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A novel strategy based on surfactant assisted electromembrane extraction for the determination of Dicamba and 2,4-DB as model herbicides in real water samples

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Abstract

In the present research, surfactant assisted electromembrane extraction (SEME) coupled with capillary electrophoresis (CE) was developed for the determination of 3,6-dichloro-2-methoxybenzoic acid (Dicamba) and 4-(2,4-dichlorophenoxy)butyric acid (2,4-DB) in real water samples. The addition of surfactant in the donor solution improved the analyte transport into the lumen of hollow fiber that resulted in an enhancement in the analytes migration into acceptor solution. To understand the effect of surfactant on the extraction efficiency, a comparative study was carried out between electromembrane extraction (EME) and SEME methods. Several parameters effective on extraction efficiency were studied and optimized (type of organic solvent, type and concentration of surfactant, pH of the donor and acceptor phases, stirring rate, time, and salt addition). In the optimum conditions, the limits of detection were obtained 6.03 ng mL^{-1} for 2,4-DB and Dicamba, respectively. The method was reproducible so that intra and inter day relative standard deviations (RSDs %) were less than 8.9 % for both analytes. Finally the optimized method was successfully employed for the determination of Dicamba and 2, 4-DB in the real water samples.

Keywords: Surfactant assisted electromembrane-extraction; 3,6-dichloro-2-methoxybenzoic acid; 4-(2,4-dichlorophenoxy)butyric acid; Capillary electrophoresis; Water samples, Herbicides.

1. Introduction

Phenoxy acid herbicides are a major class of toxics employed in agricultural and forestry applications to control the growth of different unwanted vegetable species in the crops. They can remain as residues in crops, soils, and surface waters. Their incorrect application may leave harmful residues, which involve possible health risks [1, 2]. Therefore, this research aims to introduce a new method for simultaneous determination of 2,4-DB and Dicamba as two models of these phenoxy acid herbicides. The maximum contaminant level of 2, 4-DB and Dicamba are set as 30 to 100 ng mL^{-1} in drinking water by Environmental Protection Agency (EPA) of United States (Fig. 1) [3].

Here Fig.1

The development of a rapid and specific method allowing the determination of the residue of these herbicides in different environmental samples is an important issue in human health and environmental contexts. Several analytical methods have been reported for the determination of phenoxy acid herbicides in different media such as micellar electrokinetic capillary chromatography (MEKC) [4], ion chromatography (IC) [5], high-performance liquid chromatography (HPLC) [6], and HPLC with coulometric detection [7].

It is necessary to note that the concentration of Dicamba and 2,4-DB are below the detection limit of most analytical devices. Furthermore, their direct analysis in real samples is not possible due to the presence of interfering compounds along with the desired molecules. Consequently, sample pretreatment is a critical step that must be selective and sensitive enough, especially in the case of river water samples. Different methods such as liquid–liquid extraction (LLE) [8], solid phase extraction (SPE) [9-11], stir-bar sorptive extraction (SBSE) [12], solid phase microextraction (SPME)

[13], single drop microextraction (SDME) [14], molecular imprinted polymer (MIP) [15], hollow fiber liquid phase microextraction (HF-LPME) [16], and EME [17] have been developed.

Recently, a totally new concept based on electrokinetic migration of charged analytes was introduced by the suggestion of EME. The EME system uses a power supply and two electrodes to apply the voltage across the support liquid membrane (SLM). One of the electrodes is placed in the donor phase, while the other electrode is placed in the acceptor phase inside the lumen of the fiber. The driving force in EME is the electrokinetic migration in response to the applied electrical potential. Charged analytes in the donor phase are drawn across the SLM towards the electrode of opposite charge in the acceptor phase. The pH in both sides of the SLM must be adjusted to optimized values in order to ensure sufficient ionization of the analytes in the sample and the acceptor solutions. The acceptor solution can either be an organic solvent, providing a two-phase extraction system directly compatible with gas chromatography (GC), or an aqueous solution, providing a three-phase extraction system compatible with HPLC or CE [18,19]. To increase the efficiency of extraction system in EME, sample solution or SLM can be supported with the materials that are able to make an increase in analyte migration [20, 21].

Surfactants are amphiphilic compounds that consist of both hydrophobic and hydrophilic moieties. Therefore, they have dissolved in both organic and aqueous phases. Surfactants can form amphiphilic association structures such as micelles, vesicles, microemulsions, and liquid crystals when combined with each other and with water. Because of these structures, there has been an increasing attraction in their applications in sample pretreatment techniques to improve extraction efficiency [22]. Surfactants were used in some microextraction method such as cloud point extraction, dispersive liquid-liquid microextraction, ultrasound-assisted emulsification microextraction and HF-LPME [23-26].

This study, for the first time aims to develop a SEME procedure coupled with CE for the extraction and determination of Dicamba and 2,4-DB as model herbicides from real water samples. The novelty of the present work is presence of surfactant in the sample solution that can help analyte to transfer into SLM, resulting in higher sensitivity, enrichment, and low limits of detection.

2. Experimental

2.1. Chemical and Reagents

Dicamba and 2, 4-DB were purchased from Dr Ehrenstorfer (Augsburg, Germany). Phosphate salts (KH_2PO_4, K_2HPO_4), NaOH, NaCl, HCl, Triton X-100 and X-114 from Merck (Darmstadt, Germany) and 1-octanol, toluene, nitrobenzene, 1-nonanol, n-hexane, and 1-heptanol were obtained from Fluka (Buchs, Switzerland). Tween-20 was obtained from Sigma (St. Louis, MO, USA). A digital pH-meter (Cyberscan 2100, Eutech Instruments, Singapore) was employed for pH measurements. To prevent capillary blockage, all buffers were filtered through 0.45 µm filter membranes (Millipore, Bedford, MA, USA).

2.2. Equipment for SEME

The DC power supply used was a model EPS-600Z from Paya Pajohesh (Tehran, Iran) with programmable voltage within the range of 0-300 V and current range of 0-0.50 A. Platinum wires (diameter 0.2 mm) were used as electrodes with an inter-electrode distance of 5 mm in the sample and acceptor solutions. The porous hollow fiber used for the immobilization of the SLM and housing the acceptor solution was a PP Q3/2 polypropylene hollow fiber (Membrana, Wuppertal, Germany) with an internal diameter of 0.60 mm, wall thickness of 200 µm, and 0.2 µm pores. The EME cell was stirred with a stirring rate in the range of 100-1250 rpm by a heater-magnetic stirrer model 301 from Heidolph (Kelheim, Germany) using 5×2 mm magnetic bars.

2.3. Procedure for SEME

The SEME method was performed according to follows.In order to prepare the 1-octanol immobilized membrane, the polypropylene hollow fiber were cut into 6 cm segments, cleaned in acetone and dried prior to use. The hollow fibers were then immersed in 1-octanol for 20 mins to impregnate the pores in the fiber walls with the organic solvents and excess of solvent was removed with a medical wipe. 20 μL of the NaOH (pH 13.0) was introduced into the lumen of the hollow fiber using a microsyringe. The excess of acceptor phase was removed from its end and then the end of the hollow fiber was sealed using a pair of hot flat-tip pliers. A 4.0 mL aqueous sample solution (pH 8.0) containing 100 ng mL^{-1} of each herbicides and a certain concentration of surfactant were spiked into sample vial. The whole extraction cell was placed on a stirrer and was stirred for a certain time. When the extraction was complete, the sealed end of the hollow fiber was cut with scissors, and the acceptor phase was collected with a microsyringe, and then transferred to the sample vial of CE.

Here Fig. 2

2.4. Standard solutions

Stock solutions of Dicamba and 2,4-DB with a concentration of 1000 mg L^{-1} was prepared by diluting a certain amount of concentrated solution and transferring it into a 50 mL calibrated volumetric flask, and the volume was adjusted with deionized water. A 0.1 M stock solution of each surfactant was prepared and used in subsequent experiments. The stock solutions were protected from light using aluminum foil and stored at 4 ^{0}C. Then, the required working standard solutions were freshly prepared by appropriate dilution of the stock solution to the desired concentrations. Three river water samples were collected from Jajrood, Caspian Sea, and

Sepidrood to serve as real water samples. Water samples were diluted with the 1:1 ratio with the water. The pH values were adjusted at 8.0 by the addition of 4.0 M HCl and NaOH solutions.

2.5. CE conditions

Detection procedure was carried out using a Lumex Capel 105 (Ohiolumex, Twinsburg, Russia) equipped with a UV detector operated at 214 nm. Computer-controlled Chrom & Spec software version 1.5 was used to collect and analyze the data of the electropherograms. The background electrolyte solution was 100 mM phosphate buffer adjusted to pH 7.0. The detection were carried out at 16 kV, generating a current level within the range of 120-145 μA. The acceptor solutions were injected by hydrodynamic injection at 60 mbar for 10 s. Before using, the capillary was conditioned for 20 mins with 0.5 M HCl, 5 mins with water, 30 mins with 0.5 M NaOH and 5 mins with water. Additionally, the capillary was washed for 1 min with 0.5 M NaOH, 1 min with water and 2 mins with the running buffer with positive pressure applied at the injection end before each run.

2.6. Calculation of extraction recovery and enrichment factor

The extraction recovery (ER %) of the EME procedure was calculated according to the following equation:

$$ER = \frac{n_{a,final}}{n_{s,initial}} 100\ \% = \left(\frac{V_a}{V_s}\right)\left(\frac{C_{a,final}}{C_{s,initial}}\right) \times 100\ \% \quad (1)$$

where $n_{s,initial}$ and $n_{a,final}$ are the number of moles of analyte originally present in the sample and the number of moles of analyte finally collected in the acceptor solution, respectively. V_a is the volume of the acceptor solution, V_s is the volume of sample, $C_{a,final}$is the final concentration of analyte in the acceptor solution, and $C_{s,initial}$ is the initial analyte concentration in the sample solution. The enrichment factor (EF) of EME procedure was calculated according to the following equation:

$$EF = \frac{C_{a,final}}{C_{s,initial}} \quad (2)$$

and relative recovery (RR) was acquired from the following equation:

$$RR\% = \frac{C_{found} - C_{real}}{C_{added}} \times 100 \quad (3)$$

Where C_{found}, C_{real}, and C_{added} are the concentration of analyte after addition of a known amount of the standard into the real sample, the concentration of analyte in real sample, and the concentration of known amount of standard which was spiked into the real sample, respectively.

3. Results and discussion

3.1. Optimization of SEME procedure

In order to obtain the best extraction efficiency, different parameters affecting the extraction procedure were studied and optimized.

3.1.1. Variation in the SLM composition (organic solvent)

The nature of the organic solvent plays an important role in extraction efficacy. Firstly, the organic solvent should have good affinity for target compounds to allow the enhancement of extraction migration between the donor and acceptor solutions. Secondly, its vapor pressure should be low to prevent the solvent loss during the extraction process. Furthermore, it should be immiscible with water; otherwise the organic solvent is prone to get lost in the sample solution [27]. To obtain best results, six organic solvents including 1-octanol, toluene, nitrobenzene, 1-nonanol, n-hexane, and 1-heptanol were evaluated on extraction efficiencies. Among the all tested solvents, 1-octanol was found to be most efficient for the extraction of Dicamba and 2, 4-DB in the terms of analyte peak areas while the n-hexane showed the lowest efficiency.

3.1.2. Effect of the type and concentration of surfactant

In the following step of optimization process for SEME method, the effect of the type of surfactant on the extraction efficiency was studied by three different non-ionic surfactants (Triton X-100, X-114 and tween-20). Best results were obtained by Triton X-100, therefore it was selected for subsequent experiments. Surfactants can solubilize solutes with different properties and nature. These analytes can interact electrostatically, hydrophobically or by a combination of both interactions. As shown in Fig. 3, surfactants are transferred into the SLM based on the hydrophobic nature on their tails and membrane. Surfactants can form a hydrophobic layer around the analytes (partial layer) and make an increase in their migration and tendency to SLM. Due to mentioned point, the presence of surfactant in donor phase could make an increase in extraction efficiency in comparison with conventional EME.

Here Fig. 3

The results showed that the optimum concentration of surfactant was 0.15 mM. In this work, by increasing the concentration of surfactant until 0.15 mM in sample solution, migration of analyte increases across the SLM. The results showed that above 0.15 mM, extraction efficacy decreases. This can be explained by the fact that under 0.15 mM point (Critical micelle concentration (CMC) of Trition-X100 is 0.2 mM), the increase of free surfactant monomer will lead to an improvement of the extraction procedure. This increase can be due to formation of partial hydrophobic layer around model herbicides that facilitate their migration into SLM and improve in sensitivity. However, when the surfactant concentration was higher than the 0.15 mM, a fraction of analytes can incorporate into the micelles. Therefore, an approximately complete hydrophobic layer is formed around the analytes. According to mentioned point, the effect of applied potential may be decreased on the herbicide analytes. In addition, as the concentration of surfactant in the sample solution is increased, the viscosity of sample solution is enhanced. This increase in the

viscosity of donor phase can reduce the analyte migration across the SLM. Both expressed points can be resulted in lower extraction efficacy in the high concentration of surfactant in the sample solution.

Here Fig. 4

3.1.3. Effect of voltage

In EME, the electrokinetic migration of the analytes across the SLM into the acceptor solution is greatly dependent on the applied voltage. Obviously, the applied voltage determines the strength of electrical field which the analytes sense in the solution. Then, in order to find the optimal potential, peak area was investigated as a function of the applied electrical potential difference. The voltage applied across the SLM was varied between 0 and 70 V. Results showed that the efficiency of extraction process increased as the voltage was increased from 0 to 30 V whereas in higher voltages, efficiency decreased for 2, 4-DB and it was steadily changed for Dicamba (Fig. 5). This phenomenon could be explained from two different approaches. Firstly, in the EME procedure the electrolytic reactions take place with the extraction simultaneously. With increasing the voltage, the electrolysis of water at the positive electrode increases, leading to an increase of hydronium ions; back extraction occurs. Secondly, at the higher voltages, bubble formation at the electrodes produced by electrolysis could lead to the instability of the migration of the analytes, thus, it can affect the extraction efficiency negatively. [28]

Here Fig. 5

3.1.3. Effect of time

In EME, the migration of the analytes across the SLM into the acceptor solution is strongly dependent upon the time. A series of experiments with different extraction times between 5 to 30 mins were performed to determine the best time for extraction procedure. The results are

summarized in Fig. 6. For both analytes, extraction increased up to 25 mins and beyond 25 mins, extraction decreased. Therefore, 25 mins was selected as the optimum extraction time for SEME method. Observed decrease above 25 mins can be due to the organic solvent evaporation and/or dissolution in water solution [28].

Here Fig. 6

3.1.4. Effect of pH in donor and acceptor solutions

In the next step of optimization process, the pH of both donor and acceptor solutions were studied. The extraction involves pH adjustment of the sample solution to a pH where the analytes are charged molecules and have a good tendency for going to organic membrane. Consequently; the donor phase should be basic to ionize the acidic analytes and increase their transfer from the donor phase into the SLM in EME. The pH of the sample solution was varied in the range of 4.0 and 10.0 to determine the optimum pH of donor phase for herbicides extraction while the acceptor solution pH was kept constant at 13.0. The results showed that the extraction of the two model analytes would be more efficient at pH 8.0 in the donor solution for both analytes [29].

Corresponding experiments were performed to study the effect of pH in the acceptor solution. Based on the extraction principles of EME, the acceptor solution should be strongly basic in order to ionize the acidic analytes to be able to desorb analytes from SLM into acceptor phase. On other hand, the acceptor solution should have a pH where the analytes are charged to prevent them from back diffusion into the organic solvent. For this purpose, the pH of donor phase was kept constant at 8.0 and NaOH concentration was varied in the range of 0.1–100 mM NaOH in the acceptor phase. The results showed that migration increases for the analytes with the increase of the pH value of the acceptor solution. The pH 13.0 in the acceptor solution was selected as optimum in the subsequent experiments for both analytes [28].

3.1.5. Influence of agitation speed

Agitation of the donor solution was studied between 0 and 1250 rpm. The EME system efficiency is maximized in 1000 rpm and decreased in higher stirring rates. Although extraction could perform without agitation, observed peak areas were significantly weaker than those with agitation extraction. Therefore, 1000 rpm was selected for subsequent studies. Stirring speed enhances convection in the sample solution, thus promoting the extraction. However, it can be assumed that SLM was partly depleted at higher agitation speeds and leakage of the organic solvent from the SLM may occur [30].

3.1.6. Effect of ionic strength

The effect of ionic strength of donor solution prior to extraction has been widely studied. Some studies reported that the addition of salt to the donor phase improved the extraction efficiency in microextraction procedures. Therefore, in this study, the effect of salt addition in the donor solutions on extraction system was investigated by adding NaCl to aqueous samples in the range of 0-10% (w/v). The result indicated that the addition of salt limited the extraction. This is probably due to increase of the viscosity of the donor phase which decreases the diffusion rate and tends to restrict the movement of the analyte from the bulk solution to the organic phase [31].

3.2. Method performance

In order to verify the applicability of the proposed SEME method, the analyses were evaluated under optimized conditions. The method was validated with respect to the parameters including linearity, limit of detection (LOD), repeatability as RSD% (n=3), EF and RR. The results are summarized in Table 1.

Linear dynamic ranges (LDRs) of 20-700 ng mL^{-1} for Dicamba and 2,4-DB with good linearity correlations R^2: 0.992 and 0.995 were obtained, respectively. LODs, calculated based on

signal-to-noise ratio of 3 was found to be 6.03 ng mL^{-1} for Dicamba and 2, 4-DB. Repeatability or intra-day precision was investigated by injecting five replicate of a standard solution (100 ng mL^{-1}) and inter-day precision were assessed by injecting the same sample over five consecutive days. Intra and inter day precision extractions varied between 6.3 to 8.9 % for Dicamba and 6.8 to 8.5 % for 2, 4-DB. EFs of 215 and 185 were obtained that corresponded to relative recoveries ranging from 95 to 96.5%for Dicamba and 2, 4-DB, respectively.

3.3. Analysis of real samples

The SEME technique was applied to determination of herbicides in river water and spiked samples. Figure 7 shows the electrophoromogram obtained from spiked river water sample at concentration level of 50 ng mL^{-1}.The corresponding RRs % and RSDs% are summarized in Table 2. As can be seen, the relative recoveries in spiked river water samples were between 91.2 % to 96 % for Dicamba and 2, 4-DB, respectively. This indicates that the matrix effect did not have a significant role on the extraction efficiency.

Here Fig. 7

3.4. Comparison of the proposed method with others reported methods

The analytical performance of the proposed method was compared with the previous reported methods for the analysis of Dicamba and 2, 4-DB (Table. 3). The proposed method is superior in many ways such as linear range and LODs over other reported methods either using IC [5], MEKC [4] or other direct derivatization based methods.

SEME method can make a decrease in used solvents in proposed method in comparison with sample preparation techniques including LLE [32] or SPE [33] and consequently less residues are generated. In comparison to SPME that uses of the expensive and fragile fibers, due to the low cost of hollow fibers, one hollow fiber can be used per sample in SEME method. [13] Consequently,

the carry-over effect can be eliminated. In addition, compared to previous EME reported method, SEME resulted in higher LDR and lower LODs for two herbicides. [17] Therefore, SEME can provide good and sensitive results for the preconcentration and determination of these herbicides in environmental samples.

4. Conclusion

A novel surfactant assisted EME method has been introduced for the first time to extract and determine of Dicamba and 2,4-DB as model herbicides from real water samples. To investigate the effect of surfactant on the extraction efficiency, a comparative study was carried out between EME and SEME methods. The result demonstrates that the presence of surfactant in sample solution is an excellent approach to enhance the efficacy of EME method. This is probably related to increase in hydrophobicity of herbicides and an enhancement in analytes migration into the SLM. Consequently the proposed method offers more efficient extraction and higher sensitivity in comparison with conventional EME. Under optimized conditions, this method provided low LOD (6.03 ng mL^{-1}), high EF (185-215) and high extraction RR (95-96.5%). Finally the method was successfully employed for the determination of Dicamba and 2, 4-DB in real water samples.

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Table 1: Figures of merit of SEME method.

Method	Analyte	LOD (ng mL^{-1})	LDR (ng mL^{-1})	R^2	RSD%[a] intra day	RSD%[a] Inter day	EF[b]	RR%[b]
SEME	Dicamba	6.03	20-700	0.995	6.3	8.9	215	95

2,4-D,B	6.03	20-700	0.992	6.8	8.5	185	96.5

[a] RSD% was calculated at concentration of 100 ng mL^{-1} for analyte (n=3).

[b] EF and RR% were calculated at concentration of 100 ng mL^{-1} for analyte (n=3).

Table 2: Determination of Dicamba and 2, 4-DB in real water samples.

Sample	Analyte	C_{add} (ng mL^{-1})	C_{found} (ng mL^{-1})	RR%	RSD% (n=3)
RW1	Dicamba	-	6.5	-	6.8
		50	53.5	94	7.8
	2, 4-D, B	-	-	-	-

		50	45.6	91.2	7
RW2	Dicamba	-	-	-	-
		50	46.5	93	7.2
	2, 4-D, B	-	7	-	8.1
		50	53.25	92.5	7.5
RW3	Dicamba	-	-	-	-
		50	48	96	8.1
	2, 4-D, B	-	-	-	-
		50	47.75	95.5	9.6

RSD% was calculated at concentration of 50 ng mL^{-1} for analyte (n=3).
RW1: Jajrood, RW2: Sepidrood, RW3: Caspian Sea.

Table 3: Comparison of analytical performance data of the proposed method with other methods applied for the analysis of phenoxy acid herbicides.

Method	**Sample preparation**	**Herbicides**	**Organic solvent volume (µL)**	**LOD (ng mL^{-1})**	**LDR (ng mL^{-1})**	**RSD%**	**Refs.**

IC [a]	-	Dicamba	-	20	-	-	[5]
MEKC [b]	-	Dicamba	-	0.01	-	-	[4]
GC-MS[c]	SBSE[f]	2,4-D[n], Dicamba	500	0.001-0.8	0.5-5	15-20	[12]
GC-MS	SPME[g]	2,4-D, 2,4-DB, Dicamba	-	0.004-0.03	0.1-10	4-12	[13]
GC-MS	SDME[h]	2,4-D, 2,4-DB	4	0.0012-0.007	0.01-1	4-10	[14]
CE-UV[d]	EME[j]	2,4-D, 2,4-DB, Dicamba	10	10-15	30–500	3-5	[17]
GC-MS	LLE[k]	2,4-D, 2,4-DB, Dicamba	800	0.01-0.06	0.1-10	8-15	[32]
GC-ECD[e]	SPE[l]	2,4-D, Dicamba	500	0.02-0.05	-	2-10	[33]
CE-UV	SEME[m]	2,4-DB, Dicamba	16	6.03	20-700	6.3-8.9	This work

[a] Ion chromatography; [b] micellar electrokinetic capillary chromatography, [c]gas chromatography-mass spectrometry, [d] capillary electrophoresis-ultra violet(detector), [e] gas chromatography-electron capture detector, [f] stir-bar sorptive extraction, [g] solid phase microextraction, [h] single drop microextraction, [j] electromembrane extraction, [k] liquid-liquid extraction, [l] solid phase extraction, [m] surfactant assisted electro-membrane extraction, [n] 2,4-dichlorophenoxyacetic acid.

Figure captions

Fig. 1. Chemical structures, log P and pK_a values of phenoxy acid herbicides.

Fig. 2. Schematic illustration of the SEME technique.

Fig. 3. Effect of type of nonionic surfactants (0.1 mM) on the extraction efficiency: 100 ng mL^{-1} of each herbicide, 20 µL NaOH 100 mM as the acceptor phase and donor phase(pH 8.0), 1000 rpm

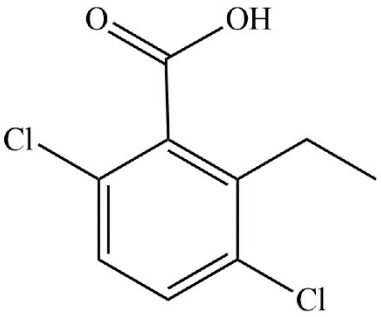
stirring rate, 20 mins extraction time, 1-octanol as SLM, and 20 V of applied potential [a: Dicamba and b: 2, 4-DB].

Fig. 4. Concentration of surfactant (Triton X-100) on the extraction efficiency: 100 ng mL^{-1} of each herbicide, 20 µL NaOH 100 mM as the acceptor phase and donor phase(pH 8.0), 1000 rpm stirring rate, 20 mins extraction time, 1-octanol as SLM, and 20 V of applied potential [a: Dicamba and b: 2, 4-DB].

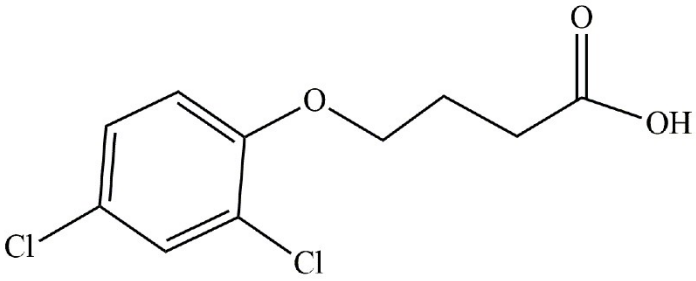
Fig. 5. Effect of applied potential on SEME efficiency; sample solution: 100 ng mL^{-1} of each herbicide, 20 µL NaOH 100 mM as the acceptor phase and donor phase(pH 8.0), 1000 rpm stirring rate, 20 mins extraction time, and 0.15 mM surfactant in sample solution [a: Dicamba and b: 2, 4-DB].

Fig. 6. Effect of extraction time on SEME method, Extraction conditions: sample solution: 100 ng mL^{-1} of analytes, 20 µL NaOH 100 mM as the acceptor phase and donor phase(pH 8.0), 1000 rpm stirring rate, SLM: 1-octanol (with 0.15 mM surfactant in sample solution), and 30 V of applied potential [a: Dicamba and b: 2, 4-DB].

Fig. 7. Electropherograms obtained SEME from non spiked (blank) and spiked samples with 50 ng mL^{-1} of each herbicides. SEME conditions: 30 V of applied potential, 20 µL NaOH 100 mM as the acceptor solution and donor solution (pH 8.0), 1000 rpm stirring rate, 25 mins extraction time, SLM: 1-octanol, and 0.15 mM surfactant in sample solution in a_1) blank of Caspian Sea a_2) spiked Caspian Sea and b_1) blank of Jajrood b_2) spiked Jajrood c_1) blank of sepidrood, and c_2) spiked of sepidrood [A: 2, 4-DB and B: Dicamba].



Dicamba
pKa: 1.97
MW: 221.04 g/mol
log P: 1.9



2,4-DB
pKa: 4.8
MW: 249.09 g/mol
log P: 3.5

Fig. 1.

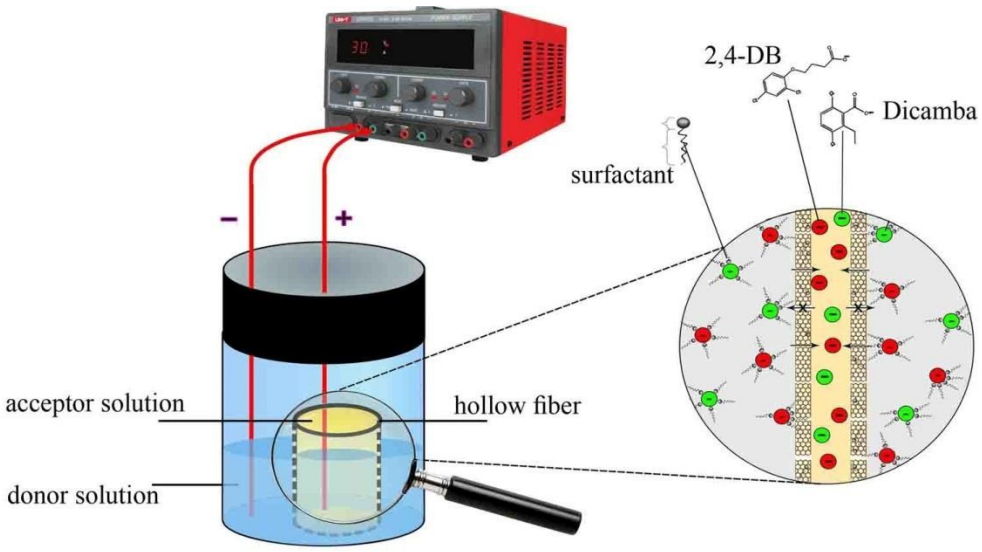


Fig. 2.

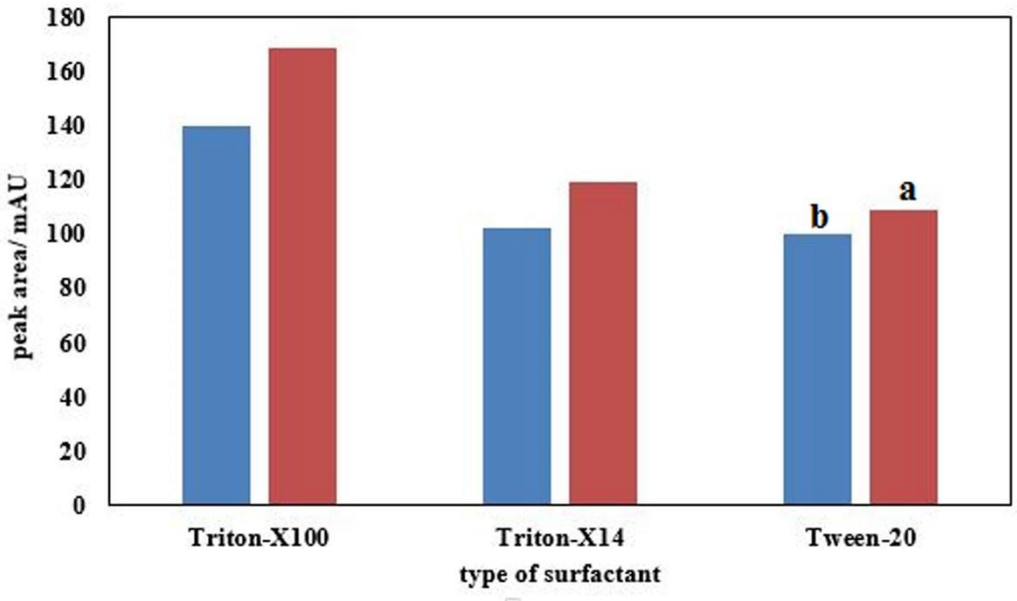


Fig. 3.

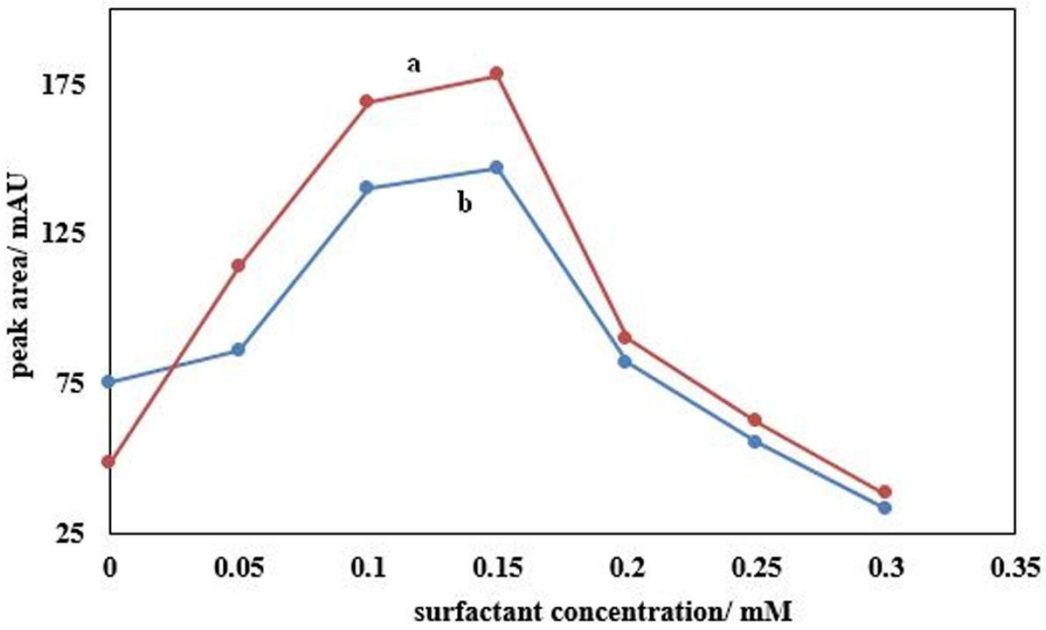


Fig. 4.

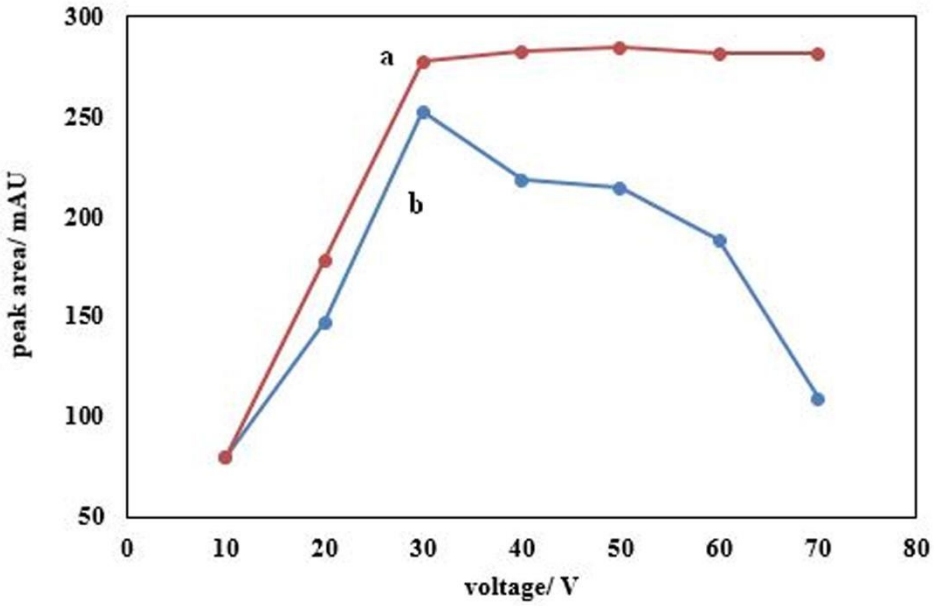


Fig. 5.

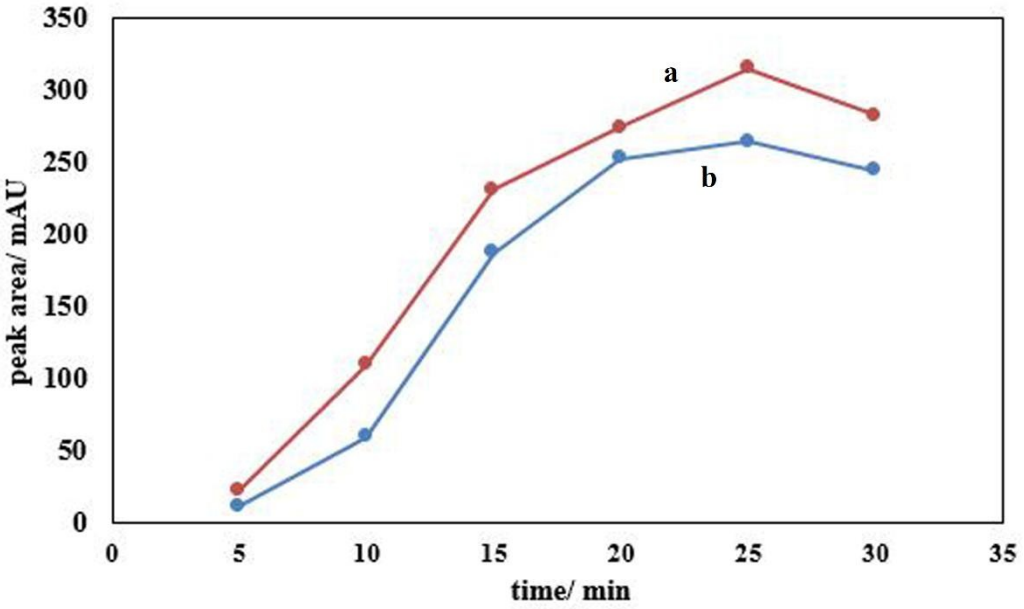


Fig. 6.

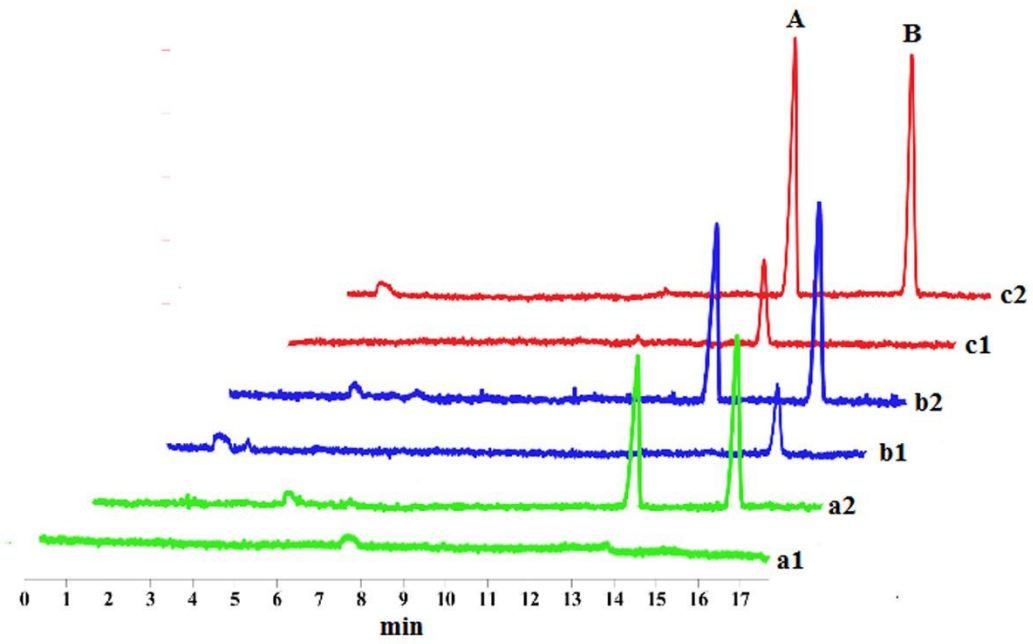


Fig. 7.

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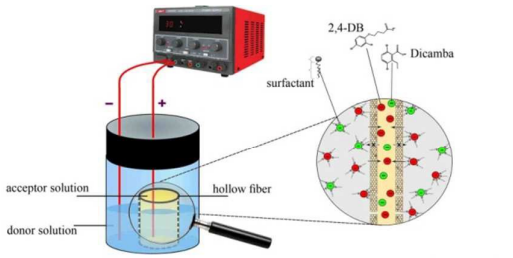

Schematic illustration of the surfactant assisted electromembrane-extraction (SEME) technique