



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Application of response surface methodology for determination of methyl red in water samples by spectrophotometry method



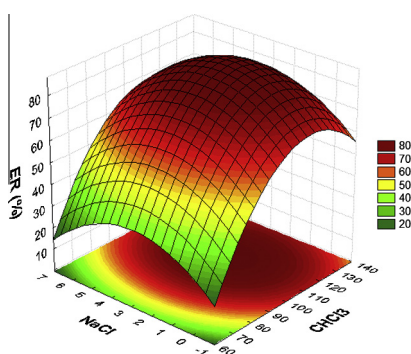
Saeid Khodadoust, Mehrorang Ghaedi*

Department of Chemistry, Yasouj University, Yasouj 75914-35, Iran

HIGHLIGHTS

- A simple method for the extraction of methyl red by using chemometrics was developed.
- The significant variables were optimized by using a BBD combined with DF.
- This technique provides good repeatability and high extraction recovery.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 4 March 2014
 Received in revised form 13 April 2014
 Accepted 22 April 2014
 Available online 30 April 2014

Keywords:

Methyl red
 Dispersive liquid–liquid microextraction
 Box–Behnken design
 Desirability function

ABSTRACT

In this study a rapid and effective method (dispersive liquid–liquid microextraction (DLLME)) was developed for extraction of methyl red (MR) prior to its determination by UV–Vis spectrophotometry. Influence variables on DLLME such as volume of chloroform (as extractant solvent) and methanol (as dispersive solvent), pH and ionic strength and extraction time were investigated. Then significant variables were optimized by using a Box–Behnken design (BBD) and desirability function (DF). The optimized conditions (100 μL of chloroform, 1.3 mL of ethanol, pH 4 and 4% (w/v) NaCl) resulted in a linear calibration graph in the range of 0.015–10.0 mg mL^{-1} of MR in initial solution with $R^2 = 0.995$ ($n = 5$). The limits of detection (LOD) and limit of quantification (LOQ) were 0.005 and 0.015 mg mL^{-1} , respectively. Finally, the DLLME method was applied for determination of MR in different water samples with relative standard deviation (RSD) less than 5% ($n = 5$).

© 2014 Elsevier B.V. All rights reserved.

Introduction

Dye and dye stuffs are extensively used in various areas such as textile, plastic, food, cosmetic, carpet and paper industries [1,2]. Wastewaters of these industries contain dye with metals, salts, and other chemicals which may be toxic to aquatic environment [3–5]. The release of colored wastewater from industry may produce an eco-toxic hazard and introduce potential danger of

bioaccumulation, which may eventually affect humans through the food chain [1]. Azo dyes are the largest group of dyes used in industry [2]. The term azo dye is applied to synthetic organic colorants that are characterized by a nitrogen-to-nitrogen double bond: $-\text{N}=\text{N}-$ [6]. Durability of azo dyes causes pollution to the environment. Besides, some azo dyes are toxic and mutagenic [7]. It is well known that methyl red (MR) dye has been used in paper printing and textile dyeing [8,9] and it causes irritation of the eye, skin and digestive tract if inhaled/swallowed [10].

Sample preparation is an important step in analytical methods for determination of analytes in various matrices. So a combination

* Corresponding author. Tel./fax: +98 741 2223048.
 E-mail address: m_ghaedi@mail.yu.ac.ir (M. Ghaedi).

of instruments with novel sample preparation methods has enabled analysis of trace amounts of analytes with higher accuracy. In the last decades design and development of miniaturized alternative methods to the older sample preparation techniques has been one of the most important challenges for analysts [11]. Liquid–liquid extraction (LLE) and Solid Phase Extraction (SPE) as the most commonly used techniques for sample preparation suffers from the disadvantages including time consuming, high cost, and need large volumes of samples and toxic organic solvents. Microextraction methods such as Solid Phase Microextraction (SPME) [12] and Liquid Phase Microextraction (LPME) [13,14] have attracted much attention in recent years as alternatives for classic liquid–liquid and solvent extraction procedures. These techniques are simple and fast, miniaturize sample pretreatment processes and minimize the use of organic solvents. However, these techniques suffer from some problems such as sample carry-over, relatively high cost, fiber fragility and relatively low precisions [15]. Dispersive liquid–liquid microextraction (DLLME) was developed to overcome these limitations [16,17]. It is based on a ternary component solvent system like homogeneous LLE and Cloud Point Extraction (CPE) [18]. In this method, the appropriate mixture of extraction and dispersive solvents are injected rapidly into aqueous sample by syringe, and a cloudy solution is formed. The analyte in the sample is extracted into fine droplets of extraction solvent. After extraction, phase separation is performed by centrifugation and the enriched analyte in the sediment phase is determined by various methods. From commercial, economical and environmental point of view, DLLME offers several important advantages over conventional solvent extraction methods: faster operation, easier manipulation, no need of large amounts of organic extraction solvents, low time and cost, high extraction recovery and enrichment factor [19–21]. There are several experimental variables affecting the DLLME procedure that must be optimized [22,23].

In recent years, chemometric tools such as response surface methodology (RSM) based on statistical Design of Experiments (DOEs) have been frequently applied to the optimization of analytical methods. Such statistical analyses are more efficient, since they account for interaction effects between the studied variables and determine more accurately the combination of levels that produces the optimum of the process [19,22]. If there is significant interaction affects between variables, the optimal conditions indicated by the univariate studies will be different from the correct results of the multivariate optimization. So the univariate procedure may fail since the effect of one variable can be dependent on the level of the others involved in the optimization process. That is why multivariate optimization schemes involve designs for which the levels of all the variables are changed simultaneously. These methods have advantages such as a reduction in the number of experiments that need be executed resulting in lower reagent consumption and considerably less laboratory work. A structured experiment design that could simultaneously take into account several variables seems a more convenient approach searching for the optimal operational conditions in a reasonable number experimental runs [24,25].

The Box–Behnken design (BBD) is a second-order multivariate technique based on three-level incomplete factorial designs that received a wide application for assessment of critical experimental conditions, that is, maximum or minimum of response function. BBD, a spherical and revolving design, has been applied in optimization of chemical and physical processes because of its reasoning design and excellent outcomes [22–24].

In the present work, DLLME followed by UV–Vis detection was applied for extraction and determination of the MR in water samples. Influence of important DLLME variables such as the kind and volume of extraction and disperser solvent, pH of the sample solution, extraction time and salt effect were investigated and

optimized by BBD and desirability function (DF). The applicability of presented method for the analysis of water samples has also been investigated.

Experimental

Reagents and instrumentation

All chemicals that used in this work were of analytical reagent grade and were used without further purification. Double distilled deionized water was used throughout which was produced by a Milli-Q system (Millipore, Bedford, MA, USA). Carbon tetrachloride, chloroform, dichloromethane, methanol, acetonitrile (HPLC grade), acetone and tetrahydrofuran (for spectroscopy) were obtained from Merck (Darmstadt, Germany). The methyl red (MR) (Fig. 1) and sodium chloride were purchased from Merck. A stock standard solution of MR (200 mg L^{-1}) was prepared in methanol. The working standard solutions were prepared in double distilled/deionized water.

Recording the absorption spectra and absorbance measurements were carried out with a UV–Vis spectrophotometer (model V-530, Jasco, Japan) using 1.0 cm quartz cells. A pH meter (model-686, thermometer Metrohm, Switzerland) equipped with a combine Ag/AgCl glass electrode was used to check the pH of the solutions. A Hermle Labortechnik GmbH centrifuge model Z206A (Germany) was used to accelerate the phase separation.

Dispersive liquid–liquid microextraction (DLLME) procedure

For DLLME, 5.0 mL aliquot of water sample was placed in a 10 mL screw cap glass tube with conic bottom and spiked at the level of 0.5 mg mL^{-1} of MR. A mixture of 1.3 mL of ethanol (as disperser solvent) and 100 μL chloroform (as extraction solvent) was injected rapidly into a sample solution by using 2.0 mL syringe and mixture was gently shaken. A cloudy solution that consists of very fine droplets of chloroform dispersed into aqueous sample was formed, and the MR was extracted into the fine droplets. After centrifugation at $4000 \text{ rpm min}^{-1}$ for 5 min the chloroform phase was sediment (about 70 μL) at the bottom of the centrifuge tube and entirely transferred into a vial using 100 μL syringe for evaporation of solvent. The residue was dissolved in 2.00 mL methanol and was conveyed to a UV–Vis spectrophotometer to measure its absorbance at λ_{max} (486 nm).

Calculation of enrichment factor and extraction recovery

The enrichment factor (EF) was defined as the ratio between the analyte concentration in the settled phase (C_{set}) and the initial concentration of the analyte (C_0) in the aqueous sample [26].

$$EF = C_{\text{set}}/C_0 \quad (1)$$

The extraction recovery (ER%) was defined as the percentage of the total analyte which was extracted in the settled phase.

$$ER\% = (C_{\text{set}} \times V_{\text{set}}/C_0 \times V_{\text{aq}}) \times 100 = EF \times V_{\text{set}}/V_{\text{aq}} \quad (2)$$

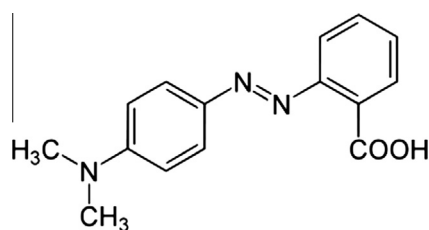


Fig. 1. Molecular structure of MR.

Download English Version:

<https://daneshyari.com/en/article/1233427>

Download Persian Version:

<https://daneshyari.com/article/1233427>

[Daneshyari.com](https://daneshyari.com)