

Evaluation and Optimization of a New Approach on Phenol Extraction from Real Water

(Penilaian dan Pengoptimuman Pendekatan yang Baharu untuk Memisahkan Fenol daripada Air Semula Jadi)

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ABSTRACT

Phenolic compounds are hazardous industrial wastes that can contaminate real water resources. Therefore, the removal of these compounds in order to reach acceptable levels before discharging becomes challenging. In this study, a combination method between dispersive liquid-liquid microextraction (DLLME) with high-performance liquid chromatography-UV detection at 280 nm with the isocratic condition was introduced as a new approach for separating phenol content in water samples. The optimized parameters that affect the extraction efficiency, such as type of solvents, the volume of extraction and dispersive, stirring speed of centrifuge and salt concentration were evaluated using response surface methodology (RSM). A central composite design (CCD) was used to investigate the effect of four independent variables parameters, as mentioned. The recovery value on the DLLME method for the water sample is in the range of 92.31 - 114.29%. Based on the recovery obtained, the DLLME-HPLC-UV is a promising method for phenol extraction because it is simple, effective and produce a high percentage of the recovery.

Keywords: Dispersive liquid-liquid microextraction; high-performance liquid-chromatography-UV; phenol; response surface methodology; water sample

ABSTRAK

Sebatian fenol adalah sisa industri berbahaya yang boleh mencemari sumber air semula jadi. Oleh itu, penyingkiran sebatian ini daripada air untuk mencapai tahap yang selamat sebelum dilepaskan menjadi suatu perkara yang mencabar. Dalam kajian ini, gabungan kaedah mikroekstraksi cecair-cecair serak (DLLME) dengan kromatografi cecair prestasi tinggi-pengesanan UV pada 280 nm dalam keadaan isokumen diperkenalkan sebagai pendekatan yang baru untuk memisahkan fenol yang terdapat di dalam sampel air. Untuk mengoptimumkan parameter yang mempengaruhi kadar kecekapan pengekstrakan, seperti jenis pelarut, jumlah pengekstrakan dan serakan, kelajuan pengadukan emparan dan juga kepekatan garam dinilai menggunakan kaedah permukaan tindak balas (RSM). Reka bentuk komposit pusat (CCD) digunakan untuk mengkaji kesan empat parameter pemboleh ubah bebas seperti yang dinyatakan. Nilai pemulihan kaedah DLLME untuk sampel air adalah dalam lingkungan 92.31% - 114.29%. Berdasarkan nilai pemulihan yang diperolehi, DLLME-HPLC-UV adalah kaedah yang menjanjikan untuk pengekstrakan fenol kerana ia adalah mudah, berkesan dan dapat menghasilkan peratusan pemulihan yang tinggi.

Kata kunci: Fenol; kaedah permukaan tindak balas ; kromatografi cecair prestasi tinggi-pengesanan UV; mikroekstraksi cecair-cecair serakan; sampel air

INTRODUCTION

Environmental issues mainly water pollution has been a major concern facing the world. Nowadays, variety of chemicals whose persistency along with their constant release into the environment raised concerns to their potential impact on wildlife and human health. In view of this, efforts have been made by researchers to introduce a new approach for water treatment (Yusoff et al. 2018).

Industrial, domestic, agricultural activities, and other environmental and global changes are the main sources of water pollution (Gupta et al. 2012; Mahdavi et al. 2018). Inorganic, organic, and biological wastes from nature are the types of water pollution issued in water pollutants (Ba-abbad et al. 2012). Heavy metals are highly toxic and carcinogenic. According to Mittal et al. (2009), nearly 20% of dyes dispensed by textile industries dumped into water

bodies are toxic and even carcinogenic to both animals and humans (Mittal et al. 2009). Based on Lua (2019), pesticides, polynuclear hydrocarbons (PAHs), detergents, oils, grease, formaldehyde, and phenols (Jiang et al. 2003; Norseyrhan et al. 2016) are examples of toxic organic pollutants. Phenols are widely used in industries as an intermediate in the productions of dyes, medicines, and pesticides (Ariffin et al. 2019). For aquatic life, phenol is lethal to fish at low concentrations and is listed as a priority pollutant by the US Environmental Protection Agency (EPA) (Abdelkreem 2013). Even at low concentrations, phenols are classified as a carcinogen and harmful to an organism (Yang et al. 2006). Phenol can actuate various reactions, cancer-causing nature, teratogenicity, and mutagenicity as exhibited in animals (Said et al. 2013). Therefore, an increase in the production of wastewater, the demand for removal of organic compounds, including phenols, has been increased (Jiang et al. 2003). Thus, an assortment of creative techniques for treatment of phenol is developed to remove undesirable phenol from water. Several methods have been developed to remove phenol from wastewater, including microbial degradation, chemical oxidation (Khalid et al. 2004), solvent extraction (Yang et al. 2006), and adsorption (Singh et al. 2008). One of the most extensively used methods for dissimilar compound analysis is high-performance liquid chromatography (HPLC). For example, in industry, HPLC is routinely used for the quality control of products, monitoring analytes in biological matrices and analysis in chemistry methods (Cabrera & Lubda 2000) as well as verification of food pollutants or food additives (Pawliszyn 2003). Nowadays, HPLC becomes more frequently used as it is performed much faster and reduce analysis time in order to obtain a higher output.

The first step and possibly the most important for analytical process usually consists of an extraction procedure resulted in isolation and enrichment of components of interest from a sample matrix is sample preparation. Extraction can vary in degree of selectivity, speed, and convenience, which is not only based on the conditions used but also on the geometric configurations of the extraction phase (Pawliszyn 2003). Currently, dispersive liquid-liquid microextraction (DLLME) (Noorashikin et al. 2017), solid-phase extraction (SPE), and liquid-liquid extraction (LLE) are the sample preparation and preconcentration of the analytes from the sample matrix that been used in previous work for solvent extraction (Sohaimi et al. 2018).

As for LLE, it is widely used for sample preparation in the analytical chemistry field due to simplicity, convenience, and broad applicability. Unfortunately, LLE is a lack of time-consuming, expensive, and involved in vast amounts of toxic organic solvents that are not

miscible with aqueous samples; it may be harmful to health and environment (Cai et al. 2007; Wu et al. 2009). SPE is simple, sensitive, time-efficient and solvent-free but SPE can still be too long, relatively pricy, and sometimes suffers from analytes breakthrough when large sample volumes are analysed (Marce & Borrull 1998; Wu et al. 2009).

DLLME is a novel sample preparation offering high enrichment factors from low water samples. The performance of DLLME is also demonstrated by the ternary solvent system in which a mixture of two types of organic solvents known as disperser solvent and extraction solvent that quickly added into target aqueous sample solution (Liu et al. 2013). DLLME provides several advantages as compared to LLE and SPE are inexpensive, simple methods, rapid, and ease of method development (Jain et al. 2013) short extraction times and low cost (Rykowska et al. 2018). According to the previous study, DLLME is a diminished LLE that uses microliter volumes of the extraction solvent compared to the classic extraction techniques together with high extraction recovery and enrichment factors (Wu et al. 2009). SPE uses small amounts of solvents compared to LLE; however, it is costly. DLLME combined with HPLC first suggested by Zhang et al. (2011). It is a separation of the organic and aqueous phases that occurs based on their different densities without centrifugation. Recently, DLLME combined with HPLC-UV is used for the extraction and determination of BPA in a water sample (Rezaee et al. 2009). This reported shows that the DLLME combined with the HPLC-UV produce the good recoveries for the organic extraction (Noorashikin et al. 2017; Yusoff et al. 2018).

Response surface methodology (RSM) is a mathematical and statistical formula used in the development of an adequate functional relationship between the response of interest, y , and several associated control (input) variables denoted by x_1, x_2, \dots, x_k (Yousefzadeh et al. 2018). Thus, RSM enables the evaluation of the effects of various process variables with their interactions on responsible variables (Liyana-pathirana & Shahidi 2005; Silva et al. 2007). The general objective of the present work was to apply the RSM approach to optimize the extraction conditions. The optimized conditions were generated from the RSM were applied to the extraction procedure (experimental). The extraction of phenol from real water were performed and the percentage of recoveries were obtained.

MATERIALS AND METHODS

REAGENT AND STANDARD

The selected reagents, such as chloroform and methanol, were obtained from Fisher Scientific (UK). Phenol,

acetonitrile (HPLC grade), dichloromethane (99%), and sodium chloride salt (NaCl) were purchased from Merck (Germany). Both ethanol and acetone were obtained from HmbG Chemical and Friendemann that were used as a dispersive solvent. Deionized water was used in the mobile phase obtained through the Millipore Milli-Q Plus water purification system. A 1000 mg/L standard solution of phenol was prepared in acetonitrile HPLC grade. The standard working solution of 1 mg/L was prepared by diluting with acetonitrile HPLC grade.

INSTRUMENTATION

The separation and determination of phenol were carried out with the waters HPLC UV-Vis detector system. The system consists of a pump, degasser, column oven, ultraviolet detector, auto-injector, and guard column. HPLC column C18 (100 × 4.6 mm, Merck, Germany) was used for Waters HPLC. A mixture of water and acetonitrile (50:60 v/v) at a flow rate of 1 mL min⁻¹ was used as a mobile phase in isocratic conditions. The detection was performed at a wavelength of 280 nm. A Sartorius centrifuge was used to accelerate the phase separation at 1000-5000 rpm.

PROCEDURE FOR DISPERSIVE LIQUID-LIQUID MICROEXTRACTION (DLLME)

Figure 1 shows the general procedure for the DLLME method, where 1 mL of sample solution was placed in a 15 mL centrifuge tube. Then, 1.5 mL of acetone, which was used as a dispersing solvent containing 750 μL chloroform (extraction solvent) and 500 μL of working

phenol solution was injected into the sample. Under the optimized procedure, the cloudy solution was centrifuged at 300 rpm for 5 min to obtain the desired formation of the two-layer phases, which are the solvent-rich phase and aqueous solution. Afterward, the volume of the solvent-rich phase (sediment) was measured and completely transferred into vials using a syringe and injected into the HPLC system for analysis.

SELECTION OF EXTRACTION AND DISPERSIVE OF SOLVENTS

Preliminary experiments were first carried out to identify the types of extraction and dispersive solvents. The selection of appropriate extraction solvent and dispersive solvent are two majors. In this study, two organic solvents (dichloromethane and chloroform) were evaluated for extractant. The extractant was selected on the basis of having a higher density than water and had a high extraction capability of the new compound. Meanwhile, three different organic solvents were selected as a dispersive solvent, namely acetone, methanol, and ethanol. The selection of dispersive solvent should have appropriate miscibility with both extraction solvent and sample solution in order to form a cloudy state. Considering the volume of sediment phase, dichloromethane in the presence of acetone as a dispersing solvent formed a low sediment phase volume, whereas the combination of acetone-chloroform formed a more stable two-phase system. In the case of methanol-dichloromethane and ethanol-chloroform, it was found that a two-phase system

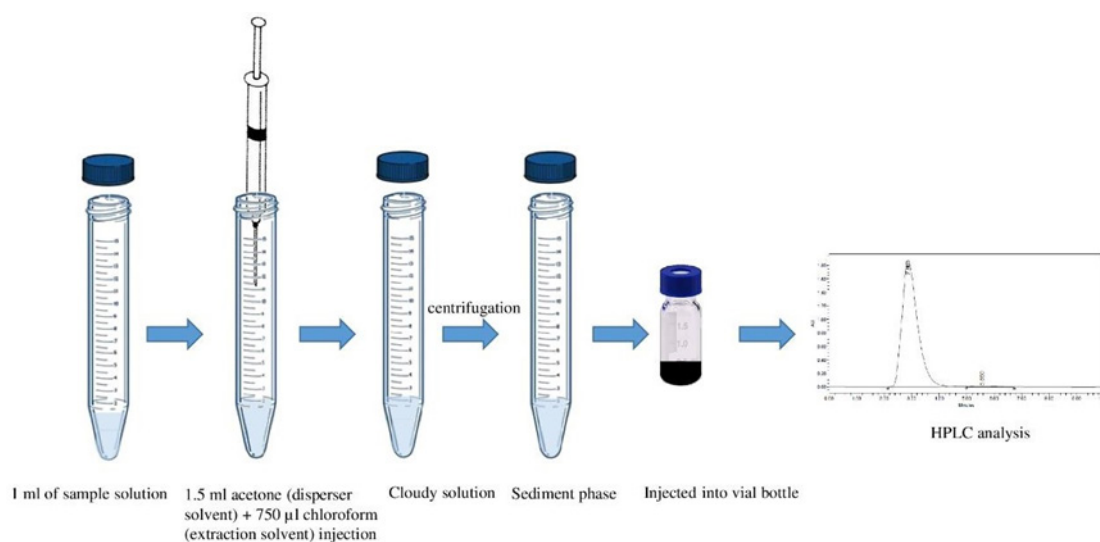


FIGURE 1. General procedure for DLLME

was not formed. Thereby, chloroform was selected as the extraction solvent and acetone as a dispersive solvent for further studies.

EXPERIMENTAL DESIGN

Several factors may affect the response of DLLME, such as the volume of extractant and dispersive solvent, the concentration of salt, and the stirring speed of centrifugation. A four factors central composite design (CCD) was applied in the experimental design to study the responses with the centre point (0, 0), which was replicated 6 times, consisting of 30 experimental runs. The experimental design and data analysis were carried out using response surface methodology with the Design Expert Software version 10.0.7.

The optimization of phenol extraction from the water sample using RSM was to minimize the number of experiments and reducing the cost of expensive analysis methods (Almeida et al. 2008). The statistical analysis was analyzed by the analysis of variance (ANOVA) and p-value, $P > 0.05$ (not significant) showed the suggested

model fit the experimental data, and independent variables influence the response (Azahar et al. 2017). The experiment was run in random order to avoid biased data.

REGRESSION AND ANOVA ANALYSIS

Analysis of variance (ANOVA) was performed on Design Expert® software version 10.0.7.

RESULTS AND DISCUSSION

OPTIMIZATION OF DLMME TECHNIQUE

To achieve the optimum condition for determination of phenol with dispersive liquid-liquid microextraction (DLLME) procedure, the optimization of four important parameters; the volume of extractant (B), dispersive solvent (D), the concentration of salt (A) and stirring speed of centrifugation (C), were selected as independent variables; and extraction recovery (Y) was the dependent response variable. Table 1 shows the factors and levels for dispersive liquid-liquid microextraction (DLLME) of phenol. A total number of 30 experiments were carried out for the response

surface modelling. The analytical responses for optimization of DLLME method of phenol are depicted in Table 2.

TABLE 1. Factor and level for dispersive liquid-liquid microextraction of phenol

Factor of independent variable	Symbol	Low Level	Central point	High level
Volume of extractant solvent (μL)	B	500	750	1000
Volume of dispersive solvent (ml)	D	1	1.5	2
Concentration of salt (mol/L)	A	0	1	2
Centrifugation speed (rpm)	C	1000	3000	5000

Sodium chloride (NaCl) is a salt that was used as the first variable factor on concentration, mol/L. According to Rezaee et al. (2009), the effect of adding salts on the extraction recovery of BPA was evaluated by the addition of 0-8%, w/v into the aqueous solution, and resulted in increased sediment phase. An increase in NaCl% will increase the volume of the sedimented phase because of the decrease in solubility of the extractant solvents in the presence of salt. Meanwhile, Maham et al. (2014) used 0 1.5 mol/L in a concentration of salts to detect the salting-out through the extraction of phenol from lakes water samples. In conventional DLLME, water should have less

density than the solvents of extraction, must have good extraction ability for a target analyte and low solubility in an aqueous sample. Based on previous research, an increase in the volume of salts would not have a significant effect on the efficiency of the extraction. In this research, the concentration of salts used are 0, 1, and 2 mol/L.

Extraction of solvents, centrifugation speeds, and dispersive of solvents were the other factors that have been tested in this study. The use of acetone as a dispersive of solvents increases the dilution of bisphenol in water (Rezaee et al. 2009). Table 2 shows the analytical for the optimization of DLMME of phenol extraction.

TABLE 2. The analytical responses for optimization of DLLME method of phenol

Run	Factor A: Concentration of salt (mol/L)	Factor B: Extraction solvent volume (μL)	Factor C: Centrifugation speed (rpm)	Factor D: Dispersive solvent volume (mL)	Extraction recovery (%)
1	0	500	5000	1	81.82
2	1	750	3000	1.5	93.18
3	0	500	1000	1	71.43
4	1	750	3000	1	74.42
5	0	1000	1000	1	118.75
6	0	500	5000	2	100
7	2	1000	5000	2	100.49
8	2	500	5000	1	40
9	0	1000	5000	1	118.75
10	1	750	3000	1.5	80.85
11	1	750	5000	1.5	73.47
12	0	500	1000	2	100
13	1	500	3000	1.5	53.85
14	2	500	1000	1	37.25
15	2	750	3000	1.5	80.85
16	1	750	3000	1.5	84.71
17	0	1000	1000	2	125
18	2	100	1000	1	62.27
19	2	1000	5000	1	81.82
20	1	750	3000	1.5	84.24
21	2	500	1000	2	43.29
22	1	750	3000	1.5	80.85
23	1	750	3000	1.5	97.67
24	1	750	3000	2	90
25	1	750	1000	1.5	66.67
26	1	1000	3000	1.5	99.72
27	2	1000	1000	2	100
28	2	500	5000	2	80
29	0	1000	5000	2	150
30	0	750	3000	1.5	82.93

REGRESSION AND ANOVA ANALYSIS

Analysis of variance (ANOVA) was performed on Design Expert® software version 10.0.7. This is a calculation technique and the main objective in this study, which is to estimate the relative contribution of each control factor to the overall response. ANOVA was also used to estimate variance errors and to determine the relative importance of various factors. It will show the effect of each of the factors investigated in the optimization criteria. The ANOVA analysis also indicated whether the observed change in response was due to changes in level adjustment or experimental standard errors. In the ANOVA analysis, squared regression (SS), degrees of freedom (DOF),

squared mean (variance), and related F-test of significance (F-value) were calculated. The sources of variance that were found in the regression model are linear, quadratic, and two interaction factors. Model significance tests, lack-of-fit tests on regression models, and individual coefficients were also analyzed by ANOVA. In the RSM, if the p-value is lacking, $p > 0.05$ (not significant), it states that the proposed model is in accordance with the experimental data, independent variables or parameters have a significant effect on the response (Alhaji et al. 2017). The quality of the model is explained by the determination of the coefficients of R^2 and R^2 adjusted (R^2_{adj}). Table 3 shows the summary of the ANOVA analysis results.

TABLE 3. Summary of ANOVA analysis

Source	Degree of freedom	Sum of squares	Mean square (variance)	F value ($\alpha=0.05$)	P-value
Model	14	15898.80	1135.63 (8.77)	< 0.0001	significant
A	1	5749.64	5749.64 (44.41)	< 0.0001	
B	1	6811.61	6811.61 (52.61)	< 0.0001	
C	1	563.25	563.25 (4.35)	0.0545	
D	1	2250.67	2250.67 (17.38)	< 0.0008	
Residual	15	1941.94	129.46		

$R^2 = 0.8912$, $R^2_{adj} = 0.7896$, Adequate Precision = 13.449

$$Y = 81.58 - 17.87A + 19.45B + 5.59C + 11.18D - 0.89AB + 1.44AC + 1.07AD - 0.36BC + 7.385E - 0.03BD + 1.91CD + 5.65A^2 + 0.54B^2 - 6.17C^2 + 5.97D^2$$

Based on Table 3, the standard deviation coefficient, $R^2 = 0.8912$, shows the high model reliability in predicting the percentage of phenol preservation yield, where the model can explain 89.12% of the response variability. The small probability value ($p < 0.001$) indicates that the model is highly significant and can be used to predict the response function accurately. Figure 2 illustrates the effect of salt concentrations, centrifugal speed, and volume of dispersive on the quadratic model obtained through Design Expert® 10.0.7. It is apparent from the results that the optimal condition of the variables to be carried out is determined by setting the phenol eigenvector to the

micro-extraction method of dispersion fluid in the range of data obtained.

Figure 2(a) shows the interaction between the concentration of salt and centrifugal speed. It shows that high in centrifugal speed leads to a high concentration of salts. The optimization value for centrifugal speed is at 5000 rpm while their concentration of salt is at 0.5 mol/L. Figure 2(b) shows the interaction between the concentration of salt and the extraction of the solvent. The extraction of phenol reached the optimum point with a salt concentration of 0 mol/L. Meanwhile, at a low concentration of salt, the volume of the extraction

solvent reached the maximum level at 2000 μL . According to Pourbasheer et al. (2017) and Rezaee et al. (2006), increasing in salt concentration will reduce the solubility of the extraction solvent due to the presence of salt in the mixture. The effects of the volume of dispersive and centrifugal speed on phenol are shown in Figure 2(c). When the compressor speed was increased from 1000

rpm to 5000 rpm, and when the dispersive solvent also increased from 1 to 2 mL, a high phenolic extraction yield produced was shown. The separation between the aqueous phase and the rich analytical phase occurred well at high compressor speed. This is because of the higher analytical density enables the removal of analytes from the aqueous phase to the rich analytical phase.

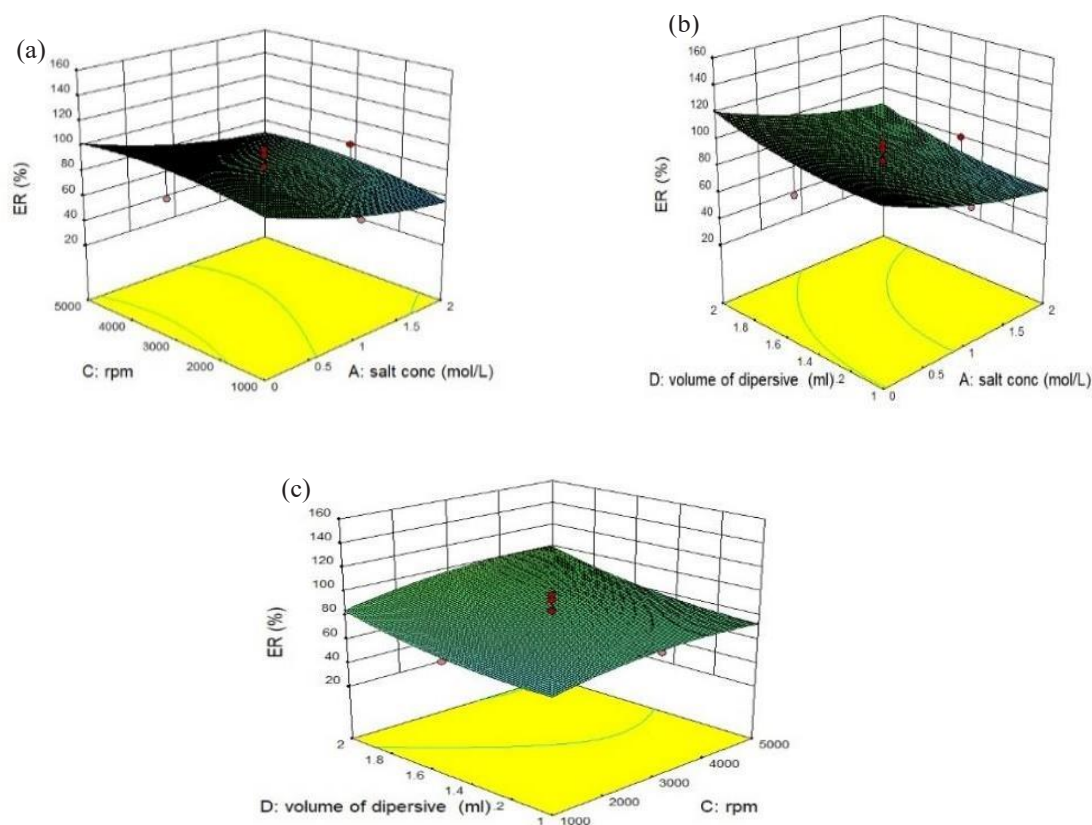


FIGURE 2. Three-dimensional response surfaces interaction between (a) centrifugal speed and salt concentration (b) volume of dispersive and salt concentration (c) volume of dispersive and centrifugal speed

VALIDATION ON REAL SAMPLE

The comparison of percentage recovery in water samples from rivers and lakes were carried out. Table 4 shows the results for the model's adequacy for predicting the recovery of phenol. Based on the optimum conditions, the recovery rate for the spiked samples was satisfactorily using the DLLME method of 92.31 and 114.29% for river water samples. Meanwhile, the recovery rate for

lake samples is between 102.7-114.29%. To determine the phenol content in the water samples, another DLLME analysis was carried out without adding (unspiked) 0.6 ppm phenol solution. The percentage of recovery (ER%) as analytical responses was calculated based on the following equation:

$$ER\% = \frac{V_{sed}}{V_{aq}} \times \frac{C_{sed}}{C_o} \times 100\% \quad (2)$$

where V_{sed} and V_{aq} are the volumes of sediment phase and volume of the aqueous sample solution, respectively. Whereas, C_{sed} and C_o are concentrations of the analyte

in the sedimented phase and initial concentration of the analyte, respectively.

TABLE 4. Percentage recovery of phenol in water sample and concentration of phenol analysis based on DLLME method

Water sample	Recovery (%) in spiked 0.6 ppm water sample	Concentration of phenol in unspiked water sample (ppm)
Sg Langat	114.29	12.156
Sg Kuyoh	114.29	16.255
Sg Ramal	92.31	11.103
Sg Buah	114.29	11.037
Sg Kantan	114.29	12.549
Tasik Cempaka	114.29	12.218
Tasik FKAB, UKM	114.29	13.534
Tasik Seri Serdang	102.70	11.999
Tasik Bandar Tun Hussein Onn	114.29	11.881
Tasik Idaman, Dengkil	102.70	13.131

From Table 4, the results tested on the water sample showed all water samples contained phenol in the range of 11.037-16.255 ppm. Sg Kuyoh showed the highest amount of phenol contamination. The source of phenol pollution in Sg Kuyoh included wastewater from a residential area in Seri Kembangan. The lakes sample area showed that FKAB, UKM contained a high

phenol concentration. According to this, it can be related to management activities surrounding the lake area that contributed to the contamination of the lake. DLLME-HPLC-UV technique has a good percentage of recovery for the determination of phenol in water samples. Figure 3 shows the result of the chromatogram of HPLC-UV spiked at 0.6 ppm at 2.214 min.

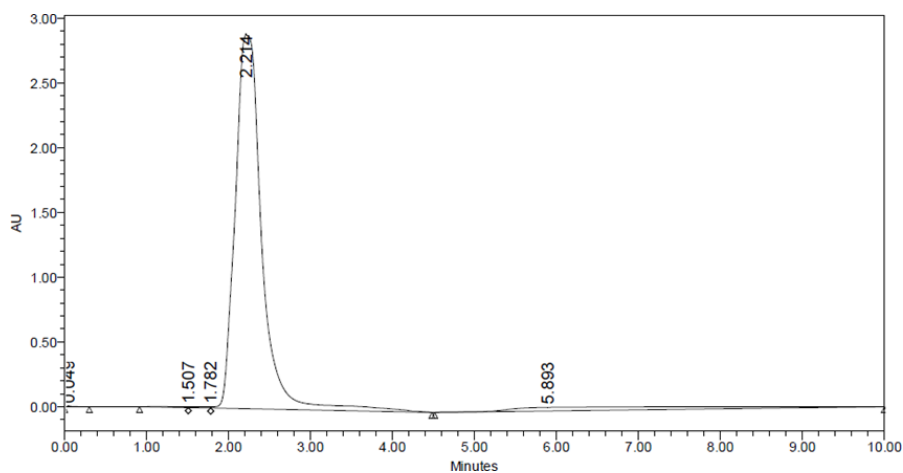


FIGURE 3. Chromatogram of HPLC-UV

CONCLUSION

The influence of operating parameters, such as the volume of extraction solvents, dispersion solvent volume, salt concentration, and compressive velocity in the determination of phenol, were observed. The composite design (RSM) type of composite design (CCD) in Design Expert® 10.0.7 software was used to evaluate and optimize the operating parameters. The optimization was performed to determine the optimum conditions for the percentage of phenol yield set in the range. The model provided by Design Expert® 10.0.7 software based on the percent phenol yield is quadratic. The values of R^2 and R^2 adj for Y1 models are 0.8912 and 0.7896, respectively. For the optimum conditions, the salt concentration was set as the minimum, while the other variables were in the range. This gave a high value, which is 1. The percentage obtained by the model at optimum condition was 103.05% while the percentage for phenol tested in river and lake water samples was between 92.31 and 114.29%. Compared with the other method, DLLME used organic solvent in a small volume. DLLME used to be more environmentally friendly, apart from that it is simple, fast, inexpensive and reduces in time.

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