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# Application of surfactant assisted dispersive liquid–liquid microextraction for sample preparation of chlorophenols in water samples

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ABSTRACT

A simple, rapid, and efficient method, based on surfactant assisted dispersive liquid–liquid microextraction (SA-DLLME), followed by high performance liquid chromatography (HPLC) has been developed for the extraction and determination of chlorophenols as model compounds in environmental water samples. A conventional cationic surfactant called cethyltrimethyl ammonium bromide (CTAB) was used as a disperser agent in the proposed approach. Thirty-five microliter of 1-octanol as an extraction solvent was injected rapidly into 11 mL aqueous sample containing 0.09 mmol $L^{-1}$ of CTAB, the mixture was then shaken for 3 min to disperse the organic phase. Having the extraction procedure been completed, the mixture was centrifuged and 20 μL of collected phase was injected into HPLC for subsequent analysis. Some parameters such as the type and volume of the extraction solvent, the type and concentration of surfactant, pH, ionic strength, shaking time, extraction temperature and centrifugation time were optimized. The preconcentration factors (PFs) in a range of 187–353 were obtained under the optimum conditions. The linear range, detection limit (S/N = 3), and precision ($n$ = 5) were 0.2–200, 0.1 μg $L^{-1}$, and 4.7–6.9%, respectively. Tap water, sea water and mineral water samples were successfully analyzed for the existence of chlorophenols using the proposed method.

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## 1. Introduction

Phenol and substituted phenols are widely distributed in natural waters because of their wide use in many industrial processes such as the manufacture of plastics, dyes, drugs and pesticides [1–3]. Among these compounds, chlorophenols are well known pollutants because of their toxicity in aquatic life and poor biotreatability, and since they make an unpleasant taste and odor in water even in very low concentrations. Chlorophenols are formed by the degradation of phenoxy herbicides, as well as by the chlorination of drinking water containing aromatic impurities [4–6]. The European Community legislation has also set a maximum allowable phenol concentration of 0.5 μg $L^{-1}$ in tap water [7]. The importance of chlorophenols in environment, calls for sensitive and reliable methods to determinate them in water samples. Many methods for analysis of chlorophenols are based on chromatographic techniques such as high performance liquid chromatography (HPLC) [8–10], gas chromatography (GC) [11–13] and capillary electrophoresis [14,15]. The GC analysis of the chlorophenols leads to tailed peaks resulting decreasing the detection limits and the reliability of the results. To alleviate this drawback, chlorophenols are usually derivatized with a suitable derivatization reagent before injection into the GC. On the other hand, HPLC is a good alternative technique, in which isocratic or gradient elution can be used to separate the compounds.

In general, the environmental samples are too diluted or too complex. Therefore, prior to analysis by HPLC, a sample preparation step is necessary to extract traces of chlorophenols from the aqueous medium, bring the analytes to a suitable concentration level, and remove them from interfering components in the matrix [16]. Typically, this would require an extraction step such as liquid–liquid extraction (LLE) or solid phase extraction (SPE). However, conventional LLE consumes large amounts of the high costing and potentially hazardous organic solvents. In addition, in trace analysis, a large volume of sample is often required and its handling can be extremely time consuming besides being tedious. SPE uses much less solvent and is less time consuming than LLE but requires column conditioning and is relatively expensive [17]. The first attempts to miniaturize the conventional LLE have been developed by Liu and Dasgupta [18,19] and Jeannot and Cantwell [20]. The first suggested method of liquid phase microextraction (LPME) was a single drop microextraction (SDME). This technique is performed by suspending a microliter drop of organic solvent in the stirred aqueous solution, in which the analytes are partitioned between the organic drop and the aqueous phase. Several different types of LPME methods have been developed, including hollow fiber LPME [21], homogeneous liquid–liquid extraction (HLLE) [22,23] and solidification of a floating organic drop (SFO) [24]. Microextraction

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techniques are fast, simple, inexpensive, environmentally friendly and compatible with many analytical instruments. In 2006, Assadi and co workers [25] developed a novel liquid phase microextraction technique, named dispersive liquid–liquid microextraction (DLLME). This method is based on a ternary component solvent system in which the extraction solvent and disperser solvent are rapidly injected into the aqueous sample by syringe. In DLLME, disperser solvent is miscible in both aqueous and organic phases. In the other hand, adding disperser solvent such as methanol in water, the interfacial tension of mixture decreases which it seems play an important role in dispersion of organic solvent in water by increasing the surface area between the organic and aqueous sample. The interfacial tension of mixtures is a physical property with great importance for mass transfer in some processes such as distillation or extraction [26].

Very recently, a novel method, ultrasound-assisted emulsification microextraction (USAEME) has been developed for extraction of organic compounds from water samples [27]. In USAEME, the appropriate extraction solvent is rapidly injected by a syringe into aqueous sample containing analytes in ultrasonic bath. A cloudy solution forms after sonication, the solution is then centrifuged and the fine droplets sediment at the bottom of the conical test tube. The determination of analytes in collected phase can be performed by instrumental analysis. The required times for emulsification in USAEME method are in the range of 5–10 min. These times are significantly higher than the time needed to disperse an organic solvent in DLLME method. Also, in both of USAEME and DLLME methods due to the difficulty to collect microvolumes of floated organic solvents, the selected extraction solvent must be denser than the aqueous samples [28]. In our previous work [29], a novel USAEME based on dispersion of microvolumes of low density organic solvents in aqueous samples was successfully developed for extraction of PAHs from water.

Surfactants are organic compounds that are amphiphilic, and they contain both hydrophobic and hydrophilic groups. Therefore, they are soluble in both organic solvent and water. Surfactant reduces the surface tension of water by adsorbing at the liquid–gas interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid–liquid interface. Many surfactants can also assemble in the bulk solution into aggregates. Examples of such aggregates are vesicles and micelles. The critical micelle concentration (CMC) is defined as the concentration of surfactants above which micelles are spontaneously formed.

The cloud point extraction (CPE) is the first extraction method in which surfactant has been used. In this technique, small volume of the surfactant-rich phase allows to extract and preconcentrate the analytes in one step. Sarafraz Yazdi and Es'haghi [30] have evaluated the performance of surfactant enhanced liquid phase microextraction (SE-LPME) for preconcentration of basic drugs of abuse in hair. They used non-ionic surfactant to transfer the target analytes to donor phase from aqueous sample. In 2010, Wu et al. represented that non-ionic surfactants can enhance the efficiency of USAEME procedure [31].

There is a similarity between disperser solvent in DLLME and surfactant from standpoints of solubility in both of organic and aqueous phases, bridging between them, and also decreasing the interfacial tension between two phases. The mentioned phenomenon can contribute in dispersion of organic solvent into aqueous phase.

The Laplace equation scrutinizes the mechanism and influent parameters in droplet formation, which the difference between the outer and inner droplet pressure is the most important among them. The pressure difference is proportionally about $\gamma/r$ in interfaces, as the Laplace equation states, which $\gamma$ is interfacial tension and $r$ is the droplet radius. Regarding constancy in pressure difference, as the interfacial tension decreases, the droplet radius also decreases. So, it is obvious that the droplets will be finer as the surfactant added to solution and subsequently surface area between organic and aqueous phase is increased.

The objective of this work was to present the application of cationic surfactant in surfactant assisted dispersive liquid–liquid microextraction (SA-DLLME) for preconcentration of chlorophenols in water samples.

## 2. Experimental

### 2.1. Chemicals and reagents

Standards of chlorophenols, 2-chlorophenol (2-CP, p$K_a$ = 8.52), 4-chlorophenol (4-CP, p$K_a$ = 9.43), 2,3-dichlorophenol (2,3-DCP, p$K_a$ = 7.7) and 2,5-dichlorophenol (2,5-DCP, p$K_a$ = 7.2) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). The ultra-pure water was prepared by a model Aqua Max-Ultra Youngling ultra-pure water purification system (Dongan-gu, South Korea). HPLC grade methanol and acetonitrile were purchased from Caledon (Ontario, Canada). Toluene, 1-octanol, 1-undecanol, and 1-dodecanol were purchased from Merck (Darmstadt, Germany) and used as extraction solvents. Cethyltrimethyl ammonium bromide, CTAB ($C_{19}H_{42}BrN$) was obtained from Merck, and tetradecyl trimethyl ammonium bromide, TTAB ($C_{17}H_{38}BrN$), Triton X-100, Triton X-114, sodium dodecyl sulfate, SDS ($C_{12}H_{25}OSO_3Na$) and sodium tetradecyl sulfate, STS ($C_{14}H_{29}OSO_3Na$) were purchased from Sigma–Aldrich. Sodium hexadecyl sulfate, SHS ($C_{16}H_{33}OSO_3Na$) was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). A stock standard solution containing 1 mg mL$^{-1}$ of chlorophenols was prepared in HPLC grade methanol. The stock solution was stored at 4 °C. Working standard solutions were prepared daily by diluting the stock standard solution with ultra-pure water to the required concentrations. Natural water samples were collected from the Caspian Sea (Mahmood Abad, Iran), tap water (Tehran, Iran) and the mineral water (Koohdasht, Iran). No filtration or any further treatment was applied in any of the samples before extraction.

### 2.2. Apparatus

Chromatographic analysis was performed with a HPLC system including a Varian 9012 HPLC pump (CA, USA), a six-port Cheminert HPLC valve from Valco (Houston, USA) with a 20 μL sample loop and equipped with a Varian 9050 UV-Vis detector. Chromatographic data were recorded and analyzed using Chromana software (version 3.6.4). An ODS-Zorbax column (250 mm × 4.6 mm, with 3 μm particle size) and an ODS-Zorbax guard column (4.6 mm × 1.25 cm) were applied to separate the chlorophenols under gradient elution conditions. A mixture of 20 mmol L$^{-1}$ phosphate buffer (pH 4) and acetonitrile (60:40) for 15 min and 100% acetonitrile for 10 min at a flow rate 1.2 mL min$^{-1}$ were used as a mobile phase and the analytes were detected at 280 nm.

### 2.3. Surfactant assisted dispersive liquid–liquid microextraction (SA-DLLME) procedure

The ionic strength and pH of the solutions were adjusted to an appropriate amount (sodium chloride, 10% (w/v); pH = 6.0). Eleven milliliter of standard solution containing 100 μg L$^{-1}$ of chlorophenols and 0.09 mmol L$^{-1}$ of CTAB was poured into a home designed centrifuge glass vial [29]. Thirty-five microliters of 1-octanol (as an extraction solvent) was rapidly injected into the aqueous sample by syringe. Then the vial was shaken to disperse the organic solvent into water sample. All steps of extraction procedure were performed at 25 ± 3 °C. A cloudy solution was formed in the vial (the cloudy state was stable for a long time). Then, the mixture was

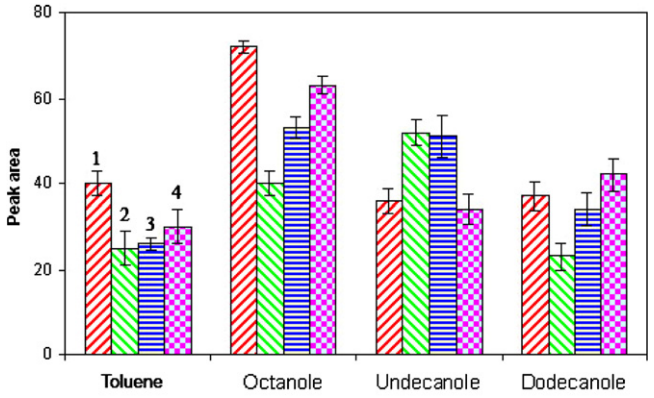


**Fig. 1.** Effect of organic solvent on the extraction efficiency. Extraction conditions: sample solution, 11.0 mL of 100 μg $L^{-1}$ of each chlorophenols; surfactant (CTAB) concentration, 0.1 mmol $L^{-1}$; extraction solvent volumes, 60 μL; pH, 3; shaking time, 2 min; centrifugation time, 5 min. (1) 2-CP, (2) 4-CP, (3) 2,3-DCP and (4) 2,5-DCP.

centrifuged for 3 min at 5000 rpm. Accordingly, the dispersed fine droplets of the extraction phase were collected on the top of the vial (22 μL ± 2). The separated phase was quantitatively transferred to a microtube with conical bottom ($V$ = 100 μL) and regarding good chromatographic behaviour of 1-octanol, 20 μL of collected phase was directly injected into HPLC for analysis.

## 3. Results and discussion

In the present study, the applicability of cationic surfactant as an agent for dispersion of organic solvent with a density lower than water in the SA-DLLME combined with HPLC-UV was considered for the determination of chlorophenols. There are several factors which affect the extraction process including the kind of extraction solvent and its volume, the kind of surfactant and its concentration, pH, the ionic strength, the shaking time, the extraction temperature, and the duration of centrifugation. The optimization was carried out using working solutions containing 100 μg $L^{-1}$ of chlorophenols. The chromatographic peak area, which is related to the number of moles of extracted analytes into the organic solvent, was used to evaluate the extraction efficiency under different experimental conditions. The injected volume of the extracted analytes into HPLC was kept constant at 20 μL throughout of the experiments.

### 3.1. Selection of extraction solvent

The first step of surfactant assisted dispersive liquid–liquid microextraction was to select a proper extraction solvent. The extraction solvent used in SA-DLLME should present the same appropriate characteristics of solvents used in conventional liquid–liquid extraction. It is desirable that this solvent has low solubility in water, high capacity for extraction of components of interest, and additionally the density lower than that of the aqueous phase. Four solvents that have these properties were tested: toluene, 1-octanol, 1-dodecanol and 1-undecanol. The extraction solvent creates a cloudy solution by shaking the container in the presence of cationic surfactant. The compatibility of these solvents with the SA-DLLME technique was studied by adding 60 μL of each mentioned solvent into 11.0 mL aqueous solution containing 100 μg $L^{-1}$ of chlorophenols and 0.1 mmol $L^{-1}$ of CTAB as disperser agent. The mixture was shaken during 2 min to complete the extraction process. After centrifugation of the solutions, 20 mL of each collected phase was injected into the HPLC-UV for subsequent analysis. The extraction efficiencies using different solvents are shown in Fig. 1. The results show that 1-octanol has the highest extraction

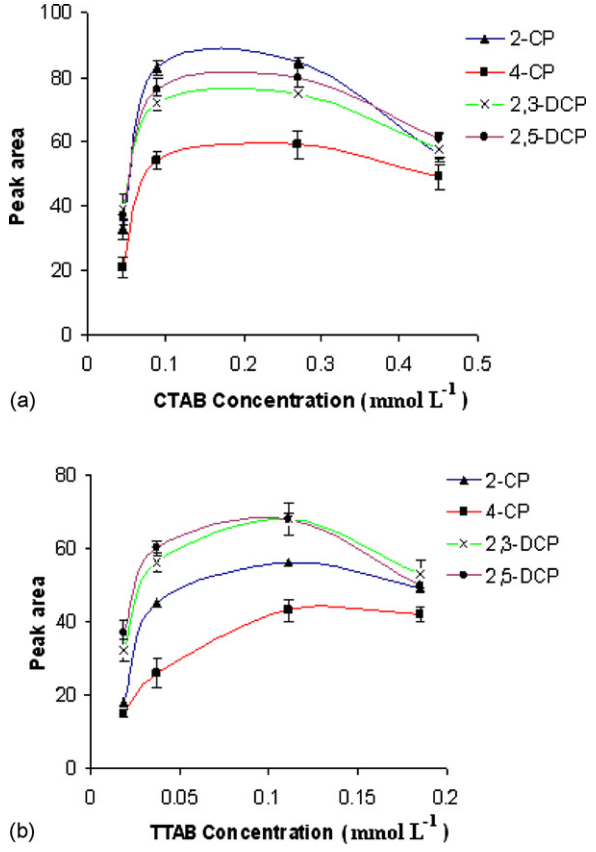


**Fig. 2.** The effect of cationic surfactant concentration (a) CTAB, (b) TTAB on the extraction efficiency. Extraction conditions: sample solution, 11.0 mL of 100 μg $L^{-1}$ of each chlorophenols; extraction solvent, 60 μL of 1-octanol; pH, 3; shaking time, 2 min; centrifugation time, 5 min.

efficiency among the examined solvents. Therefore, 1-octanol was selected as an optimum extraction solvent for further optimization studies.

### 3.2. Effect of type and concentration of surfactant

The main selection criterion of disperser solvent for traditional DLLME is its miscibility in both extraction solvent and water. As described in Section 1, all of the studied surfactants are soluble in both organic solvent and water. The cationic surfactants including a cationic head group and the hydrophobic hydrocarbon chain are appropriate ones. The most well known surfactants of this type are CTAB and TTAB. The two mentioned surfactants have been used to evaluate the extraction efficiency of chlorophenols in this study.

Surfactant concentration is an important parameter which affects the extraction efficiency. As explained before, the concentration at which surfactants begin to form micelles is known as the CMC (CMC of CTAB and TTAB are 0.91, 3.7 mmol $L^{-1}$, respectively). The effects of CTAB and TTAB on the extraction efficiency at four concentration levels of the analytes were studied. According the obtained repeatabilities and sensitivities (Fig. 2), CTAB provided better extraction efficiency than TTAB. The extraction efficiency was dramatically increased from 0.05 CMC to 0.1 CMC due to increase of free surfactant monomer causing an improved dispersion procedure, while extraction efficiency was remained constant in the range of 0.1 CMC to 0.3 CMC. Some aggregations like pre-micelles are formed as the surfactant concentration reaches CMC which cause a decrease in extraction efficiency probably as a result of interaction between analytes with pre-micelles. In addition the foam is formed as the surfactant concentration increases which

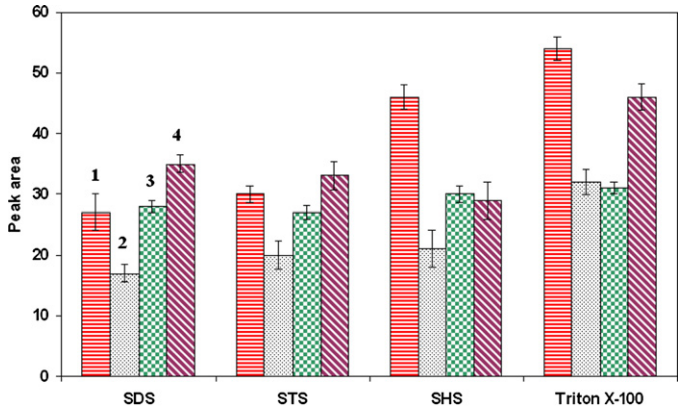


**Fig. 3.** The effect of non-ionic and anionic surfactant on the extraction efficiency: extraction conditions: sample solution, 11.0 mL of 100 μg $L^{-1}$ of each chlorophenols; surfactant concentration, 0.09 mmol $L^{-1}$; extraction solvent, 60 μL of 1-octanol; pH, 3; shaking time, 2 min; centrifugation time, 5 min. (1) 2-CP, (2) 4-CP, (3) 2,3-DCP and (4) 2,5-DCP.

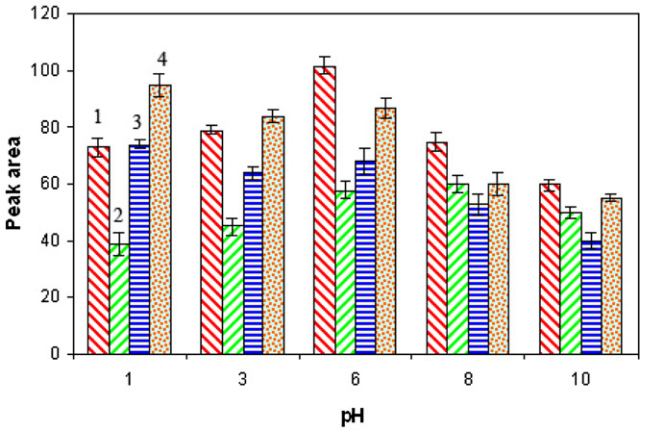


**Fig. 4.** The effect of pH on the extraction efficiency of chlorophenols. Extraction conditions: sample solution, 11.0 mL of 100 μg $L^{-1}$ of each chlorophenols; surfactant (CTAB) concentration, 0.09 mmol $L^{-1}$; extraction solvent, 60 μL of 1-octanol; shaking time, 2 min; centrifugation time, 5 min. (1) 2-CP, (2) 4-CP, (3) 2,3-DCP and (4) 2,5-DCP.

make the phase separation hardly occur even after centrifugation and the sediment collection is quantitatively impossible.

Consequently, the data showed that CTAB with optimized concentration of 0.09 mmol $L^{-1}$ creates the best conditions for extraction of chlorophenols.

To study the effect of other surfactants on the extraction efficiency of the analytes several types of non-ionic (Triton X-100 and Triton X-114) and anionic (SDS, STS and SHS) surfactants were tested as disperser agents. Unfortunately in the presence of Triton X-114 cloud point phenomenon was observed which interfered with dispersion phenomenon. The results are shown for other surfactants in Fig. 3. The chlorophenols are acidic compounds and are presented in their deprotonated form in alkaline medium. Thus non-ionic and anionic surfactants cannot form ion pairs with target analytes to increase the extraction efficiency, so the extraction efficiency of chlorophenols in the presence of anionic and non-ionic surfactants is less efficient in comparison with cationic surfactants. Regarding the obtained results, CTAB was used as an appropriate disperser agent in further experiments.

### 3.3. Influence of pH

Sample pH plays a unique role to transfer the target analytes into organic phase in many LPME methods. Because of acid–base properties of phenolic compounds and the importance of the pH effect on their extraction, this effect was studied within the pH range of 1.0–10.0. As can be seen in Fig. 4, the best extraction efficiency of chlorophenols was obtained at pH 6.0. So, it seems that both neutral and ionized chlorophenols were efficiently extracted to organic phase. The extraction of neutral protonated analyte into organic phase is eligible because of conventional interactions but the extraction of deprotonated charged species seems as an interesting phenomenon which has occurred in alkaline medium for chlorophenols which can be as a result of ion pair formation between cationic surfactant and deprotonated analytes. Therefore, pH 6.0 was selected for further studies.

### 3.4. Influence of ionic strength

The addition of salt to aqueous solution generally causes a decrease in solubility of the organic compounds in water and has been widely used to enhance the extraction efficiency of analytes. This effect was mainly observed for high polarity compounds. To investigate the influence of ionic strength on SA-DLLME performance, various experiments were performed in the presence of different amounts of NaCl (0–15%, w/v). The results demonstrated an improvement of the extraction efficiency for all of the analytes up to 10% (w/v) of NaCl because of salting out effect. The signal remains constant in the concentration range of 10–15% (w/v) of NaCl. One of advantages of salt addition in SA-DLLME besides improving extraction efficiency is preventing foam forming which causes an appropriate phase separation after centrifugation, so, the extraction solvent is quantitatively collected in top of the vial. Therefore, 10% NaCl (w/v) was used in further experiments.

### 3.5. Influence of extraction solvent volume

In order to obtain the effect of extraction solvent volume on the SA-DLLME of the chlorophenols, different volumes of 1-octanol (from 32 to 60 μL) were added to 11 mL sample solutions. The results showed that the volume of collected phase increased (20–47 μL) by increasing of the extraction solvent volume. On the other hand, the peak areas of the analytes were decreased as the collected phase volume was increased. Therefore, the best results were achieved using 32 μL of 1-octanol. But, due to difficulty of the collection of 20 μL of floated 1-octanol a poorer precision was produced. So, 35 μL of organic solvent was selected as the optimum volume of the extraction solvent.

### 3.6. Influences of shaking time, extraction temperature and centrifugation time

Three other parameters which affect on the extraction efficiency were optimized step by step. Shaking the solution is a necessary step for dispersion of organic solvent into the aqueous phase and breaking up of organic phase into fine droplets. Solvent microextraction methods are equilibrium methods and mass transfer within the organic phase is a limiting step. These fine droplets could extract analytes rapidly because of the shorter diffusion distance and large specific surface area [32]. Accordingly, the effect of the shaking time on the SA-DLLME of chlorophenols was investigated at six levels in the range of 0–5 min. The "0 min" experimental point corresponded to the extraction where the water–octanol mixture was not subjected to shaking and preconcentration of the analytes was depended upon diffusion during the centrifugation step. The mass transfer into extraction solvent was significantly increased as the shaking time was increased up to 3 min so was the extraction efficiency. The extraction efficiency does not change as the shaking time was increased up to 5 min. Therefore, the shaking

**Table 1**
Figures of merit for the SA-DLLME of chlorophenols.

| Analyte | Linearity | | LOD ($\mu g\,L^{-1}$) | Precision[a] (RSD%, $n=5$) | | PF[a] |
|---|---|---|---|---|---|---|
| | LDR ($\mu g\,L^{-1}$) | $R^2$ | | Between-day | Within-day | |
| 2-CP | 0.2–200 | 0.9994 | 0.1 | 9.4 | 5.4 | 187 |
| 4-CP | 0.5–200 | 0.9985 | 0.1 | 10.3 | 6.2 | 285 |
| 2,3-DCP | 0.2–200 | 0.9991 | 0.1 | 8.2 | 6.9 | 350 |
| 2,5-DCP | 0.2–200 | 0.9999 | 0.1 | 12.3 | 4.7 | 353 |

[a] Data were calculated based on extraction of 10 $\mu g\,L^{-1}$ of each chlorophenol.

**Table 2**
Comparison of the proposed method with other proposed methods for extraction and determination of chlorophenols.

| Analyte | Method | LOD ($\mu g\,L^{-1}$) | LDR ($\mu g\,L^{-1}$) | RSD% | Time (min) | PF | Ref |
|---|---|---|---|---|---|---|---|
| 2-CP, 4-CP, 2,3-DCP, 2,5-DCP | SPME–HPLC-UV | 0.005–0.009 | 0.05–65 | 4–7 | 50 | – | [33] |
| 2-CP | [a]CPE–HPLC-EC | 3.0 | 5.0–200 | 10 | 20 | 13 | [34] |
| 2-CP, 4-CP, 2,3-DCP | DLLME–GC-ECD | 0.5–2 | 1–400 | 2.4–4.7 | 2 | 287–628 | [35] |
| 2-CP, 4-CP | [b]SPME-MD–HPLC-DAD | 1.6–1.9 | 1–200 | 6.3–7.9 | 40–60 | – | [36] |
| 4-CP | [c]EME–HPLC-UV | 0.1 | 0.5–1000 | 6.8 | 10 | – | [37] |
| 2-CP | [d]SDCME–HPLC-UV | 0.1 | 2–500 | 5.6 | 15 | – | [38] |
| 2-CP, 4-CP, 2,3-DCP | SPE–DLLME–GC-ECD | 0.02–0.05 | 0.05–20 | 2.6–4.3 | <10 | 11,030–4390 | [39] |
| 2-CP, 4-CP, 2,3-DCP, 2,5-DCP | SA-DLLME–HPLC-UV | 0.1 | 0.2–200 | 4.7–6.9 | 6 | 187–353 | Proposed method |

[a] Cloud point extraction.
[b] Solid phase microextraction micellar desorption.
[c] Electro membrane extraction.
[d] Single-drop coacervative microextraction.

of the solution was carried out for 3 min in further experiments. It is worthy to note that by applying a Vortex instrument the needed time can be reduced as short as <1 min.

Temperature could affect both mass transfer and dispersion process, thus the effect of temperature on the extraction efficiency was investigated by varying temperatures from 25 to 50 °C after the shaking step. The experimental results indicated that solution temperature has no significant effect on the extraction efficiency of the chlorophenols. This is because that, complete dispersion of organic solvent into water was occurred in whole temperatures. So, for the convenience of the experiment, the extractions were carried out at room temperature (25 ± 3 °C).

The final parameter which optimized was centrifugation time. If the centrifugation time is not enough, the organic phase cannot be completely collected on top of the vial. A series of extraction with varying centrifugation times from 1 to 5 min at a rate of 5000 rpm were performed. The extraction efficiency for the analytes was lower when the centrifugation time was shorter than 3 min. But, longer centrifugation has not significant effect on the extraction efficiency of the chlorophenols. Therefore 3 min centrifuging time duration was selected in the further experiments.

### 3.7. Performance of the SA-DLLME procedure

The analytical performance of the proposed SA-DLLME method under optimum conditions was validated through the determination of preconcentration factors (PFs), limit of detections (LODs), linear dynamic ranges (LDRs), and precision (RSDs) for the

**Table 3**
Analytical results for the extraction and determination of chlorophenols in natural water samples.

| Samples | Chlorophenols | Added ($\mu g\,L^{-1}$) | Found[a] ($\mu g\,L^{-1}$) | Error (%) | RSD (%) ($n=3$) |
|---|---|---|---|---|---|
| Tap water | 2-CP | 0 | <LOD | – | – |
| | | 5.0 | $5.3_2$ | 6.4 | 5.1 |
| | 4-CP | 0 | <LOD | – | – |
| | | 5.0 | $4.9_8$ | −4.0 | 3.4 |
| | 2,3-DCP | 0 | <LOD | – | – |
| | | 5.0 | $4.9_0$ | −2.0 | 5.8 |
| | 2,5-DCP | 0 | <LOD | – | – |
| | | 5.0 | $5.4_3$ | 8.6 | 10.4 |
| Sea water | 2-CP | 0 | <LOD | – | – |
| | | 5.0 | $5.5_1$ | 10.2 | 7.0 |
| | 4-CP | 0 | <LOD | – | – |
| | | 5.0 | $5.0_2$ | 0.4 | 6.4 |
| | 2,3-DCP | 0 | <LOD | – | – |
| | | 5.0 | $4.8_9$ | −2.2 | 4.9 |
| | 2,5-DCP | 0 | <LOD | – | – |
| | | 5.0 | $5.3_2$ | 6.4 | 6.1 |
| Mineral water | 2-CP | 0 | <LOD | – | – |
| | | 5.0 | $5.4_4$ | 8.8 | 5.9 |
| | 4-CP | 0 | <LOD | – | – |
| | | 5.0 | $4.8_7$ | 2.6 | 6.8 |
| | 2,3-DCP | 0 | <LOD | – | – |
| | | 5.0 | $5.1_9$ | 3.8 | 6.2 |
| | 2,5-DCP | 0 | <LOD | – | – |
| | | 5.0 | $5.0_8$ | 1.6 | 9.6 |

[a] Concentration of chlorophenols in spiked samples that was founded by the proposed SA-DLLME method.

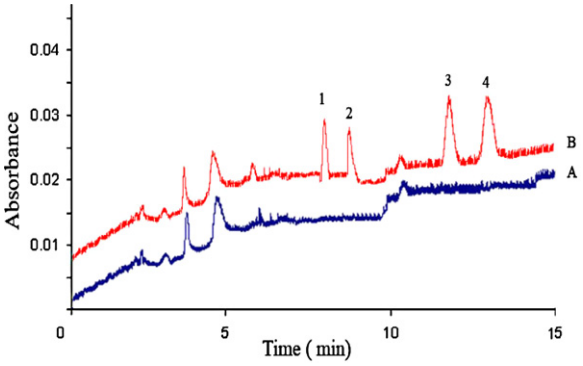


**Fig. 5.** HPLC-UV chromatograms of the (A) non-spiked and (B) spiked sea water by 5 $\mu g\,L^{-1}$ of the target analytes, after SA-DLLME. (1) 2-CP, (2) 4-CP, (3) 2,3-DCP and (4) 2,5-DCP.

chlorophenols. To evaluate the linearity of the method, a series of solutions at fifteen different concentrations (ranging from 0.01 to 200 $\mu g\,L^{-1}$) were prepared by spiking ultra-pure water with four chlorophenols. The results are summarized in Table 1. Linearity was observed over the range of 0.2–200 $\mu g\,L^{-1}$ with correlations of determinations better than 0.9985. LOD for each chlorophenol, based on a signal to noise ratio (S/N) of 3, was 0.1 $\mu g\,L^{-1}$. The within-day precisions ranged from 4.7 to 6.9% and the between-day precisions ranged of 8.2–12.3% based on the peak areas for five replicates. The PFs were varied between 187 and 353. Some characteristic of previously reported methods such as LOD, DLR, PF and extraction time for extraction and determination of chlorophenols are summarized in Table 2 for comparison. As can be seen, LODs, LDRs and PFs of the current method are comparable with the other microextraction methods. In addition, the extraction time of the proposed method is shorter than some of other methods.

### 3.8. Analysis of the real samples

To demonstrate the capability of the proposed method, the procedure was applied to the analysis of chlorophenols in sea, tap and mineral waters. The results showed that the analyzed samples were free of chlorophenols. The water samples were spiked with the analytes at 5 $\mu g\,L^{-1}$ levels and the SA-DLLME–HPLC method was applied to assess the matrix effect. Accuracy was calculated as the relative errors (errors%) for the analysis of known amounts of target analyte added to actual water samples using the proposed method (Table 3). The relative standard deviations for determination of chlorophenols in the examined real water samples were located in the range of 3.4–10.4%. The typical chromatograms of the non-spiked and spiked sea water sample obtained by the SA-DLLME are shown in Fig. 5.

### 3.9. Application range

SA-DLLME is a simple and rapid extraction procedure and can be used to extract a wide range of organic compounds without need to exact pH adjustment from water samples. To elucidate the applicability range of the proposed method, the capability of SA-DLLME was investigated for the extraction of analytes by dispersion of extraction solvent into water–surfactant system using vortex apparatus, and also dispersion of surfactant–extraction solvent mixture into aqueous phase like traditional DLLME to simplify the SA-DLLME procedure. The results showed the ability of SA-DLLME technique for the extraction of analytes from water samples is similar to other options of DLLME.

## 4. Conclusion

In the present study, cationic surfactant was used as a disperser agent in DLLME procedure named surfactant assisted dispersive liquid–liquid microextraction (SA-DLLME) as a sample preparation step before determination of chlorophenols in natural water samples by HPLC-UV. The experimental results revealed that this method provides high recovery and preconcentration factor within a short time and good linearity over the investigated concentration range. The performance of this procedure in the extraction of chlorophenols from natural waters was also satisfactory. The LODs of target chlorophenols was 0.1 $\mu g\,L^{-1}$, which showed a high sensitivity of the proposed method. A comparison of the SA-DLLME technique with other microextraction techniques showed that it is somewhat comparable with them, and SA-DLLME appears to be a useful tool for rapid extraction of organic compounds.

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