

Passive Sampling of Polycyclic Aromatic Hydrocarbons in Johor Strait by Sol-gel Polydimethylsiloxane

Cian Ying Tung^a, Razali Ismail^a, Jafariah Jaafar^{a*}

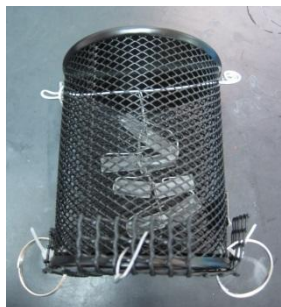
^aDepartment of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

*Corresponding author: jafariah@kimia.fs.utm.my

Article history

Received : 18 March 2013
Received in revised form :
26 April 2013
Accepted : 17 May 2013

Graphical abstract



Abstract

Passive sampling technique is an alternative technique in the monitoring of organic pollutants in aqueous environment. This technique is able to overcome several drawbacks of the conventional grab sampling technique. In this study, passive sampler consists of glass tubes coated with sol-gel polydimethylsiloxane (PDMS) were fabricated in the laboratory. The passive samplers were used to study the level and distribution of 15 polycyclic aromatic hydrocarbons (PAHs) in Johor Strait. Performance of the passive sampler was tested in the laboratory with an exposure system that has similar flow rate, temperature and water salinity with Johor Strait. Then, the passive sampler was deployed to five sampling stations located in Johor Strait for 7 and 30 days to accumulate PAHs in seawater. High performance liquid chromatography with fluorescence detector was used to analyze PAHs in the samples. All PAHs spiked in the exposure system were found to accumulate in the PDMS coating. Mass of 15 PAHs extracted from the passive sampler after deployment to Johor Strait was in the range of 0.372-1.131 ng/PDMS glass tube. Findings obtained from passive sampling method and seawater analysis were comparable. Passive sampling technique is low cost, simple and less solvent consumption.

Keywords: Passive sampling; polydimethylsiloxane; polycyclic aromatic hydrocarbons; Johor Strait

Abstrak

Teknik pensampelan pasif ialah satu teknik alternatif dalam pemantauan pencemar organik di persekitaran. Teknik ini dapat mengatasi beberapa kelemahan teknik pensampelan konvensional. Dalam kajian ini, pensampel pasif yang terdiri daripada tiub kaca yang disalut dengan sol-gel polidimetilsiloksana (PDMS) telah direka di makmal. Pensampel pasif ini telah digunakan untuk mengkaji tahap dan pengagihan 15 hidrokarbon aromatik polisiklik (PAH) di Selat Johor. Prestasi pensampel pasif telah diuji di makmal dengan menggunakan satu sistem pendedahan yang mempunyai kadar aliran, suhu dan kemasinan serupa dengan Selat Johor. Kemudian, pensampel pasif diletakkan di lima stesen pensampelan yang bertempatan di Selat Johor selama 7 dan 30 hari untuk mengumpul PAH dalam air laut. Kromatografi cecair prestasi tinggi dengan pengesan pendarfluor telah digunakan untuk menganalisis PAH dalam sampel. Semua PAH yang dicampur ke dalam sistem ujian makmal telah ditemui berkumpul di salutan PDMS. Jisim jumlah 15 PAH yang diekstrak dari pensampel pasif selepas penempatan di Selat Johor adalah dalam lingkungan 0.372-1.131 ng/PDMS tiub kaca. Keputusan yang diperolehi daripada kaedah pensampelan pasif dan analisis air laut adalah selaras. Teknik pensampelan pasif adalah berkos rendah, mudah diguna dan mengurangkan kegunaan pelarut.

Kata kunci: Pensampel pasif; polidimetilsiloksana; hidrokarbon aromatik polisiklik; Selat Johor

© 2013 Penerbit UTM Press. All rights reserved.

1.0 INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are carcinogenic pollutants that are widespread in the environment. Sixteen PAHs have been selected as the priority PAHs by United States Environmental Protection Agency (USEPA) [1]. PAHs enter surface waters mainly via atmospheric fallout, municipal effluents, urban run-off, oil spillage and industrial effluents [2]. Since the concentration of PAHs in water is extremely low (part-per-billion to part-per-trillion), analysis of

PAHs in water involves complex sampling and extraction procedures. Conventionally, bottle or grab sampling technique is applied to collect water samples from the study area and the samples are transported to the laboratory for extraction and analysis. This method has several disadvantages such as high cost, time consuming, labour intensive, high solvent consumption, and the concentration of individual spot water sample only represents the level of pollutants at the moment of sample collection [3-5].

Alternatively, passive sampler (PS) have been sought to overcome the limitations of conventional analysis method.

Initially, passive sampling technique has been developed to monitor airborne pollutants in work place air since 1927. The first PS used for monitoring of organic micro-pollutants in aqueous environment was introduced in 1987 [6-7]. PS is any device that consists of a receiving phase for sampling of the free flow analyte molecules from the sampled medium such as air, water and soil. The receiving phase can be a solvent, chemical reagent or a porous adsorbent [8]. Various PSs such as semi-permeable membrane device [9], triolein embedded acetate membranes [10], polyethylene device [11-12], Chemcatcher™ [13], membrane-enclosed silica material [14-16], silicon rubber [5, 17-18], PDMS rod [4] and polyoxymethylene sheet [19] have been developed for passive sampling of PAHs in aquatic environment. The advantages of PS are low cost, simple, miniature and do not require power supply. Besides, passive sampling technique usually combines sampling and enrichment of analyte into one step. Hence, extraction of pollutants in PS is faster, solventless and environmental friendly [20].

PAHs pollution in marine environment is a global scale issue and Johor Strait should be highlighted for pollution assessment due to the rapid development along the coastal area in recent years. Johor Strait is located at the southern-most tip of Peninsular Malaysia and it is a narrow stretch of water separating Peninsular Malaysia from Singapore. In 2006, Iskandar Development Region (IDR) was officially launched to develop an area of 2217 sq km land covering the whole southern part of the Johor State [21]. Large scale clearing of land is undergoing rapidly along the coastal of Johor Strait. Land reclamation, dredging of sediment, deforestation and shipment of construction materials increase the risk of PAHs pollution in Johor Strait. Furthermore, Johor Strait is receiving effluent from several polluted rivers in Johor such as Sungai Skudai, Sungai Danga and Sungai Segget. This situation is threatening the fishery industries especially the green mussel aquaculture in Johor Strait.

The aim of this study is to develop a sol-gel PDMS PS that is to be used to determine the level and distribution of 15 PAHs in Johor Strait. Sol-gel PDMS coating was firstly used in this study as a receiving phase for PS because most of the PSs reported in previous studies were constructed with commercially available polymer sorbents. In comparison with other polymeric materials, sol-gel PDMS has higher surface area and it can be made in the laboratory with relatively low cost. An exposure system was constructed in the laboratory to determine the capability of the PS to accumulate PAHs. This system consists of a glass tank filled with artificial seawater and the water was spiked with PAHs. The flow rate, salinity and temperature of water were adjusted according to the conditions in Johor Strait. The PS was then deployed in Johor Strait for 7 and 30 days to accumulate PAHs in seawater. Seawater samples were taken from the deployment sites during the collection of PS after 7 and 30 days of exposure. Concentrations of PAHs in seawater samples collected from Johor Strait were analysed and correlated with the findings of PS

2.0 EXPERIMENTAL

2.1 Materials

PDMS sol solution was prepared from hydroxyl-terminated polydimethylsiloxane (OH-PDMS), trimethoxymethylsilane (MTMOS), poly(methylhydrosiloxane) (PMHS) and trifluoroacetic acid (TFA) that were purchased from Sigma-Aldrich (USA) and JT Baker (USA). Analytical reagent grade chemicals such as dichloromethane, n-hexane, hydrochloric acid 35%, sulphuric acid 95%, sodium hydroxide pallet and anhydrous sodium sulphate were obtained from QReC (New Zealand).

Standard solution of 15 PAHs was prepared from EPA 610-N PAH kit (Supelco, USA). The kit containing standard materials of 15 PAHs include acenaphthene (ACNAP), anthracene (ANTH), benzo(a)anthracene (BAA), benzo(b)fluoranthene (BBF), benzo(k)fluoranthene (BKF), benzo(ghi)perylene (BGHIP), benzo(a)pyrene (BAP), chrysene (CHY), dibenzo(ah)anthracene (DAHA), fluoranthene (FLTH), fluorine (FLU), indeno(1,2,3-cd)pyrene (IND), naphthalene (NAP), phenanthrene (PHE) and pyrene (PYR). HPLC grade acetonitrile (ACN) and water were purchased from Tedia (USA) and Merck (Germany) respectively. Clean-up of seawater extract was performed using a 6 mL empty solid phase extraction cartridge (Macherey-Nagel, Germany) filled with 2 g of silica gel (Merck, Germany).

2.2 Preparation of PDMS Coated Glass Tubes

The glass tubes (2 cm length) were pre-treated with successive immersion of the tubes into purified water, dichloromethane, 1M NaOH and 0.1M HCl solution for 30 minutes respectively. After that, the tubes were rinsed with purified water and dried in oven at 120°C for 2 hours. Sol solution of PDMS was prepared according to procedure reported by Liu *et al.* [22]. In brief, a 400 mg of OH-PDMS was dissolved by 400 μ L dichloromethane in a micro-centrifuge tube. Then, 75 μ L MTMOS and 75 μ L PMHS were added and mixed with vortex. Lastly, 75 μ L aqueous TFA (95%) was mixed into the mixture by fast vortex for 1 minute. The pre-cleaned glass tube was immersed into the sol solution for 20 minutes. Coating process was repeated twice with fresh sol solution. The coating process must be carried out consistently in order to obtain glass tubes with constant weight. The coated glass tubes were placed in a desiccator at room temperature for 1 day to allow gelation. The remaining sol solution was characterised for infrared spectroscopy (IR) and scanning electron microscopy (SEM). Conditioning of coated glass tubes was carried out by dipping the glass tubes in acetonitrile and sonicated for 20 minutes.

2.3 Construction of PDMS Sol-gel Passive Sampler

The casing of the PS was a stainless steel canister with 5 mm holes. Eight PDMS coated glass tubes were tied together with stainless steel wire and attached into the canister. The outer layer of canister was protected with plastic fine mesh to reduce bio-fouling on the surface of sol-gel PDMS coating. Top of the canister was attached with a 1.5 m nylon rope to suspend the PS on the raft of green mussel farm or jetty. A brick was tied at the bottom of canister to allow full immersion of PS into seawater. Each PS was sealed in a plastic bag during transportation to the deployment sites to avoid contamination from atmosphere. Schematic diagram of the PS is shown in Figure 1.

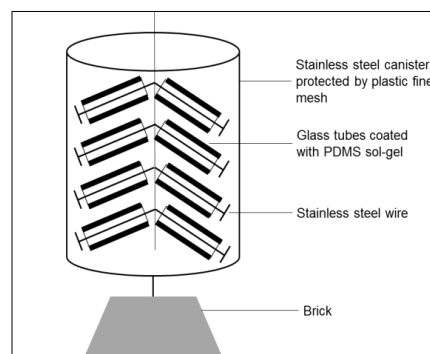


Figure 1 Schematic diagram of sol-gel PDMS passive sampler

2.4 Exposure System

The exposure system was constructed with a 20 L glass tank filled with 15 L artificial seawater. The water was adjusted to 26 g/L salinity using sea salt and temperature was maintained at 30 ± 3 °C with a temperature controller. Water flow rate of 30 mL/min was generated using a peristaltic pump. A 25 mL acetonitrile containing 7.5 ng/mL of each PAH compound was added to 15 L artificial seawater in the tank every day. Fifteen PDMS coated glass tubes were immersed into the tank for ten days and three glass tubes were collected from the tank at days 2, 4, 6, 8 and 10. Glass tubes were wrapped in aluminium foil and stored in freezer until analysis was carried out.

2.5 Deployment of Passive Sampler

Deployment of PSs was conducted from April to May 2012 along the coastal of Johor Strait. Five sampling stations are illustrated in Figure 2. The sampling stations are near to the green mussel farm (S2, S3 & S4), coastal construction areas (S1, S2 & S5) and jetty (S2, S3 & S5). At the sampling station, PS was taken out from plastic bag and immediately immersed into water at 0.5 m depth. Seawater samples were taken during the collection of PS after 7 and 30 days of deployment. Four glass tubes were collected from each PS after 7 days of deployment, another four glass tubes were collected after 30 days of deployment. Glass tubes were wrapped in aluminium foil and stored at 4°C in a cooler box during transportation to the laboratory. All glass tubes were stored in freezer until analysis was carried out.

2.6 Sample Analysis

PDMS coated glass tubes collected from exposure system and sampling stations were rinsed with purified water and wiped with lint-free tissue to remove bio-film attached on the coating. Each glass tube was immersed into 1 mL acetonitrile in a micro-centrifuge tube and PAHs in the PDMS coating were desorbed into acetonitrile by sonication for 30 minutes. The extract was enriched by a gentle stream of nitrogen gas until a volume of 300 µL.

Water samples collected from Johor Strait were extracted according to British Standard method, BS EN ISO 17993 [23]. In brief, a 1000 mL water sample was stirred with 25 mL n-hexane in an amber glass bottle for 60 minutes. The n-hexane layer was removed from water sample by using a separation funnel. The extract was concentrated to approximately 2 mL with rotary evaporator. Clean-up of extract was performed using 2 g of silica gel filled in an empty solid phase extraction cartridge. Elution of PAHs was carried out using 2×5 mL dichloromethane:n-hexane (1:1 v/v). The eluate was enriched to dryness under a gentle stream of nitrogen gas and the residue was reconstituted with 200 µL acetonitrile.

All sample extracts were filtered through a 0.2 µm pore size nylon membrane prior to HPLC analysis. PAHs were analysed by Agilent 1100 series HPLC with fluorescence detector. Separation of 15 PAHs was performed by Agilent ZORBAX Eclipse C18 PAH HPLC column (150 mm \times 4.6 mm I.D, 5 µm particle size). Gradient elution was applied to separate the PAHs in constant flow rate of 1.0 mL/min. The mobile phase gradient was programmed with initial mobile phase composition of acetonitrile:water (50:50 v/v) and held for 1 min, then the acetonitrile content was gradually increased to 100% at 17 min and held for 10 min at 100% acetonitrile. A 10 µL sample was injected to HPLC system and a programmed wavelength was used to detect the PAHs. Data acquisition was performed using Chemstation software.

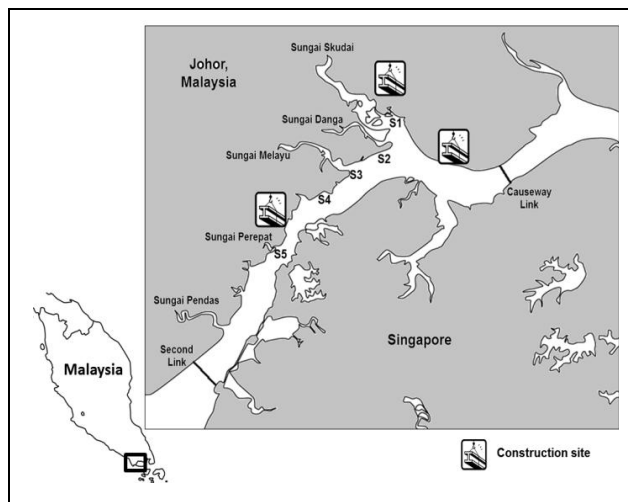


Figure 2 Sampling stations of passive sampler deployment in Johor Strait. S1: Sungai Skudai; S2: Green mussel farm 1; S3: Green mussel farm 2; S4: Green mussel farm 3; S5: Nusajaya

2.7 Quality Control

For blank analysis, glass tubes coated with sol-gel PDMS were deployed into the exposure system filled with blank artificial seawater. Method detection limit (MDLs) of PAHs were determined from the injection of spiked PS blank extracts and calculated using the lowest concentration of analyte which produced a peak with a signal-to-noise ratio of 3. Repeatability of PS reported as relative standard deviation (RSD) was calculated from the standard deviations obtained from the analysis of 3 glass tubes collected at the same days in the exposure system and after the field deployment. For recovery study, three glass tubes were deployed to the exposure system that filled with artificial seawater containing PAHs.

3.0 RESULTS AND DISCUSSION

PDMS is a silicone polymer that consists of a flexible Si-O backbone and a repeating Si(CH₃)₂O unit. The properties of PDMS are highly hydrophobic, non-toxic and not bio-accumulate [24]. PDMS is commercially available polymer that has wide applications and sol-gel technology can be used to prepare PDMS coating on a glass surface. Sol-gel coating has high thermal and chemical stability because chemical bonding occurs in between the sol-gel network and silanol groups on glass surface. Besides, sol-gel coating exhibits a porous surface structure with high surface areas that can provide more binding sites for analytes adsorption [25]. Therefore, sol-gel PDMS can be used as a polymeric sorbent for PS.

Before the coating process, glass tubes were pre-cleaned with 1M NaOH and 0.1M HCl in order to expose most of the silanol groups on glass surface for chemical bonding with sol-gel network [22]. In the preparation of PDMS sol solution, OH-PDMS was used as coating phase and MTMOS act as a sol-gel precursor. TFA was added to the sol solution to catalyse the combination of more OH-PDMS on the glass tube surface and form a loose sol-gel network. The role of PMHS is deactivation of surface and network. The sol-gel process starts with the hydrolysis of the sol-gel precursor, followed by polycondensation of hydrolyse products into a sol-gel network. After that, the sol-gel polymer is bonded to the silanol groups on the glass surface.

The active hydrogen atoms react with silanol groups to end-cap the remaining silanol groups [22].

IR was used to determine the functional group of the coating. The IR spectrum (Figure 3) of the PDMS coating showed a medium intensity peak at 2965.12 cm^{-1} which was attributed to C-H bond in methyl group. Peak for Si-H stretching occurred at 2165.54 and 912.30 cm^{-1} . Two strong peaks were observed at frequency of 1262.12 and 799.56 cm^{-1} , these peaks were contributed by the Me₂SiO group in the PDMS. The characteristic peaks of Si-O-Si were showed at 1098.33 and 1020.22 cm^{-1} in the spectrum. The broad peak at 3444.12 cm^{-1} was contributed by hydroxyl (-OH) stretching. Hydroxyl group occurred in PDMS coating because the TFA catalyst consist of 5% of water and polycondensation happened during the sol-gel coating process. IR spectrum obtained was comparable with the reference IR spectrum of pure PDMS polymer.

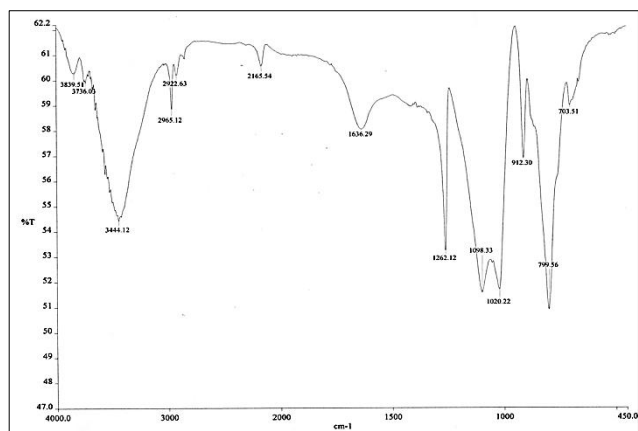


Figure 3 IR spectrum of PDMS sol-gel coating

PDMS coating checked by SEM with magnification $250\times$ (Figure 4(a)) illustrated the porous surface of sol-gel PDMS coating. The diameter of pores captured under a magnification $4000\times$ (Figure 4(b)) was approximately $3.4\text{ }\mu\text{m}$. The SEM micrograph shows homogenous pores of the sol-gel PDMS coating. The porous structure of the coating is able to enhance the surface area for solute-solid phase interactions and the PAH accumulation rate [22].

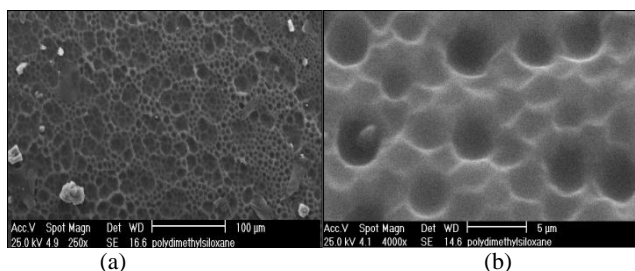


Figure 4 SEM of PDMS sol-gel coating under magnifications (a) $250\times$ and (b) $4000\times$

The exposure system was constructed to investigate the ability and performance of PS coating before it was deployed to the real study field in Johor Strait. Water turbulence generated by the peristaltic pump in the system allowed the diffusion of PAHs in artificial seawater to the sol-gel PDMS coating. Figure 5 shows

the increasing trend of PAHs accumulation in the PDMS coating when the exposure period was increased from 2 days to 10 days. Mass of total PAHs accumulated in the PDMS coating was in the range of 1.35 to 34.12 ng per PDMS coated glass tube. The accumulation of analytes depends on the sampler design, physicochemical properties of the analytes and environmental variables (i.e., water turbulence, water temperature and bio-fouling) [7, 27]. Figure 5 shows that accumulations of NAP, ACNAP, FLU, PHE, ANTH and FLTH ($\log Kow < 5$) were lower than the accumulation of PYR, BAA, CHY, BBF, BKF and BAP ($\log Kow > 5$) in the PDMS coating. These differences could be attributed to the difference in the octanol-water partitioning coefficient (Kow) between the PAH compounds. According to the study by Baltussen *et al.* [28], compounds with $\log Kow > 5$ showed better recovery by using stir bar sorptive extraction method with $55\text{ }\mu\text{L}$ of PDMS fiber. It is in agreement with the findings in this study. However, low accumulation rate for PAHs with high hydrophobicity such as DAHA, BGHIP and IND was observed. It could be due to the strong adsorption of these compounds onto the glass surface and other suspended particles and causing analyte loss [28].

RSD obtained from the analysis of three glass tubes collected from the PAHs spiked exposure system was 1.3-13.5%. MDL and recovery were in the range of 0.0048-0.0652 ng/PDMS glass tube and 41.5-103.6% respectively. No detectable PAHs were found in the PDMS coated glass tubes that were deployed to the blank exposure system. RSD obtained from triplicate analysis of glass tubes collected from field study was 0.4-17.2%.

In the field study, the mass of total PAHs retained in the PDMS glass tubes after 7 days and 30 days of deployment were 0.372-0.610 and 0.464-1.131 ng/PDMS respectively as indicated in Table 1. Lower molecular weight (LMW) PAHs were dominant over higher molecular weight (HMW) PAHs in the PDMS coating. Table 1 indicates that LMW PAHs such as NAP, ACNAP, FLU, PHE, ANTH, FLTH and PYR were frequently detected in the PS coating. The mass of LMW PAHs was 1.2-4.1 folds higher than the mass of HMW PAHs. LMW PAHs are abundant in crude and petroleum refinery products, while HMW PAHs are usually produced through incomplete combustion process. Therefore, pollution of LMW PAHs in Johor Strait might be associated with the oil leakage from poor maintenance fishermen boats and ships that use to transport the construction materials.

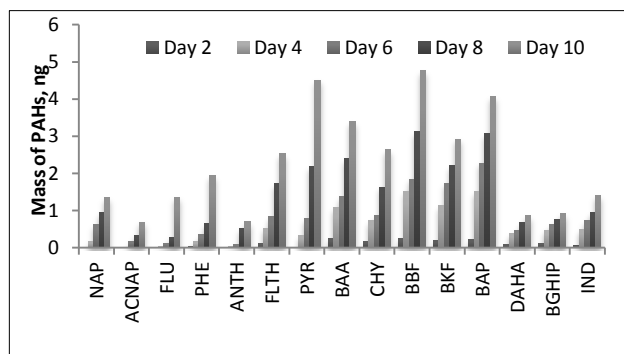


Figure 5 Mass of PAHs accumulated in the PDMS coating of passive sampler after an exposure of 2 to 10 days in a laboratory test system

In addition, Table 1 indicates that mass of total PAHs accumulated in PS that deployed for 30 days was higher than the 7 days. However, the increase in mass of PAHs in between two deployment periods was not significant. This could be due to the

establishment of thermodynamic equilibrium in between water and PDMS coating, if longer deployment period was applied. The net flow of PAHs from water to PDMS coating increased during the initial phase of exposure until equilibrium is achieved in the system [7]. Furthermore, uptake rate of PAHs by PS affected by bio-fouling on the PDMS coating. Bacteria and various flora and fauna were colonised to form a biofilm on the unprotected surface of PDMS coating that submersed in water. Biofilm formed a layer of barrier on the PS and affects the overall resistance to mass transfer [7]. In the preliminary study, PS was deployed directly

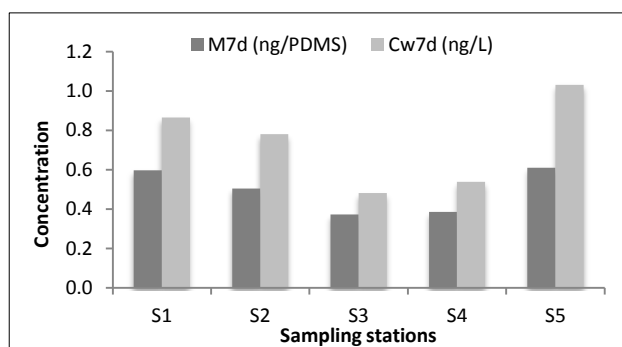
without protection of plastic mesh. Thick biofilm was observed on the PDMS coating after 30 days of deployment and most of the PAHs were not detected. In the second deployment, the PS was deployed with protection of plastic mesh and bio-film on the PDMS coating was reduced significantly. Sol-gel coating was not damaged by the colonising organism because it is water resistant, tough and not biodegradable. Thus, it is suitable to be used as a receiving phase for PS that will be usually deployed to drastic environment.

Table 1 Mass of PAHs (ng/PDMS) accumulated in PDMS coating of passive sampler deployed in Johor Strait for 7 days (M_{7d}) and 30 days (M_{30d})

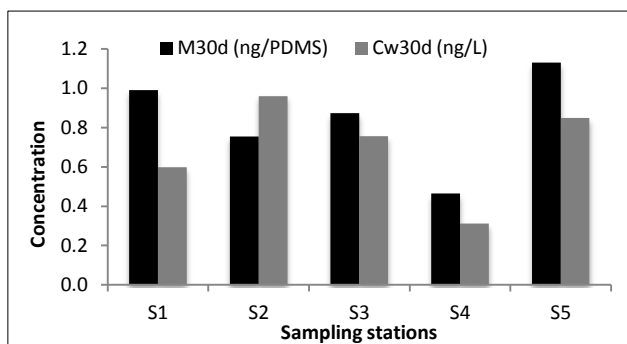
	S1		S2		S3		S4		S5	
	M_{7d}	M_{30d}	M_{7d}	M_{30d}	M_{7d}	M_{30d}	M_{7d}	M_{30d}	M_{7d}	M_{30d}
NAP	nd	0.157	nd	nd	nd	nd	nd	0.152	nd	0.221
ACNAP	nd	nd	nd	0.034	nd	nd	0.030	0.052	nd	0.045
FLU	nd	0.051	nd	nd	nd	0.046	nd	nd	nd	0.048
PHE	0.070	0.133	nd	nd	0.120	0.125	nd	0.033	0.189	0.110
ANTH	nd	nd	0.021	0.006	0.017	0.020	0.019	nd	nd	0.029
FLUTH	0.072	0.138	0.174	0.086	nd	0.226	0.174	nd	0.144	0.127
PYR	0.196	0.221	nd	0.135	nd	0.120	nd	0.110	nd	0.328
BAA	0.044	0.039	0.045	0.084	nd	nd	nd	nd	0.047	0.065
CHY	0.086	nd	0.118	0.085	0.065	0.103	nd	nd	nd	nd
BBF	0.065	0.052	0.090	0.074	nd	0.064	0.044	0.019	0.092	0.016
BKF	nd	0.012	0.017	0.016	nd	0.011	0.011	0.007	0.013	nd
BAP	0.033	0.044	0.040	0.061	0.065	0.042	0.035	0.039	0.043	0.046
DAHA	0.032	0.050	nd	0.050	0.083	0.050	nd	nd	0.083	0.053
BGHIP	nd	0.038	nd	0.058	nd	0.066	0.073	0.026	nd	nd
IND	nd	0.058	nd	0.066	0.022	nd	nd	0.026	nd	0.044
$\Sigma_{15\text{PAH}}$	0.597	0.991	0.505	0.755	0.372	0.873	0.386	0.464	0.610	1.131

nd – not detected

Seawater samples were taken during the collection of PS after 7 and 30 days of exposure. Figure 6 shows the comparison of total PAHs concentration in seawater and mass of total PAHs accumulated in PS after the deployment in Johor Strait. Concentrations of total PAHs in seawater collected at 7 and 30 days deployment period were in the range of 0.481-1.031 ng/L and 0.312-0.960 ng/L respectively. Figure 6 (a) shows that concentration of total PAHs in seawater was higher than mass of total PAHs accumulated in PS. In contrast, opposite trend was observed for the 30 days deployment as shown in Figure 6 (b). Mass of PAHs accumulated in PS was derived from the truly dissolved fraction of PAHs in seawater and concentration of PAHs detected in seawater samples was contributed by both dissolved PAHs and PAHs that associated with suspended solid [7]. Besides, the PDMS coating is more selective for pollutants with log Kow 5-6. Therefore, the concentrations of PAHs in seawater samples were slightly higher than the PS. Higher PAHs mass obtained in PS after 30 days of deployment was probably due to in-situ enrichment of PAHs by the PDMS coating.



(a)



(b)

Figure 6 Mass of total PAHs (M_{7d} & M_{30d}) accumulated in passive sampler deployed in Johor Strait and concentration of total PAHs (C_{w7d} & C_{w30d}) detected in seawater sample collected during the harvest of passive sampler after (a) 7 days deployment and (b) 30 days deployment

Overall, findings obtained from PS and seawater analysis presented a similar trend on the distribution of PAHs in Johor Strait. Levels of PAHs in sampling stations S1, S2, S3 and S5 were higher compare to S4. Distribution of PAHs is mostly influenced by anthropogenic activities around the sampling stations. Sampling stations S1, S2, S3 and S5 are located near with the coastal construction sites of Iskandar Malaysia (as shown in Figure 2). Land development activities such as dredging of sediment, land reclamation and shipment of construction materials are introducing pollutants to Johor Strait.

Moreover, PAHs pollution in S1 and S2 could be contributed by the wastes discharged from Johor Bahru through Sungai Skudai and Sungai Danga. Both rivers are flowing through several high population and intensive human activities areas in Johor States. In contrast, low PAHs level in station S4 was observed because this sampling station is located near with the coastal of undeveloped land that covered by mangrove forest.

4.0 CONCLUSION

PDMS coating was successfully produced using the sol-gel coating method. The porous sol-gel PDMS coating provides large surface area for PAHs adsorption. Findings obtained from the exposure system showed that the PDMS coating is efficient in the accumulation of PAHs with log Kow 5-6. PAHs were detected in PS exposed to waters in Johor Strait for 7 and 30 days. Long deployment period (e.g. 30 days) was suggested so that the PS was sufficiently adsorbed during the equilibrium phase. Further studies are recommended to determine the factors such as bio-fouling, flow rate and temperature that affect the PAHs uptake by PS. Results obtained from seawater analysis and passive sampling by sol-gel PDMS coated PS were compatible. Level and distribution of PAHs in Johor Strait were related with the anthropogenic activities along the coastline. Passive sampling method is a good alternative method for monitoring of organic pollutants in marine environment. The design of PS is simple, small, lightweight and low cost. In comparison with conventional methods, extraction of PAHs from PS is faster, solventless and less labour intensive.

Acknowledgement

We grateful for financial support received from the Ministry of Higher Education, Malaysia (MOHE); Universiti Teknologi Malaysia (UTM), Johor Bahru under vote number Q.J.130000.2626.03J46 and the School of Postgraduate Study, UTM for Zamalah UTM scholarship.

References

- [1] Hodgson, J. W., Bashe, W. J. & Bakar, T. V. 1990. *USEPA*. Method 550.
- [2] Srogi, K. 2007. *Environ. Chem. Lett.* 5: 169–195.
- [3] Deschamps, M. B., Daudin, J. J. & Barriuso, E. 2007. *J. Chromatog. A*. 1167: 143–153.
- [4] Zhao, W., Ouyang, G., Alae, M. & Pawliszyn, J. 2006. *J. Chromatog. A*. 1124: 112–120.
- [5] Prokes, R., Vrana, B. & Klanova, J. 2012. *Environ. Pollut.* 166: 157–166.
- [6] Namiesnik, J., Zabiegala, B., Kot-Wasik, A., Partyka, M. & Wasik, A. 2005. *Anal. Bioanal. Chem.* 381: 279.
- [7] Vrana, B., Mills, G. A., Allan, I. J., Dominiak, E., Svensson, K., Knutsson, J., Morrison, G. & Greenwood, R. 2005. *Trends Anal. Chem.* 24: 845–868.
- [8] Gorecki, T. & Namiesnik, J. 2002. *Trends Anal. Chem.* 21: 276–291.
- [9] Harman, C., Thomas, K. V., Tollefsen, K. E., Meier, S., Boyum, O. & Grung, M. 2009. *Mar. Pollut. Bull.* 58: 1671–1679.
- [10] Tang, J., Chen, S., Xu, Y., Zhong, W., Ma, M. & Wang, Z. 2012. *Environ. Pollut.* 164: 158–163.
- [11] Adams, R. G., Lohmann, R., Fernandez, L. A., Macfarlane, J. K. & Gschwend, P. M. 2007. *Environ. Sci. Technol.* 41: 1317–1323.
- [12] Fries, E. & Zarfl, C. 2012. *Environ. Sci. Pollut. Res.* 19: 1296–1304.
- [13] Vrana, B., Mills, G. A., Dominiak, E. & Greenwood, R. 2006. *Environ. Pollut.* 142: 333–343.
- [14] Vrana, B., Popp, P., Paschke, A. & Schuurmann, G. 2001. *Anal. Chem.* 73: 5191–5200.

- [15] Vrana, B., Paschke, A. & Popp, P. 2006. *Environ. Pollut.* 144: 296–307.
- [16] Paschke, A., Schwab, K., Brummer, J., Schuurmann, G., Paschke, H. & Popp, P. 2006. *J. Chromatog. A.* 1124: 187–195.
- [17] Rusina, T. P., Smedes, F., Koblizkova, M. & Klanova, J. 2010. *Environ. Sci. Technol.* 44: 362–367.
- [18] Yates, K., Davies, I., Webster, L., Pollard, P., Lawton, L. & Moffat, C. 2007. *J. Environ. Monit.* 9: 1116–1121.
- [19] Hawthorne, S. B., Jonker, M. T. O., Heijden, S. A., Grabanski, C. B., Azzolina, N. A. & Miller, D. J. 2011. *Anal. Chem.* 83: 6754–6761.
- [20] Zeng, E. Y., Tsukada, D. & Diehl, D. W. 2004. *Environ. Sci. Technol.* 38: 5737–5743.
- [21] Iskandar Regional Development Authority. 2010. *Annual report 2010*. Johor, Malaysia: IRDA. 16–17.
- [22] Liu, W., Wang, H. And Guan, Y. 2004. *J. Chromatog. A.* 1045: 15–22.
- [23] British Standard Institution. 2003. London. BS 17993: 2003.
- [24] Seethapathy, S. & Gorecki, T. 2012. *Anal. Chim. Acta.* 750: 48–62.
- [25] Yu, J., Dong, L., Wu, C., Wu, L. & Xing, J. 2002. *J. Chromatog. A.* 978: 37–48.
- [26] Guo, Y. & Colon, L. A. 1995. *Anal. Chem.* 67: 2511–2516.
- [27] Lobpreis, T., Vrana, B., Dominiak, E., Dercova, K., Mills, G. A. & Greenwood, R. 2008. *Environ. Pollut.* 153: 706–710.
- [28] Baltussen, E., Sandra, P., David, F. & Cramers, C. 1999. *J. Microcolumn Separations.* 11: 737–747.