

Analysis of Methylphenol Concentration in Selangor Rivers, Malaysia using Solid Phase Extraction Technique Coupled with UV-Vis Spectroscopy

(Analisis Kepekatan Metilfenol di Sungai-Sungai Selangor, Malaysia menggunakan Teknik Pengekstrakan Fasa Pepejal Digandingkan dengan Spektroskopi UV-Vis)

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ABSTRACT

Methylphenol is extensively produced from pharmaceuticals, agriculture, textiles, cosmetics, and petrochemicals industries. It is a pollutant that can adversely affect public health and the ecosystem. Following the issues raised, methylphenol extraction from Selangor rivers need to be done to avoid adverse consequences. In this study, solid phase extraction (SPE) combined with ultraviolet-visible spectroscopy (UV-Vis) detection at 271 nm was utilized to extract methylphenol from Selangor rivers. The challenges reported by applying the SPE technique was to identify the optimum conditions for extraction to guarantee effective recovery of the extracted methylphenol. Therefore, this research aimed to develop an extraction technique to extract methylphenol from Selangor rivers. In this study, 3 mL Supel Swift-HLB cartridges with bed weight of 60 mg were used as SPE cartridges. The optimum conditions for methylphenol SPE were 3 mL methanol as a conditioning solvent, 6 mL of pH 5 water sample with a contact time of 4 min with adsorbent bed was practiced during sample loading, 3 mL of acetonitrile as washing solvent, and 12 mL of acetone as the elution solvent. The concentrations of methylphenol detected at five different locations collected from Sungai Klang, Sungai Selangor, and Sungai Langat ranged from 5 to 6 mg L⁻¹. SPE coupled with UV-Vis is an appropriate method for methylphenol extraction as it simplifies sample preparation, is time saving, and can achieve a high percentage recovery of methylphenol.

Keywords: Methylphenol; pollutant extraction; Selangor river water; solid phase extraction; UV-Vis analysis

ABSTRAK

Kepadatan penduduk yang semakin meningkat di Selangor telah menyebabkan pembangunan pesat dalam aktiviti perindustrian dan domestik. Perkembangan ini telah menyebabkan kesan negatif terhadap alam sekitar terutamanya di sungai-sungai Selangor. Metilfenol yang dihasilkan secara meluas daripada industri farmaseutikal, pertanian, tekstil, kosmetik dan petrokimia merupakan bahan pencemar yang boleh menjejaskan kesihatan awam dan ekosistem. Berikutan isu yang dibangkitkan, pengekstrakan metil fenol di sungai Selangor perlu dilakukan bagi mengelakkan kesan buruk. Dalam kajian ini, gabungan pengekstrakan fasa pepejal (SPE) dengan pengesanan spektrofotometri ultralembayung nampak (UV-Vis) pada 271 nm digunakan untuk mengekstrak metil fenol dalam sampel air sungai Selangor. Cabaran yang dilaporkan dalam menggunakan teknik SPE termasuk mengenal pasti keadaan terbaik untuk digunakan semasa pengekstrakan bagi menjamin pemulihan berkesan metil fenol yang diekstrak. Justeru, kajian ini bertujuan untuk menentukan gabungan parameter optimum bagi SPE metil fenol dan untuk menentukan kepekatan

metil fenol dalam sampel air sungai di Selangor. Kartrij SPE yang digunakan dalam kajian ini ialah kartrij Supel™ Swift-HLB 3 mL dengan berat lapisan penjerap 60 mg. Keadaan optimum yang ditentukan bagi SPE metil fenol ialah 3 mL metanol sebagai pelarut keadaan, 6 mL sampel air pada pH 5 serta masa sentuhan 4 minit dengan lapisan penjerap digunakan semasa langkah pemuatan sampel, 3 mL aseton sebagai pelarut pencuci dan isi padu 12 mL aseton digunakan sebagai pelarut elusi. Kepekatan metil fenol yang dikesan di Sungai Klang, Sungai Selangor serta Sungai Langat adalah dalam lingkungan 5 hingga 6 mg L⁻¹. SPE-UV-Vis ialah kaedah yang sesuai untuk pengekstrakan metil fenol kerana ia memudahkan penyediaan sampel, menjimatkan masa serta membolehkan peratusan pemulihan metil fenol yang tinggi dicapai.

Kata kunci: Air Sungai di Selangor; analisis UV-Vis; metilfenol; pencemar; pengekstrakan fasa pepejal

INTRODUCTION

Rivers are one of the most crucial elements in the Malaysian ecosystem since they deliver a variety of roles, such as providing water for agricultural activities, domestic usage, numerous industries, and as a source of energy (Farid et al. 2016). However, the extensive growth of industries has raised the degree of water pollution in Malaysia. Particularly in Selangor, the rise in population due to rapid development in the state has contributed to the intensification in human activities which utilized lands alongside the riverbanks. This in turn has a detrimental effect on the water quality of Selangor rivers (Basheer, Hanafiah & Abdulhasan 2017).

Methylphenol, an organic molecule that binds directly to hydroxyl groups and has poor solubility in water (8.3 g/100 mL), is among the most widely detected pollutants in rivers due to its broad use in most industrial processes (Norseyrihan et al. 2016). Methylphenol compounds are residues from the manufacturing of pesticides, dyes, medications, perfumes, the petrochemical industry as well as photographic film developers (Noorashikin et al. 2014). Nonetheless, methylphenol is not just produced by human activities, but it is also generated naturally, such as from the decomposition of wood or leaves (He et al. 2014). Due to this natural process, methylphenol is also discovered in soils and sediments which lead to groundwater and wastewater pollution (Soto-Hernandez, Palma-Tenango & Garcia-Mateos 2017).

The presence of methylphenol in water systems is now a major global issue owing to its adverse effects on the environment (Norseyrihan et al. 2016). River water that has been contaminated by these compounds will threaten public health and the ecosystems (Farhan & Sapawe 2020). Methylphenol compounds are highly toxic even at low concentrations and have low

biodegradability properties. It has been recognized as one of the key contaminants in aquatic ecosystems by the US Environmental Protection Agency (EPA) and the European Union (EU). In Malaysia, 0.001 mgL⁻¹ is the tolerable bound of methylphenol concentration in wastewater. The European Community (EC) mandates the fixation of 0.5 µg/L for each phenol as the legal tolerance level in water intended for human intake (Hazrina et al. 2018; Nik Nur Atiqah et al. 2020). Furthermore, methylphenol has also been classified as a chemical that has the potential to cause carcinogenic effects. Therefore, it is very crucial to extract methylphenol from Selangor rivers to determine its concentration (Norseyrihan et al. 2016).

In recent years, various methods have been developed to extract contaminants from river water samples. This has helped in reducing the quantity of methylphenol that enters the waterways, especially in Selangor rivers. The most popular techniques for extracting methylphenol include solid-phase extraction (SPE), solid-phase micro extraction (SPME), liquid-liquid extraction (LLE) and several more (Ariffin et al. 2019). Conversely, LLE requires the use of large amounts of toxic organic solvents that are hazardous to health and form emulsions that complicate the target analyte extraction process (Ariffin et al. 2019; Belay et al. 2016). On the other hand, SPME has the drawbacks of analyte carryover, fiber breakdown at high pH value, as well as sensitivity and selectivity limits in complex matrices (Jalili, Barkhordari & Ghasvand 2020; Mercin et al. 2021; Noorashikin, Mohamad & Abas 2013).

SPE is an extraction technique that can extract various types of organic analytes from various types of samples from non-polar to highly polar (Emiroglu et al. 2021). Furthermore, it provides analyte extraction with high analyte concentration, producing highly pure

extracts and use less organic solvents as compared to other techniques which has a positive impact due to reduction of hazardous waste generation (Hazrina et al. 2018; Veloo & Ibrahim 2021). The extracted methylphenol then was analyzed with UV-Vis spectroscopy at detection of 271 nm. SPE emphasizes the significance of accurate selection of conditioning, washing, elution solvents and their volumes to achieve high percentage recovery of extracted analyte.

Cartridge of SPE such as Supel™ Swift HLB, a co-polymer SPE phase with both hydrophilic and lipophilic functional groups, was utilized as the adsorbent in this research. This phase is ideal for extracting a wide range of chemicals from aqueous samples such as food, environmental, and biological samples. The polymer material can retain a wide range of compounds with diverse polarity and LogP values due to its hydrophilic and lipophilic balanced (HLB) characteristics (Kraševac & Prosen 2018; Wang et al. 2022). This product is time saving in terms of simple sample preparation, thus reduces sample processing errors.

In this study, the optimization of parameters was implemented to determine the optimum condition of extracting methylphenol in water. Parameters such as pH value of sample as well as its volume, type of conditioning solvent, washing solvent, elution solvent, elution solvent volume, and contact time between sample and the adsorbent bed were studied to investigate the relation between these parameters with the percentage of extraction. The optimized parameters were utilized to determine the best combinations of SPE conditions to be tested with the real water samples from Sungai Klang, Sungai Selangor, and Sungai Langat at 271 nm wavelength.

MATERIALS AND METHODS

CHEMICALS AND REAGENTS

Methylphenol standard liquid with a concentration of 1000 mg/L was purchased from Sigma Aldrich (Germany). Methanol, which was used to dilute the methylphenol solution was bought from JT Baker (Malaysia). Apart from that, conditioning, washing, and elution solvents such as acetonitrile, acetone, and ethyl acetate were obtained from Fisher Scientific (Malaysia). A 100 mg L⁻¹ standard methylphenol solution was prepared in methanol and was diluted into 5, 10, 15, 20, and 25 mg L⁻¹ of working solutions. The pH value of the solution samples was adjusted with diluted hydrochloric acid or diluted sodium hydroxide solutions.

INSTRUMENTATION

Solid phase extraction of methylphenol was done by using Supel™ Swift HLB cartridge and Supelco Preppy™ Manifold which were purchased from Merck (Germany). Spectrum SP-UV 300SRB Spectrophotometer that was bought from Spectrum Instruments (Shanghai, China) was utilized to determine absorbance of methylphenol in the standard methylphenol solutions and the concentration of methylphenol in the Selangor rivers water samples. The detection was carried out at 271 nm wavelength.

PROCEDURE OF SOLID PHASE EXTRACTION

Generally, the SPE technique consists of four main steps which are conditioning, sample loading, washing, and eluting. Firstly, the SPE cartridge was installed on the SPE manifold. Three mL of methanol, which acted as the conditioning solvent, was added to the SPE cartridge. Next, 6 mL of pH 5 water sample was loaded into the cartridge and left retained for four minutes of contact time with the adsorbent bed. Thereafter, 3 mL of acetone which acted as the washing solvent was added to the cartridge and removed at 3 mL/min. Then, the vial was placed into the SPE manifold for eluent collections. Twelve mL of acetone as elution solvent was added to the cartridge to elute the methylphenol into the vial. Finally, the eluent was analyzed by using UV-Vis at 271 nm wavelength.

OPTIMIZATION OF PARAMETERS FOR METHYLPHENOL SOLID PHASE EXTRACTION

Conditioning Solvent

Three distinctive solvents (methanol, ethyl acetate and acetonitrile) were chosen to be tested for the optimization of methylphenol extraction conditioning step.

Washing Solvent

Different solvents (methanol, acetone, and acetonitrile) were utilized to optimize the washing step of SPE.

Elution Solvent

The elution step for the extraction of methylphenol was conducted using three different types of solvents (methanol, acetone, and ethyl acetate).

Sample pH

The methylphenol solutions were adjusted to five different

pH values (3, 6, 7, 9, and 12) with the use of dilute acid (hydrochloric acid) or dilute alkaline solution (sodium hydroxide) that were tested during sampling.

Sample Volume

To study the effect of sample volume on methylphenol SPE, different volumes of methylphenol solutions (3 mL, 6 mL, 9 mL, 12 mL, and 15 mL) were tested during the sample loading step.

Elution Solvent Volume

The impact of elution solvent volume on methylphenol extraction was investigated by using five different volumes for the elution step (3 mL, 6 mL, 9 mL, 12 mL, and 15 mL).

Contact Time

The extraction of methylphenol was conducted at different contact time between the methylphenol solutions

and the adsorbent layer (2 min, 4 min, 6 min, 8 min, and 10 min).

Water Sample Collection

Sampling for the determination of methyl phenol concentration in Selangor River water samples was collected from five different locations for each of the three rivers in Selangor, namely Sungai Klang, Sungai Selangor and Sungai Langat. Table 1 shows the locations where river water samples were taken. The amber glass bottle was cleaned three times before taking the river water sample. 500 mL of river water samples were collected using amber glass bottles that had been labelled in advance according to the name of the river, the location of the river and the date the sample was taken. The samples were then filtered using grade 1 Whatman filter paper to separate the large particles that were suspended with the water sample during the sampling process. Samples were stored in a cool place below 4 °C before SPE was performed.

TABLE 1. Information on sampling location of water samples

| River name | Sample name | Location |
|-----------------|-------------|--|
| Sungai Klang | SK1 | Tengku Ampuan Promenade Bridge, Shah Alam |
| | SK2 | Connaught Bridge, Klang |
| | SK3 | Pengkalan Pier of Kampung Delek, Klang |
| | SK4 | Sultan Suleiman Town, Port Klang |
| | SK5 | North Klang Straits Industrial Area, Port Klang |
| Sungai Selangor | SS1 | Tanjong Keramat Road, Kuala Selangor |
| | SS2 | Sungai Yu Fisherman's Market, Kuala Selangor |
| | SS3 | Pasir Penambang, Kuala Selangor |
| | SS4 | Bintara Jetty, Kuala Selangor |
| | SS5 | Batu 8 Kampung Asahan Jetty, Bestari Jaya |
| Sungai Langat | SS1 | Industrial Area Sg. Balak |
| | SS2 | Bangi Batu 18 Road, Sungai Tangkas |
| | SS3 | West Country Residential Area, Bandar Baru Bangi |
| | SS4 | Taman Sri Kejora, Kajang |
| | SS5 | Industrial Area Cheras Jaya |

RESULTS AND DISCUSSION

OPTIMIZATION PARAMETERS FOR EXTRACTION OF METHYLPHENOL IN WATER USING SOLID PHASE EXTRACTION

Effect of Type of Elution Solvent

Figure 1 shows the absorption of methylphenol when methanol, acetone, and ethyl acetate were used as elution solvents. The absorption values were 0.02, 3.12, and 0.85, respectively. Methanol and acetone are polarity solvents while ethyl acetate is a low polarity solvent (Han et al. 2019; Wang et al. 2022). From the absorbance value in the graph, acetone was more suitable for extraction of methylphenol. The interaction that occurred between methylphenol and the adsorbent which is HLB cartridge is hydrogen bonding, which is a strong interaction. This is because the methylphenol consists of hydrophilic group (OH) that interact with the Oxygen atom (O) from the hydrophilic part of the HLB cartridge. Supel™ Swift HLB SPE is a copolymer having both hydrophilic and lipophilic functional groups. Thus, the strong hydrogen interaction produced in this interaction makes the good results on methylphenol extraction was obtained. Therefore, this might be accomplished by employing a solvent that has high polarity to ensure the extraction of methylphenol from water become successful. Therefore, this indicated that acetone was a better elution solvent as compared to methanol and ethyl acetate.

Acetone with the highest absorption value proves its ability to disrupt the hydrogen bonding interaction between methylphenol and the adsorbent layer. This allows methylphenol which is a polar analyte to be eluted from a polar matrix such as water sample. Therefore, acetone was selected as the elution solvent that was optimal to be used during application on real water samples.

Based on previous research (Shakir et al. 2021), several solvents such as acetonitrile, methanol, methanol/ammonia (80/20, v/v), and methanol/acetic acid (80/20, v/v) were investigated. Based on outcome, the methanol/acetic acid (80/20, v/v) combination with the maximum extraction efficiency was selected as the best elution solvent type.

EFFECT OF SAMPLE pH

As illustrated in Figure 2, below is the absorbance against pH of solution at specific pH 3, 5, 7, 9, and 12. It clearly shows the low absorption of methylphenol at pH 3. This is due to the protonation of methylphenol species, which contributed to an increase in the ionic properties of methylphenol (Ahmad et al. 2022; Shakir et al. 2021). As a result of the less interaction between methylphenol and the adsorbent layer, only a limited quantity of methylphenol can be extracted from the adsorbent layer.

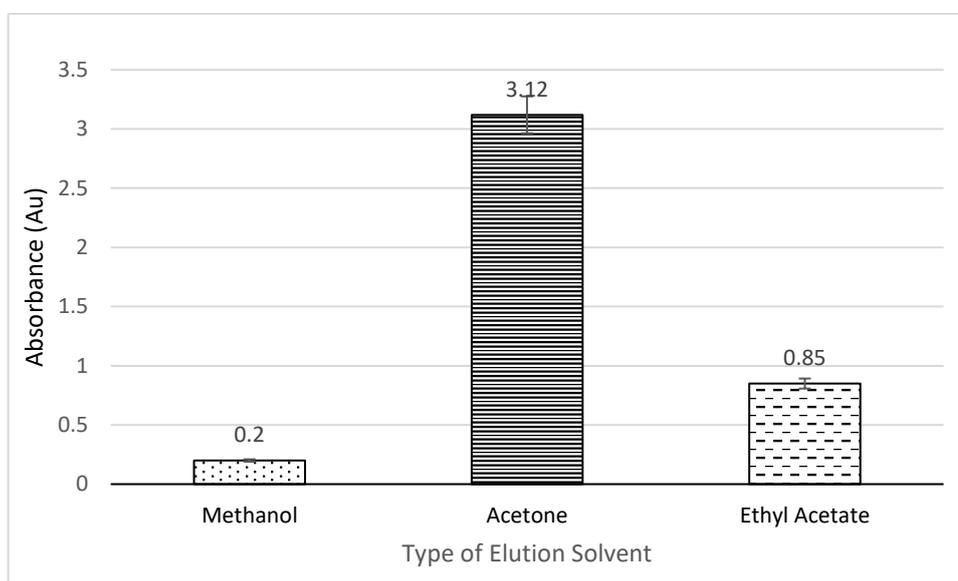


FIGURE 1. Graph of absorbance against type of elution solvent

This explanation is based on the pKa value of methylphenol which is 10.0 (pKa value: 10.0). At low pH (pH 3), the protonation of methylphenol started at acidic pH and due to the results show the low extraction of methylphenol lower compared to pH 5, which is at higher pH value for acidic state reduced the likelihood of protonation occurrence of methylphenol and in turn enhanced the interaction between methylphenol with the adsorbent layer. With that, more methylphenol was extracted, producing high methylphenol absorption values. Thus, there was an increase in the absorption value with increasing of pH value from pH 3 to pH 5.

The absorption of methylphenol that was extracted declined significantly from pH 5 to pH 7, as methylphenol existed in a neutral state at pH 7. This happened because uncharged methylphenol allowed it to less interact with the adsorbent layer which caused methylphenol to less bound to the adsorbent layer. This made methylphenol absorbance was the lowest at pH 7. The absorption of methylphenol at pH 9 to pH 12 was considered low because at this condition, the methylphenol was at deprotonation condition, therefore less interaction happened between the adsorbent and the methylphenol. This is significant with the pKa value of the methylphenol at pH 10. At the basic condition, the methylphenol is under deprotonation, thus the interaction is reduced

between the adsorbent and the methylphenol. This led to the lack of methylphenol amount that was extracted, which in turn produced a low value of absorption at pH 12. For the pH optimum, pH 5 has been selected for the best condition study in methylphenol extraction.

EFFECT OF TYPE OF CONDITIONING SOLVENT

Three types of polar solvents, which were methanol, ethyl acetate, and acetonitrile were selected for optimization of conditioning solvent for extracting methylphenol, as shown in Figure 3. This was because of the polar solvent promoted interaction between analytes and functional groups on the surface of the adsorbent by repelling the analyte out of the solution phase and made it more strongly attracted to the surface of the adsorbent (Ahmad et al. 2022; Shakir et al. 2021).

Figure 3 shows that the absorption value of methylphenol were 2.96 for methanol, 2.83 for ethyl acetate, and 2.93 for acetonitrile when these solvents were utilized as conditioning solvents. Methanol which produced the highest absorption value demonstrated that it was more efficient than ethyl acetate and acetonitrile in activating functional groups of adsorbents. This might be due to methanol's stronger polarity and lower viscosity as compared to the other two solvents (Ntombela & Mahlambi 2019).

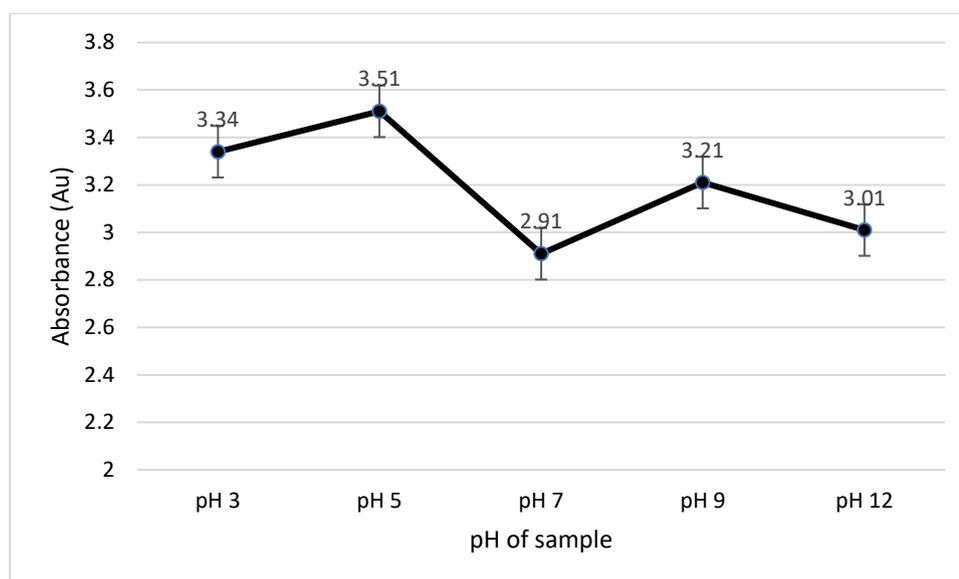


FIGURE 2. Graph of absorbance against pH of sample

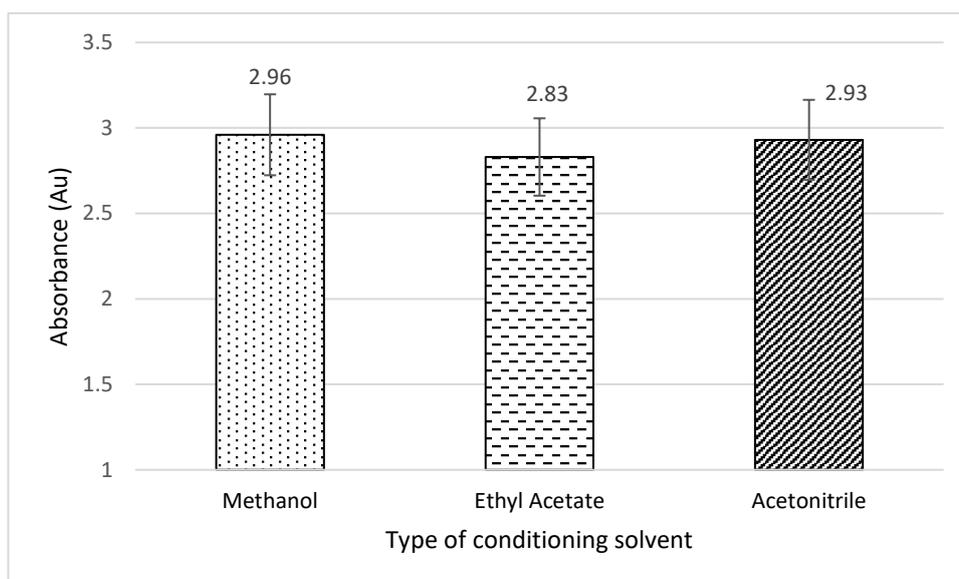


FIGURE 3. Graph of absorbance against the type of conditioning solvent

These properties made it more effective in penetrating adsorbent layers and opening up the pores on the surface of the adsorbent to produce effective interaction with analytes. This in turn increased the amount of methylphenol that was extracted. Therefore, methanol was selected as the best conditioning solvent to be utilized during the conditioning step for the extraction of methylphenol from real water samples. Based on Danato et al. (2015)'s findings, methanol was used as the conditioning solvent and the recoveries ranged from 70% to 117.3%.

EFFECT OF TYPE OF WASHING SOLVENT

The interference components usually remain bonded together with the analyte during sample loading. To remove interference components without eluting the desired analyte ahead of time before the elution step, a washing step is required. Figure 4 shows the graph of absorbance against the type of washing solvent.

All tested washing solvents allowed the removal of interference components. As shown in Figure 4, the reading for the absorption value for washing solvent used, namely methanol, acetonitrile, and acetone were 2.98, 3.86 and 2.88, respectively. Acetonitrile showed the highest absorption value as compared to methanol and acetonitrile. This was because when a solvent can remove more interference components, it will provide

more space for methylphenol to be adsorbed on the surface of the adsorbent (Arias et al. 2020; Dan et al. 2022). Due to its highest methylphenol absorption value, acetonitrile was chosen as the best washing solvent to be utilized on the extraction of real water samples.

According to the previous study (Arias et al. 2020), a solvent commonly used as a cleaning solvent was a porogenic solvent. Therefore, acetonitrile and water-acetonitrile mixtures were evaluated in the experiments, where acetonitrile was chosen as it produced the highest recovery at 94% to 100%.

EFFECT OF SAMPLE VOLUME

Figure 5 shows a graph of absorbance against sample volume. The volume of samples loaded on the SPE cartridge needs to be ensured to allow the maximum amount of methylphenol to interact with the active site of the adsorbent and consequently contribute to a high methylphenol absorption value.

The absorbance against sample volume graph above displays the absorption values of 3.00, 3.33, 3.06, 3.10, and 2.95 for sample volumes of 3 mL, 6 mL, 9 mL, 12 mL, and 15 mL, accordingly. In this study, it was found that the absorption of methylphenol increased from 3 mL to 6 mL, and thereafter, the absorption value decreased moderately. Absorption of methylphenol with a low sample loading volume of 3 mL indicated an

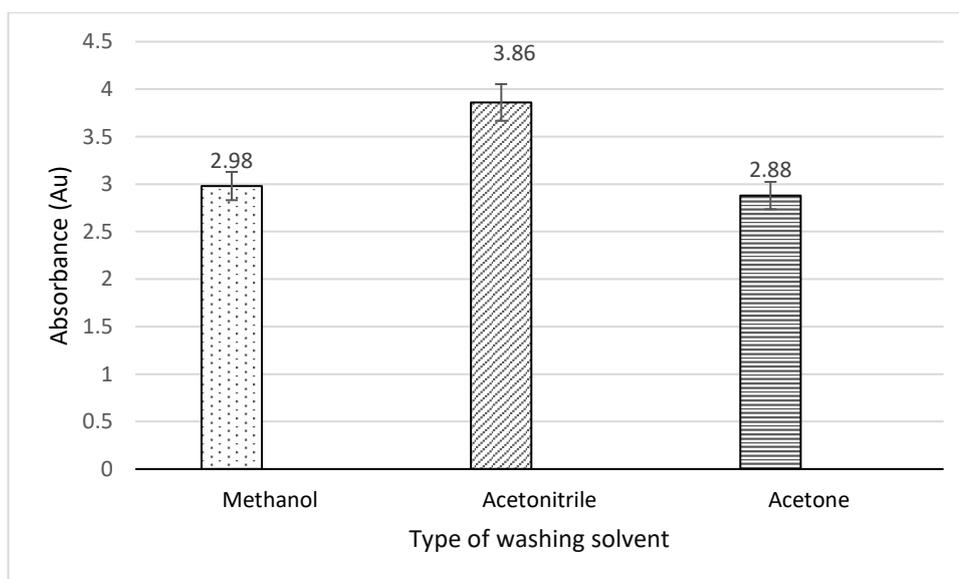


FIGURE 4. Graph of absorbance against type of washing solvent

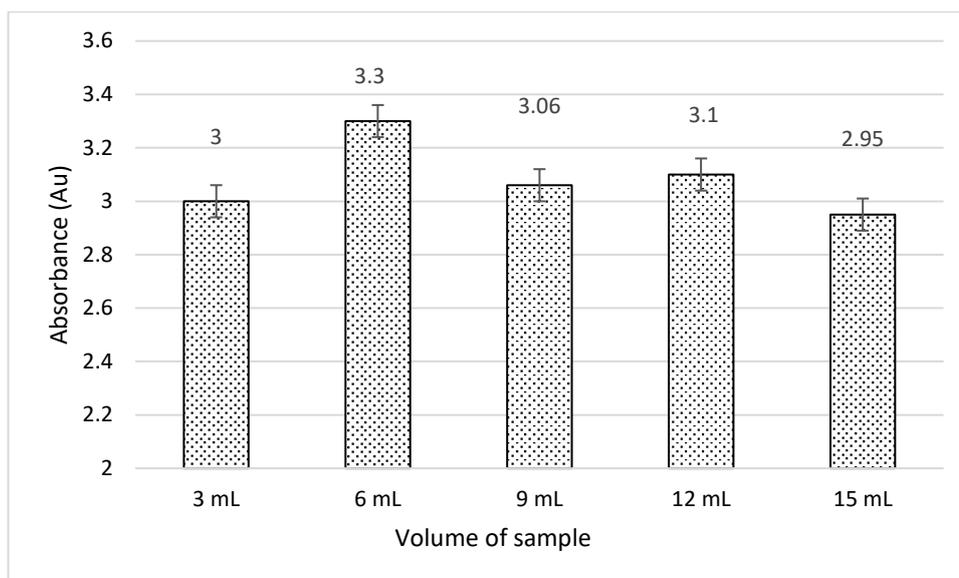


FIGURE 5. Graph of absorbance against volume of sample

insufficient amount of methylphenol that interacted with the active site of the adsorbent layer.

The best absorption value for the SPE adsorbent was determined on the loading volume of 6 mL, which indicated that the analyte was fully bonded to the active site. When a volume greater than 6 mL was loaded, the

analyte absorption deteriorated, and this was due to the active site of the adsorbent had become too saturated. Active sites that had become too saturated result in excess methylphenol that cannot be bounded to the active site. Therefore, 6 mL of sample volume was

considered the optimal sample volume for real water sample extraction.

The optimal volume of the sample was determined in the research of Belay (2016) using multiple sample quantities ranging from 5 mL to 80 mL. According to the findings, the extraction efficiency gradually improved from 10 mL to 50 mL and showed minimal variation. As a result, 50 mL was determined to be the optimal sample volume in their experiments.

EFFECT OF ELUTION SOLVENT VOLUME

Five different volumes were tested for the elution solvent volume optimization experiment, which were 3 mL, 6 mL, 9 mL, 12 mL, as well as 15 mL. Figure 6 shows the graph of absorbance against the volume of the elution solvent.

According to Figure 6, the obtained absorbance value for each of the mentioned volumes were 2.99, 3.08, 3.08, 3.72, and 3.11, respectively. The graph shows the trend of increased absorption value from a volume of 3 mL to 12 mL. When the volume of the elution solvent used was greater than 12 mL, the absorption value of methylphenol began to decrease. This may be due to the high volume of elution solvent that caused methylphenol to dissolve in the adsorbent layer (Ariffin et al. 2019; Maranata, Surya & Hasanah 2021). Therefore,

12 mL was preferred as the volume of elution solvent to be applied during the SPE elution step on real water samples.

In terms of the strength factors of all parameters optimized, the elution solvent required adequate volume to elute all target analytes from the adsorbent layer. Therefore, 0.8 mL was the optimal volume of solvent reported to be able to totally elute the desired analytes.

EFFECT OF CONTACT TIME

The effect of contact time between methylphenol with the adsorbent layer was tested at 2 min, 4 min, 6 min, 8 min, and 10 min. In this study, a short contact time is very beneficial for saving extraction time. The optimal contact time will allow maximum retention of methylphenol at the active site of adsorbent which will contribute to the effective separation of methylphenol from water samples. Figure 7 shows a graph of absorbance against contact time.

Based on Figure 7, the absorption values at the periods of 2 min, 4 min, 6 min, 8 min, and 10 min were 3.11, 3.59, 3.24, 2.99, and 2.91, respectively. The graph also indicates that a contact time of 4 min gave the maximum absorption value. These 4 min of contact time allowed methylphenol to interact with the adsorbent layer of the SPE cartridge at the optimum level and enabled it

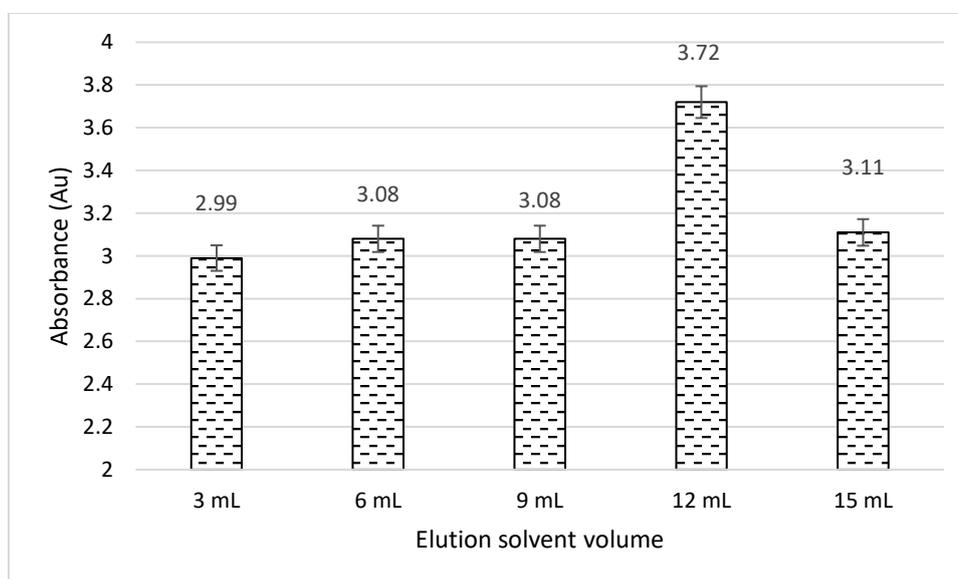


FIGURE 6. Graph of absorbance against volume of elution solvent

to break the hydrogen bond between methylphenol and the sample water molecule effectively. Disrupting the bond between methylphenol and water samples increases the quantity of methylphenol bound to the adsorbent layer, thus enhancing the amount of methylphenol extracted (Ferial et al 2021; Hazrina et al. 2018; Idris et al. 2019; Zhang et al. 2018).

Contact time exceeding 6 min denoted a downward trend in the absorption value. This is most likely due to excess contact time with the adsorbent layer caused the analyte to dissolve in the adsorbent layer or evaporate into the air. With that, 4 min was chosen as the contact time between methylphenol with the adsorbent layer for the SPE technique as it produced the highest absorption peak as compared to the other time period.

In a study by Othman and Harry (2021) and Tsukagoshi et al. (2002), the effect of contact time was investigated from contact time ranging from 5 min to 40 min. The extraction recovery reached more than 90% after only 5 min of contact time and increased gradually up to 20 min. After 20 min, the recovery of extraction remained consistent as the time period increased. Therefore, 20 min was selected as the best value based on the results.

METHOD VALIDATION AND ANALYSIS OF METHYLPHENOL IN REAL WATER SAMPLES

Under optimised conditions, a series of experiments based on linearity, limit of detection, limit of quantification, and precision were evaluated to validate the developed method. It can be seen from Table 2 that the present method has a wide linear range and good method precision. In this case, the methylphenol exhibited good linearity with correlation coefficient which is 0.9998. The LOD and LOQ values of the parabens were found in the range of 0.045 $\mu\text{g/L}$ and from 0.78 $\mu\text{g/L}$. Precision which was expressed as relative standard deviation (RSD) was presented in terms of repeatability (from five independent sample preparations, intra-day RSD) and reproducibility (studied during three consecutive days, inter-day RSD); the values for intra-day RSD% were 2.7% and those of inter-day RSD% were in the range of 1.8%.

As noted earlier, actual water samples were taken from five different locations at Sungai Klang, Sungai Selangor and Sungai Langat. Figures 8 and 9 show examples of absorbance against wavelength graphs for sample SK4 and sample SL2 which both exhibited the highest peak at 271 nm.

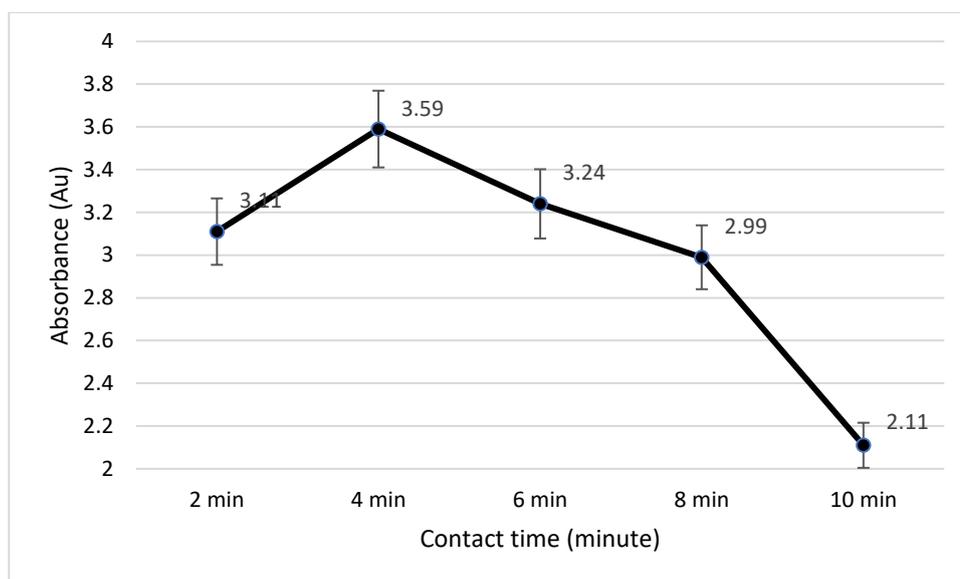


FIGURE 7. Graph of absorbance against contact time

TABLE 2. Information of method validation of methylphenol

| Analyte | Linearity ($\mu\text{g/L}$) | R^2 | LOD ($\mu\text{g/L}$) | LOQ ($\mu\text{g/L}$) | Precision | | Recovery of spiked amount (1 $\mu\text{g/L}$), %RSD) |
|--------------|----------------------------------|--------|----------------------------|----------------------------|-----------------------------|-----------------------------|--|
| | | | | | Intra-day (RSD%, n=5) | Inter-day (RSD%, n=3) | |
| Methylphenol | 0.2-1.0 | 0.9998 | 0.045 | 0.76 | 2.7 | 1.8 | 95% (2.1%) |

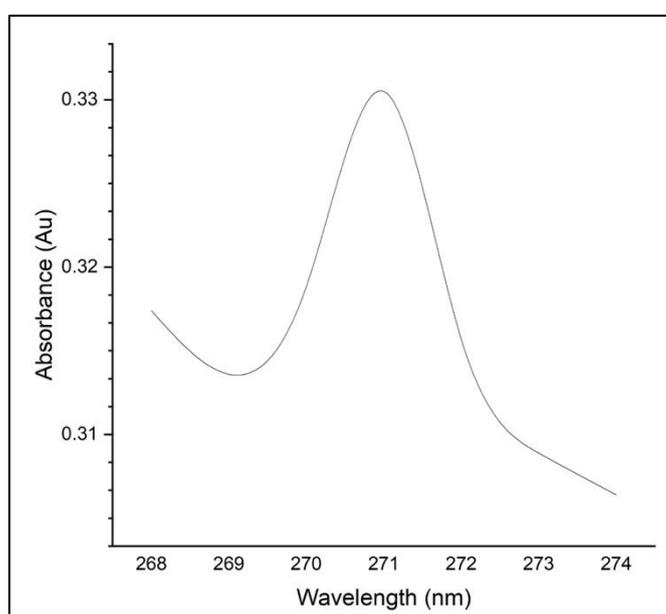


FIGURE 8. Graph of absorbance for SK4

Methylphenols are used by businesses in a variety of industries, including agriculture, medicine, the food industry, and chemistry. As shown in Tables 3, 4, and 5, all water samples showed excellent concentrations in the range of 0.20 mg L^{-1} to 0.69 mg L^{-1} . The results showed the accuracy of SPE method, and the concentrations detected validated the effectiveness of the SPE method for real water samples. The SK4 sample showed the highest detected concentration detected of 0.69 mg L^{-1} , where the sample was taken from the Sungai Klang, specifically at Sultan Suleiman Town, Pelabuhan Klang. The highest

concentration of methylphenol was detected in SK4 Kuang due to an agriculture, food processing company that is located upstream of the river. Any solid/liquid waste produced by that company might be the reason for this. The lowest concentration detected in Sungai Klang was from the SK3 sample with a concentration of 0.52 mg L^{-1} and it was collected from Pengkalan Kampung Delek Jetty, Klang.

The highest concentration of methylphenol extracted from Sungai Selangor was 0.82 mg L^{-1} , which was the SS1 sample collected from Tanjung Keramat

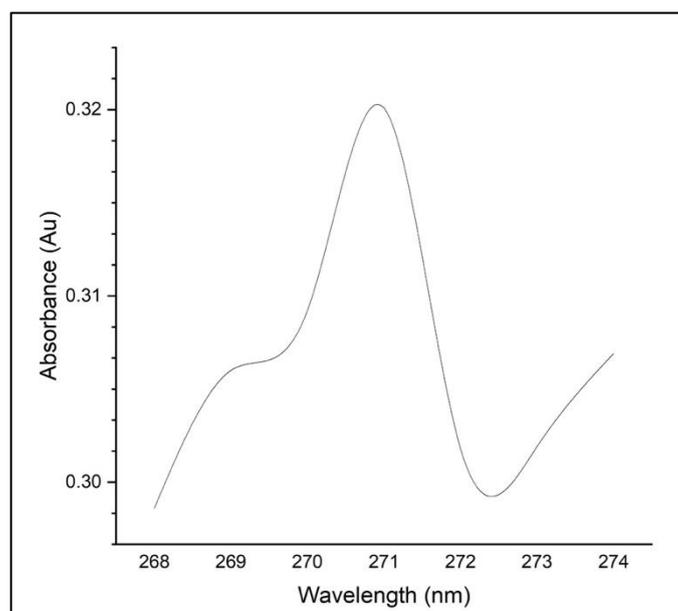


FIGURE 9. Graph of absorbance for SL2

Road, Kuala Selangor. SS1 is accumulated with large amounts of plastic rubbish and debris from housing areas and restaurants, which might also cause the leach of a large amount methylphenol. High concentration of methylphenol in SS1 is mainly caused by food and beverage factories, commercial centers, storm water releases from residential areas, and public sewage treatment plants. The lowest concentration detected in Sungai Selangor was in the SS5 sample from Batu 8 Jetty Kampung Asaham, Bestari Jaya with a concentration value of 0.20 mg L⁻¹.

Finally, samples SL1 and SL5 showed the same value of concentrations that were 0.65 mg L⁻¹ and at the same time were the highest concentrations of methylphenol identified in Sungai Langat. Both SL1 and SL5 samples were, respectively, collected from Sungai Balak Industrial Area and Industrial Area Cheras Jaya. These areas show the highest concentration of

methylphenol because there are the food industry and chemistry production factories were involved mostly.

On contrary, the lowest concentration of methylphenol in Sungai Langat was 0.23 mg L⁻¹ attained from SL2 samples acquired from the Bangi Batu 18 Road, Sungai Tangkas. This is the residential area and the restaurants, most probably the methylphenol produced from the reactions that involved others compounds from the industrial area nearby to this residential area. Tables 3, 4, and 5 show the concentrations of methylphenol in Sungai Klang, Sungai Selangor, and Sungai Langat that had been determined.

It was found that all methylphenol concentrations in the 15 samples that were tested exceeded the 0.001 mg L⁻¹ acceptable limit of methylphenol concentration in water in Malaysia. In conclusion, the optimized SPE method developed can be used to monitor methylphenol compounds in environmental water samples.

TABLE 3. Concentration of methylphenol in Sungai Klang

| Sungai Klang sample | Methylphenol concentration (mg/L) |
|---------------------|-----------------------------------|
| SK1 | 0.52 |
| SK2 | 0.56 |
| SK3 | 0.52 |
| SK4 | 0.69 |
| SK5 | 0.55 |

TABLE 4. Concentration of methylphenol in Sungai Selangor

| Sungai Selangor sample | Methylphenol concentration (mg/L) |
|------------------------|-----------------------------------|
| SS1 | 0.82 |
| SS2 | 0.26 |
| SS3 | 0.24 |
| SS4 | 0.28 |
| SS5 | 0.20 |

TABLE 5. Concentration of methylphenol in Sungai Langat

| Sungai Langat sample | Methylphenol concentration (mg/L) |
|----------------------|-----------------------------------|
| SL1 | 0.65 |
| SL2 | 0.20 |
| SL3 | 0.25 |
| SL4 | 0.33 |
| SL5 | 0.65 |

COMPARISON OF DEVELOPED METHOD FOR EXTRACTION OF METHYLPHENOL IN REAL WATER

The method developed was compared with the methods of previous studies reported in literature reviews for the determination of analyte concentrations in ambient water samples. This SPE-UV-Vis's method was compared with other studies in terms of the type of SPE cartridges used, types and volumes of conditioning solvent, washing solvent and elution solvent, pH and volume of sample, analytical techniques utilized to determine analyte concentrations, as well as concentrations detected from the SPE technique (Fiehn & Jekel 1997; Shazana, Masturah & Noorashikin 2022). The study focused on the comparison of concentration values obtained from the developed method showed a better concentration than the concentrations reported in the literature review.

Table 6 shows the comparison of SPE applications in another research. The advantages of the listed method in Table 6 is most of the method can detected the low concentration of analyte has been extracted using SPE method from various samples. It shows that the sensitivity of the SPE cartridge is acceptable in determination of various pollutants from various samples. Currently, there have a variety of cartridge in the market, but the suitability of samples, analytes with the SPE cartridge is also importance factors that need to be focused before study been started.

The limitations of the listed method in Table 6 is most of the methods using high volume of sample which is around 100 mL to 200 mL. This range of sample volume is considered bulky in the current research and not easy to collect and kept the high samples volume at the laboratory.

TABLE 6. Comparison of SPE application in another research

| Analyte | Matrix | Cartridge type | Sample pH and volume | Type and volume of conditioning solvent | Type and volume of washing solvent | Type and volume of elution solvent | Analytical technique | Concentration ($\mu\text{g L}^{-1}$) | Reference |
|--|-----------------------------------|----------------------|----------------------|---|---|---|----------------------|--|----------------------------|
| Methylphenol | River water | Supel Swift HLB | 5 (6 mL) | Methanol (3 mL) | Acetone (3 mL) | Acetone (12 mL) | UV-Vis | 5000-6000 | Current method |
| Priority pesticides and organic pollutants | River water | Oasis HLB | - (200 mL) | Dichloromethane (6 mL), acetonitrile (6 mL), Water (6 mL) | Water (1 mL) | Acetonitrile-dichloromethane (2.5 mL), dichloromethane (3.2 mL) | GC-MS | 0.05-2 | (Veloo & Ibrahim 2021) |
| Chlorophenol | River water | SDS-alumina | 2 (200 mL) | - | Water (50 mL) | Acetonitrile (1 mL) | LC-UV-Vis | 0.05-1 | (Tsukagoshi et al. 2002) |
| Phenolic compound | Surface water, reused water | LiChrolut EN | - (1000 mL) | Acetone (6 mL), Air (6 mL) | Water (3 mL) | Acetone (1 mL) | CE-CL | 0.02-0.082 | (Tsukagoshi et al. 2002) |
| Chlorophenol | Well, tap and river water samples | Bond Elut PPL | 2.5 (100 mL) | Acetone (2 mL), Water (2 mL) Methanoll | Water (2 mL) | Acetone (1 mL) | GC-ECD | 0.0000005-0.0001 | (Farhan & Sapawe 2020) |
| Phenolic compound | Waste-water effluent | Supelclean EnviChrom | 4.5 (250 mL) | (7 mL) Water (10 mL) | Water (10 mL) | Methanol (7 mL) | HPLC | 0.001-0.02 | (Fiehn & Jekel 1997) |
| Ibuprofen, diclofenac, acetylsalicylic acid, acetaminophen, caffeine adulterants | Herbal medicines | Oasis HLB | 4.5 (100 mL) | Acetonitrile (3 mL) Methanol (3 mL), Water (3 mL) | Water (3 mL) | Formic acid in acetonitrile (4 mL) | LC-MS/MS | 0.0006 | (Emirođlu et al. 2021) |
| Pesticides | Surface water | Oasis HLB | - (100 mL) | (3 mL), Water (3 mL) (3 mL) | Water (3 mL) | Methanol (10 mL) | GC-MS | 0.224-3.509 | (Ntombela & Mahlambi 2019) |
| Pesticides | Surface water | Strata™-X SPE | 2.5 (100 mL) | Methanol (3 mL) | Ultrapure water (6 mL) | Dichloromethane: Methanol (1:1 v/v) (2 mL) | GC-MS/MS | 0.02-0.55 | (Kraševac & Prosen 2018) |
| Pesticides | Surface water | Oasis HLB | - (250 ml) | Methanol: dichloromethane mixture, deionised water (10 mL) Methanol (3 mL), Distilled water (6 mL) | Distilled water (5 mL) | Methanol: dichloromethane (10 mL) | LC-MS | 0.0059-0.0178 | (Donato et al. 2015) |
| Pesticides | Waste-water effluent | C ₁₈ | - (10 mL) | (3 mL), Distilled water (6 mL) | Methanol: water (10:90 v/v) (10 mL) | Methanol (5 mL) | LC-MS/MS | 0.016-0.017 | (Arias et al. 2020) |

CONCLUSION

SPE coupled with UV-VIS Spectroscopy technique using Supel™ Swift HLB cartridges for extraction of methylphenol in Sungai Klang, Sungai Selangor, and Sungai Langat has been successfully developed with the range of concentration extracted of 5 to 6 mg L⁻¹. In conclusion, the method developed has great potential in analytical analysis of real water samples.

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