hybrid as an alternative adsorbent for analysis of the selected polar dyes.

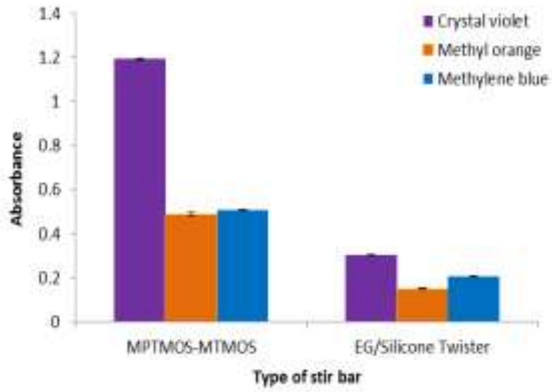


Figure 8 Comparison of extraction efficiency (based on absorbance) of the sol-gel hybrid MPTMOS-MTMOS as SBSE coating material and commercial EG-silicone Twister™ towards the three selected dyes under optimum conditions.

3.4 Method Validation

Calibration graph of analyte absorbance versus its concentration was performed to validate the SBSE-UV-Vis method towards CV, MO and MB dyes. The optimum SBSE conditions was applied to the extraction of three selected dyes from deionized water at varying concentrations (1-5 µg mL^{-1}) for CV and MB, and (2-10 µg mL^{-1}) for MO. Good coefficient of determination were obtained for CV (R^2= 0.9966), MB (R^2= 0.994) and MO (R^2= 0.9958). The LOD obtained for CV, MB and MO were 0.34, 0.42 and 0.75 µg mL^{-1}, respectively. The LOQ obtained were 1.12, 1.40 and 2.49 µg mL^{-1}, respectively.

3.5 Real Sample Analysis

River water sample was spiked with 2 µg mL^{-1} of each CV and MB and 4 µg mL^{-1} of MO to determine the accuracy and precision of the MPTMS-MTMOS-SBSE method. Average recoveries (72-85%) with RSD (3.4-4.1%) were obtained using the developed sol-gel hybrid MPTMS-MTMOS. Table 1 shows the average recoveries and precision of three selected organic dyes from river water using sol-gel hybrid MPTMS-MTMOS and commercial EG-silicone Twister™. The sol-gel hybrid MPTMS-MTMOS SBSE gave a better recovery (72.3 – 85.7%) and good precision (RSD <4.1%) compared to EG-silicone Twister™ stir bar (recovery: 61.7-68.3% and precision: RSD < 5.8%).

Table 1 Average recoveries (%) and precision (RSD) of three selected organic dyes from spiked river water

	MPTMS-MTMOS		EG-Silicone Twister™	
Organic Dyes	**Average Recovery (%)**	**RSD (%, *n* = 3)**	**Average Recovery (%)**	**RSD (%, *n* = 3)**
Crystal violet	85.7	4.1	68.3	5.4
Methyl orange	72.3	3.4	65.9	5.8
Methylene blue	74.2	3.9	61.7	5.3

4.0 CONCLUSION

A new sol-gel hybrid silica-based MPTMS-MTMOS as SBSE adsorbent for the extraction of three selected organic dyes namely crystal violet, methylene blue and methyl orange in water sample was successfully demonstrated. The MPTMS-MTMOS sol-gel hybrid coating showed better extraction performance for the selected organic dyes compared to commercial EG-silicone Twister™ coating. The introduction of MPTMS to MTMOS helped to increase the hydrophilicity of the material prepared and promote dipole-dipole interaction between polar dyes and the adsorbent material. The MPTMOS-MTMOS-SBSE method is safer in comparison to LLE, economical and environmental friendly and serves as promising alternative adsorbent for analysis of organic dyes in various aqueous matrices.

Acknowledgement

The authors would like to express an appreciation to Ministry of Education Malaysia under the Research University Grant (GUP) (Vote No: 04H22) for funding the project.

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