Desalination and Water Treatment
www.deswater.com
doi:10.5004/dwt.2018.22740

120 (2018) 173–179
July

Development and optimization of chemometric assisted micro-cloud point extraction for preconcentration and separation of Eriochrome black T in water and wastewater samples

Abolfazl Rakhshani Aval, Mashaallah Rahmani*, Elham Ghasemi

Department of Chemistry, Faculty of Sciences, University of Sistan and Baluchestan, Zahedan 98135-674, Iran, email: abolfazlrakhshaniavval@gmail.com (A.R. Aval), Tel. +98 54 31132662, email: Rahmani341@hamoon.usb.ac.ir (M. Rahmani), ghasemi@pgs.usb.ac.ir (E. Ghasemi)

Received 21 November 2017; 3 July 2018

ABSTRACT

In this work, a new inexpensive and easy to use micro-cloud point extraction (MCPE) method is proposed for the extraction and preconcentration of Eriochrome black T (EBT) before spectrophotometric determination. To increase the extraction efficiency, the effecting factors on the MCPE procedure were investigated and optimized using the Taguchi design method and Response surface methodology (RSM). A second-order response surface model for micro-cloud point extraction of Eriochrome black T is developed to predict responses. Under optimum conditions, the calibration curve was linear in the range of 0.20–2.00 mg L^{-1} with a detection limit of 59 μg L^{-1} for EBT.

Keywords: Micro-cloud point extraction; Taguchi design method and Response surface methodology; Eriochrome black T; Water and wastewater analysis

1. Introduction

Environmental pollution with organic dyes poses dire effects on living beings [1]. Most of these dyes are released to the environment by large industries such as textiles, leather, paper, and food. This is due to the broad application of dyes in such industries [2] and because most factories do not apply appropriate refine on their wastewater. Considering their hazard to the environment, the determination of organic dyes in environmental samples has become very important in recent decades, and many methods have been proposed for the determination of dyes in water and wastewater samples [3]. One industrial dye which has a lot of applications in different industries is Eriochrome black T (EBT) [4]. This dye is an azo dye which means it contains -N=N-bond in its structure (Fig. 1). Eriochrome black T (EBT) or Mordant Black 11 is a popular pH indicator. Eriochrome black T is applied in dyeing wool fabric, silk, and nylon [5]. Therefore, it was considered worthwhile to make efforts to develop a simple method for the determination of EBT in water and wastewater samples. Due to the low concentration of dyes in water, usually, a sample preparation step is necessary before the introduction of the sample to analytical instruments. Many techniques have been developed for this purpose including solid phase extraction (SPE) [6], solid phase microextraction (SPME) [7], molecularly imprinted solid phase extraction (MISPE) [8], dispersive liquid-liquid microextraction (DLLME) [9], hollow fiber-liquid phase microextraction (HF-LPME) [10], and cloud point extraction (CPE) [11]. CPE is a simple, inexpensive and easy to operate extraction method, which a surfactant is used as extractant solvent.

Usually, batch and dynamic adsorption processes have been applied for the removal of EBT from waste effluents. Among the variety of adsorbents, microwave radiation-treated almond shell [12], hydrophobic cross-linked polyzwitterionic acid (HCPZA) [13], β-cyclodextrins/polyurethane foam material [14], magnetic/silica/pectin nanoparticles [15], bottom ash [16], NiFe-calcined layered double hydroxides [17], activated carbon [18] and maize stem tissue [19] have been used for the removal of EBT from wastewater. Moreover, very few works are available

---

*Corresponding author.

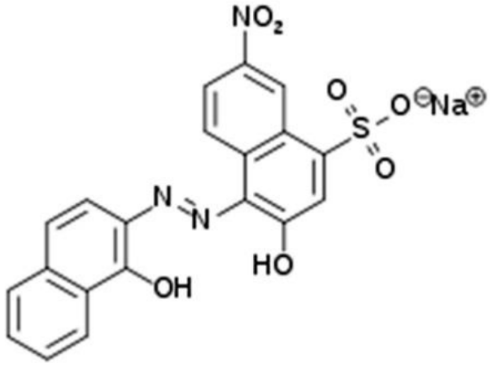


Fig. 1. Structure of EBT.

for the extraction and preconcentration of Eriochrome black T in aqueous solution [20]. In this work, a new micro-cloud point extraction (MCPE) method is applied for the first time in the extraction and preconcentration of EBT before spectrophotometric determination. MCPE is an extraction method based on CPE. In this method, the whole CPE procedure is carried out in brine, and consequently, the water bath step is eliminated [21]. MCPE consists of a few simple steps: addition of surfactant to sample solution, the addition of salt to form a cloudy solution (micelle formation), and separating of enriched micellar phase from the aqueous phase with centrifugation. In all the extraction methods, there are some factors that can affect the extraction efficiency. To reach the highest efficiency of extraction, these factors must be optimized. Therefore, the optimization process is very important. Optimization process requires an understanding of which factors are important and to what level they should be set. Usually, optimization is done by a univariate method which means changing one variable at a time. Because of the high number of experiments that must be done, univariate methods of optimization are expensive and time-consuming. Multivariate studies of effective factors where factors are studied simultaneously appear to be good replacements for univariate methods [22]. This can be achieved by applying the design of experiments (DoE) methods [22]. In this way, the optimization process will be done with the least number of experiments. DoE have the ability to determine the importance of factors and their contribution to the results. Then based on the contribution of factors, it will set the best settings of factors as an optimized condition. Of the popular DoE methods frequently used by analytical chemists, we can name Fractional factorial design (FFD) [23], Response surface methodology (RSM) [24], and Taguchi design [25]. The Taguchi method is a very powerful user-friendly method, which has some advantages in comparison with traditional univariate optimization method such as keeping the experimental cost at a minimum level, by reducing the time of experimental investigation and being able to study the influence of individual factors to determine the most effective parameter in the procedure. In this paper, MCPE was applied for preconcentration and spectrophotometric determination of EBT in aqueous samples. To find out the optimal conditions for the proposed method, the Taguchi design method and Response surface methodology are used. A second-order response surface model for micro-cloud point extraction of Eriochrome black T is developed to predict responses.

2. Experimental

2.1. Instrument

A Shimadzu UV/Vis spectrophotometer model UV-160 (Japan) equipped with two 10 µL microcells (Starna, UK) was used for measuring the absorbance and recording the spectra of EBT. A Metrohm pH meter model EasySeven (Switzerland) was used for pH measurements.

2.2. Reagents and chemicals

All chemicals used in this research were of analytical grade and were used as received. They were purchased from Merck KGaA (Germany). Triton X-114 (1% w/v) and Na_2SO_4 (5% w/v) solutions were prepared in doubly distilled water. A stock solution of EBT (500 mg L^{-1}) was prepared in 100 mL of doubly distilled water. Working solutions were obtained by daily dilution of the stock solutions. All solutions were kept in a refrigerator at 4°C.

2.3. Micro-cloud point extraction procedure

To perform MCPE procedures, five mL sample solution containing EBT in the range of 0.20–2.00 mg L^{-1} was prepared in a centrifuge tube. The pH of the sample solution was adjusted to 3 with the help of HCl and NaOH solutions (0.1 mol L^{-1}), and then Triton X-114 (0.2% w/v) was added to it. To form a cloudy solution, a proper volume of Na_2SO_4 solution (1.5% w/v) was added to the mixture. After addition of the salt, the solution became cloudy, and the dye was extracted into micelles. This mixture was centrifuged for 7 minutes at 5000 rpm to separate the enriched micellar phase and aqueous solution. 20 µL of high density enriched micellar phase which was settled at the bottom of the tube, was transferred to a vial and dissolved in 50 µL of the diluting solvent. Ten µL of this mixture was transferred to the microcell for spectrophotometric determination. The absorbance of this solution was recorded against the blank at the maximum absorption wavelength of EBT in 575 nm.

2.4. Design of experiments

Taguchi method is a powerful design of the experiment method, which has been used widely by the analytical chemist in optimization procedures [26]. In the Taguchi method, the number of experiments that can increase the time and cost of analysis can be reduced by using an orthogonal array. Based on the orthogonal array, Taguchi can learn the entire parameters space. Taguchi uses the signal to noise (S/N) ratio to identify the quality characteristics. The S/N ratio is quoted in dB units can be defined in three forms: the smaller the better, the nominal best, and the larger the better. Where larger is the better, which is the case in the present research, S/N ratio can be defined as [27]:

$$\frac{S}{N}=\frac{-10\log\left(\frac{1}{y_1^2}+\frac{1}{y_2^2}+\ldots+\frac{1}{y_n^2}\right)}{n} \tag{1}$$

where n is the replication number of the experiment and y_i is the characteristic property.

For MCPE, it was necessary to dilute the enriched micellar phase in an organic solvent. For this purpose, four solvents namely acetone, ethanol, methanol, and acetonitrile were investigated. Therefore, 20 µL of enriched micellar phase which was settled at the bottom of centrifuge tube after centrifugation was diluted with 50 µL of dilution solvent. Some important factors were considered in the selection of dilution solvent: the ability of the selected solvent to dissolve the sedimented phase completely and rapidly, its absorbance, repeatability of results. Dissolution of the sedimented phase in acetone took place difficulty. On the other hand, the absorbance of EBT and its repeatability using ethanol was high. Therefore, we selected ethanol as dilution solvent for MCPE of EBT (Fig. 2).

The effecting factors and levels used for Taguchi design are shown in Table 1. The L16 orthogonal array, absorption and S/N ratios obtained for each experiment are shown in Table 2.

Response surface methodology is an important branch of experimental design. It is to find a suitable approximation for the true functional relationship between y and the set of independent variables used. The RSM uses the interaction between statistical and mathematical techniques that are useful for modeling and analyzing engineering problems and developing, improving, and optimizing processes. Usually, a second-order model is used in RSM.

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i \chi_i + \sum_{i=1}^{k} \beta_i x_i^2 + \sum_{i} \sum_{j} \beta_{ij} \chi_i \chi_j + \varepsilon \qquad (2)$$

The β factors applied in the mentioned model can be estimated by the least square method.

3. Result and discussion

3.1. Effect of pH

The pH can potentially influence enrichment factor of extraction of the analyte. In this study, Triton X-114 was used for micro-cloud point extraction of EBT. The different forms of the EBT have a different tendency for extraction in the micellar phase of the Triton X-114 as a non-ionic surfactant that can give different results by spectroscopy analysis. The ionic form of the analyte normally does not interact or bind as strongly as its neutral form with a non-ionic surfactant [28]. The sulfonate group of EBT turn to be anionic in the aqueous solution, and a decrease in pH of EBT aqueous solution turn azo group to be protonated. Moreover, pKa of EBT is 6.2, and its anionic form dominates in pH > pKa. In pH = 3, EBT has a higher tendency for extraction in micellar phase. This could be explained by the presence of a lesser ionized form of EBT, which bind strongly with Triton X-114 as a non-ionic surfactant.

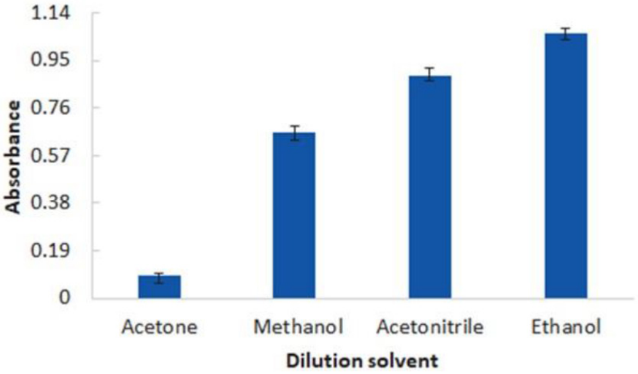


Fig. 2. Effect of dilution solvent on MCPE of EBT.

3.2. Effect of salt concentration

In the cloud point extraction, the micelle formation is achieved by placing the sample solution in a hot water bath for a period. However, in the present work, MCPE was performed at room temperature simply by increasing the ionic strength of the sample solution. To study the effect of ionic strength on the formation of micelles and efficiency of MCPE, different brine solutions of Na_2SO_4 in the range of 0.05–1.50% (w/v) were studied (Fig. 4). At 0.5% of w/v salt, the recovery was reduced. This result might be related to increasing the viscosity of the surfactant-rich phase, leading to a decrease in the signal. Further addition of salt from 0.5 to 1.50% (w/v), reduced the solubility of EBT in the aqueous phase through a salting-out effect and decreased the "free water" concentration in the micelle phase. Consequently, the extraction efficiency improved as the salt concentration increased, but above a concentration of 1.50% (w/v) of salt, the signals remained stable and sometimes even decreased.

3.3. Effect of volume of sample solution

The volume of the sample solution can effect micelle formation and its dispersion throughout the sample solution. Therefore, it can have a great influence on the efficiency of MCPE. To find out the best volume of the sample solution, samples with different volumes (5–15 mL) were prepared, according to Table 2, and the MCPE procedures were applied to them. Based on obtained results, five mL of sample solution showed the best efficiency for MCPE of EBT (Fig. 5).

3.4. Optimization results and statistical analysis

According to the results shown in Figs. 3–5 and Table 3, the most effective factor in MCPE of EBT is pH, and the least effective factor is the volume of the sample solution. Table 4 presents the optimum conditions chosen based on the L16 orthogonal array of Taguchi design for EBT. Con-

Table 1
Factors and levels used for Taguchi design of MCPE for EBT

Factor	Level 1	Level 2	Level 3	Level 4
(A) pH	3	5	7	9
(B) Concentration of salt (%)	0.05	0.50	1.00	1.50
(C) Volume of sample solution (mL)	5	8	10	15

Table 2
L16 Orthogonal array and experimental results for EBT

Test	A	B	C	Abs	SNR
1	1	1	1	1.33	2.477033
2	1	2	2	1.24	1.868434
3	1	3	3	1.25	1.938200
4	1	4	4	1.4	2.922561
5	2	1	2	1.18	1.437640
6	2	2	1	1.1	0.827854
7	2	3	4	1.03	0.256744
8	2	4	3	1.15	1.213957
9	3	1	3	0.883	–1.08079
10	3	2	4	0.698	–3.12289
11	3	3	1	0.812	–1.80888
12	3	4	2	0.846	–1.45259
13	4	1	4	0.372	–8.58914
14	4	2	3	0.341	–9.34491
15	4	3	2	0.345	–9.24362
16	4	4	1	0.495	–6.10790

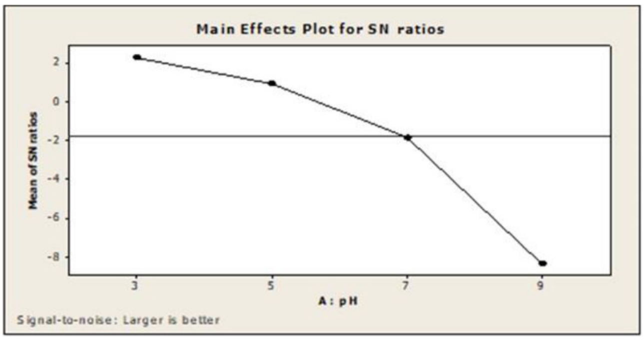


Fig. 3. Effect of pH on MCPE of EBT based on S/N.

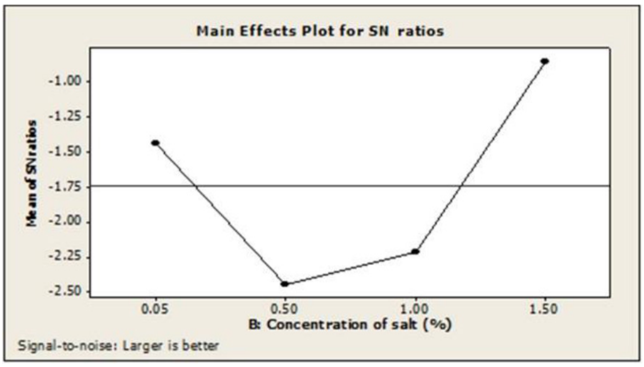


Fig. 4. Effect of salt concentration on MCPE of EBT based on S/N.

tribution results indicate that the most effective and least effective factors in the MCPE of EBT are the pH and volume of the sample solution.

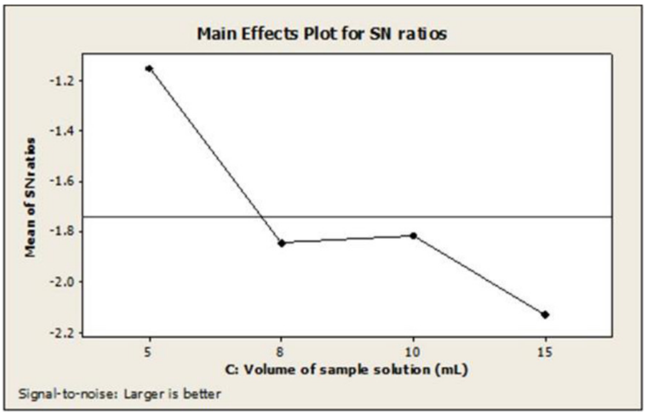


Fig. 5. Effect of volume of sample solution on MCPE of EBT based on S/N.

Table 3
Responses based on S/N for each level of factors

Level	A	B	C
1	2.3016	–1.4388	–1.1530
2	0.9340	–2.4429	–1.8475
3	–1.8663	–2.2144	–1.8184
4	–8.3214	–0.8560	–2.1332
Max–min	10.6229	1.5869	0.9802

Table 4
Optimized condition for determination of EBT with MCPE

Factor	Level	Level description	contribution
A	1	3	0.4
B	4	1.5 (%w/v)	0.068
C	1	5 (mL)	0.029
Total contribution from all factors			0.497
Expected result at optimum condition			1.401

After obtaining the optimal parameters for the MCPE of EBT, the final equation was defined using Response surface methodology. A quadratic model (second-order polynomial equation) for the response surface was developed to explain the effects of the parameters. The model coefficients were obtained using statistical software of MINITAB Version 17 and Design-Expert Software Version 10. The second-order surface response of the MCPE can be expressed as a function of extraction parameters such as pH (A), salt concentration (B), and sample solution (C) volume. From the observed data for MCPE of EBT, the response function was determined in uncoded units as:

Absorbance = + 1.25855 + 0.077552* A – 0.28112* B + 8.72109E-003* C – 0.017020 *A *B – 4.60939E – 003 *A *C – 9.29398E-005 *B *C – 0.014469 *A^2 + 0.22874 *B^2 + 4.47737E-004 *C^2

This model for MCPE of EBT could predict the experiment results. Analysis of variance (ANOVA) has been applied for any parameter to distinguish the significance of the effects and interactions between the parameters. Fur-

Table 5
ANOVA for response surface model

Source	SS	DF	MS	F-value	p-value	
Model	1.99	9	0.22	83053.45	< 0.0001	significant
A	0.63	1	0.63	2.365E+005	< 0.0001	
B	1.350E-003	1	1.350E-003	508.09	< 0.0001	
C	8.167E-003	1	8.167E-003	3074.53	< 0.0001	
AB	2.629E-003	1	2.629E-003	989.72	< 0.0001	
AC	7.632E-003	1	7.632E-003	2873.12	< 0.0001	
BC	1.821E-007	1	1.821E-007	0.069	0.8022	
A^2	0.054	1	0.054	20174.58	< 0.0001	
B^2	0.045	1	0.045	16852.76	< 0.0001	
C^2	4.045E-004	1	4.045E-004	152.30	< 0.0001	
Residual	1.594E-005	6	2.656E-006			
Cor Total	1.99	15				

R-squared = 0.9907, Adjusted R-squared = 0.9739, Predicted R-squared = 0.9704

thermore, a p-value lower than 0.05 has been statistically considered significant. Results from ANOVA (Table 5) for the quadratic model showed that the polynomial model was highly statistically significant, as suggested by low P value ($P < 0.0001$). The adjusted R-squared (R^2 adj) of 0.9739 and the predicted R-squared (R^2 pre) of 0.9704 are in good agreement, indicating the experimental data suitability with the generated second-order model.

To evaluate the interaction between the various independent variables and their corresponding effect on the response, we draw three-dimensional (3D) and two-dimensional (2D) contour plots (Figs.6 a–c). To study the effect of pH (A) on the extraction efficiency, a few experiments with a pH of 3–9 at a salt concentration (B) of 0.05, 0.50, 1.00, 1.50 and the volume of the sample solution (C) of 5, 8, 10, 15 were performed. Figs. 6a, b show that by increasing the amount of pH (A), the extraction efficiency decreased (see also section 3.1).To see the effect of concentration of salt (B) on the extraction efficiency, few experiments were carried out with a constant pH value at a varying concentration of salt (B) of 0.05, 0.50, 1.00, 1.50 at the volume of the sample solution (C) of 5, 8, 10, 15 Figs. 6a, c. It was observed that with increasing concentration of salt (B) from 0.5 to 1.50% (w/v), the extraction efficiency increased (see also section 3.2).

3.5. Linear range, limit of detection and precision

To study the effectiveness of the proposed method, the analytical figures for the MCPE of EBT were obtained under optimum conditions (Table 6). The limit of detection (LOD) was calculated based on $3S_b/m$, where S_b is the standard deviation of 10 blank measurements and m is the slope of the calibration graph (Table 6). The relative standard deviation (RSD) was calculated for five replicates of the standard sample at an intermediate concentration of the calibration curve of the dye (1.0 mg L^{-1} for EBT). The enrichment factor (EF) was calculated as the slope of the calibration curve after and before the MCPE. It found to be 123.78 fold for EBT.

3.6. Analysis of real samples

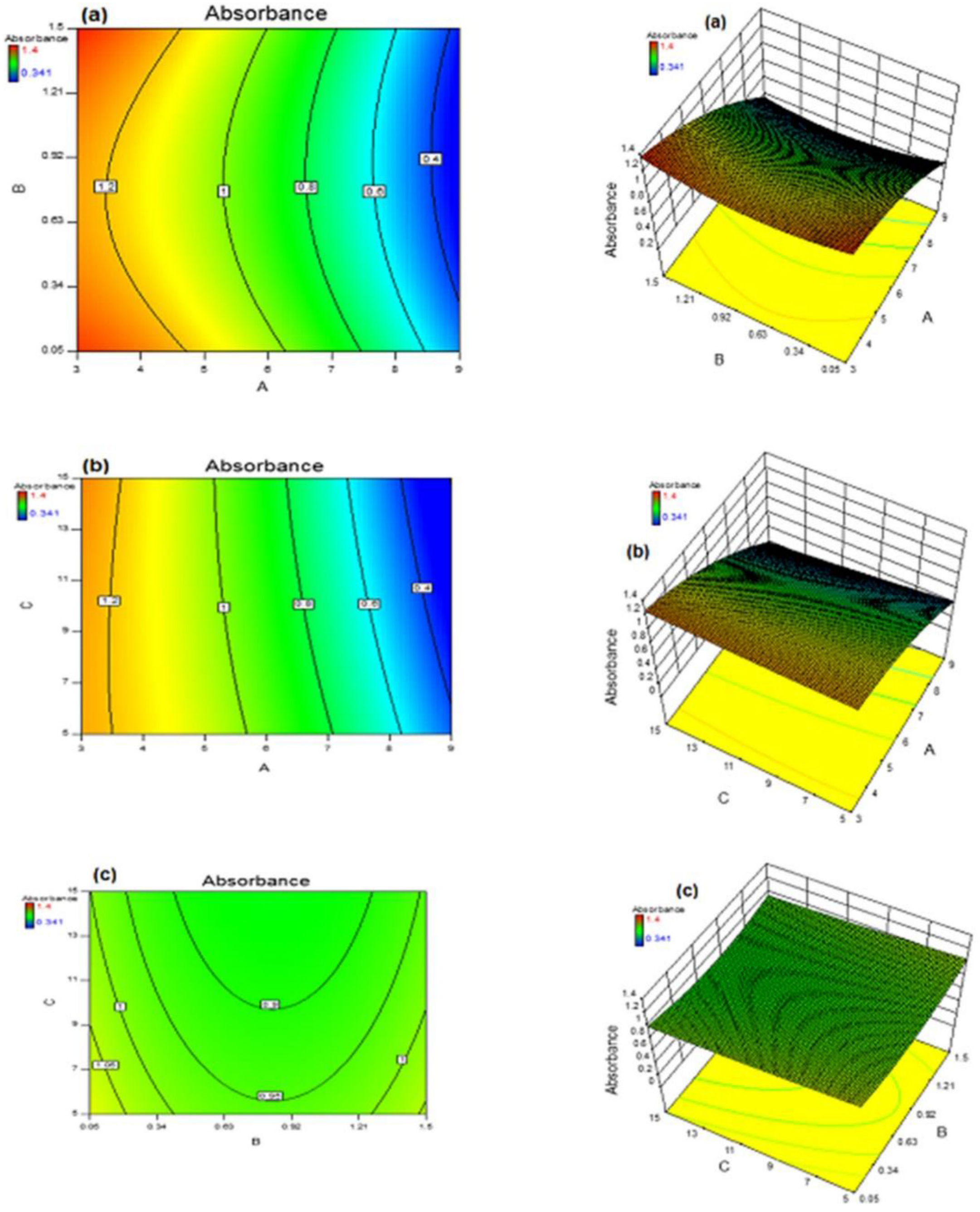
The MCPE procedure was applied to tap water and wastewater samples for determination of EBT as described for standard solutions in Section 2.3. Wastewater samples (from the recycling wastewater system of The University of Sistan and Baluchestan) were filtered through 0.45 µm nylon membranes and then subjected to centrifugation for 5 min at 5000 rpm prior to analysis. Since no dye pollution was observed in both samples, the samples were spiked with three different concentrations of EBT to investigate the matrix effect on its determination. The results are shown in Table 7. As can be seen, good recoveries were obtained for EBT.

4. Conclusions

In this study, a fast, economical, efficient and easy to operate method based on micro-cloud point extraction was evaluated for the preconcentration and determination of traces of Eriochrome black T. Triton X-114 was used as a non-ionic and green extractant solvent. In the present work, we coupled the MCPE method with UV-Vis spectrophotometry as an inexpensive, fast, and available instrument. With using microcells, the consumption of toxicorganic solvent was reduced, and consequently, enrichment factor and sensitivity of the method for target analyte was increased. The total analysis time including microextraction and spectrophotometric determination was less than 8 min. In this study, the optimization of effective factors on MCPE was carried out with the help of Taguchi design method and Response surface methodology. A second-order response surface model for micro-cloud point extraction of Eriochrome black T is developed to predict responses.

Acknowledgment

This research was supported by the University of Sistan and Baluchestan.



Figs 6. (a–c). 3D and 2D plots showing the effects of parameters.

Table 6
Analytical figures of merit for MCPE of EBT

Parameter	MCPE
Equation of calibration curve	$A = 0.6865C_{EBT} + 0.0583$
Dynamic range (mg L^{-1})	0.20–2.00
R^2	0.9842
RSD (%, n = 5)	1.54
Limit of detection (µg L^{-1})	59
Enrichment factor (fold)	123.78

Table 7
Data analysis for determination of EBT in tap water and wastewater samples by MCPE

Analyte	Tap water		Wastewater	
	Added (mg L^{-1})	Relative recovery%	Added (mg L^{-1})	Relative recovery%
EBT	0.20	89.98	0.20	92.80
	1.00	90.79	1.00	93.00
	2.000	98.94	2.00	101.98

References

[1] A. Reife, H.S. Freeman, Environmental Chemistry of Dyes and Pigments, John Wiley & Sons, 1996.

[2] W. Herbst, K. Hunger, Industrial Organic Pigments: Production, Properties, Applications, John Wiley & Sons, 2006.

[3] X.Q. Li, Q.H. Zhang, K. Ma, H.M. Li, Z. Guo, Identification and determination of 34 water-soluble synthetic dyes in foodstuff by high performance liquid chromatography–diode array detection–ion trap time-of-flight tandem mass spectrometry, Food Chem., 182 (2015) 316–326.

[4] K. Hunger, Industrial Dyes: Chemistry, Properties, Applications, John Wiley & Sons, 2007.

[5] K. Lacasse, W. Baumann, Textile Chemicals: Environmental data and facts, Springer Science & Business Media, 2004.

[6] Y.E. Unsal, M. Soylak, M. Tuzen, Column solid-phase extraction of sunset yellow and spectrophotometric determination of its use in powdered beverage and confectionery products, Int. J. Food Sci. Technol., 47 (2012) 1253–1258.

[7] F. Cioni, G. Bartolucci, G. Pieraccini, S. Meloni, G. Moneti, Development of a solid phase microextraction method for detection of the use of banned azo dyes in coloured textiles and leather, Rapid Commun. Mass Spectrom., 13 (1999) 1833–1837.

[8] H. Yan, J. Qiao, Y. Pei, T. Long, W. Ding, K. Xie, Molecularly imprinted solid-phase extraction coupled to liquid chromatography for determination of Sudan dyes in preserved beancurds, Food Chem., 132 (2012) 649–654.

[9] N. Xiao, J. Deng, K. Huang, S. Ju, C. Hu, J. Liang, Application of derivative and derivative ratio spectrophotometry to simultaneous trace determination of rhodamine B and rhodamine 6G after dispersive liquid–liquid microextraction, Spectrochim. Acta Mol. Biomol. Spectrosc., 128 (2014) 312–318.

[10] C. Yu, Q. Liu, L. Lan, B. Hu, Comparison of dual solvent-stir bars microextraction and U-shaped hollow fiber–liquid phase microextraction for the analysis of Sudan dyes in food samples by high performance liquid chromatography–ultraviolet/mass spectrometry, J. Chromatogr. A, 1188 (2008) 124–131.

[11] E. Heidarizadi, R. Tabaraki, Simultaneous spectrophotometric determination of synthetic dyes in food samples after cloud point extraction using multiple response optimizations, Talanta, 148 (2016) 237–246.

[12] O. Sahin, C. Saka, S. Kutluay, Cold plasma and microwave radiation applications on almond shell surface and its effects on the adsorption of Eriochrome Black T, J. Ind. Eng. Chem., 19 (2013) 1617–1623.

[13] T.A. Saleh, A.M. Muhammad, S.A. Ali, Synthesis of hydrophobic cross-linked polyzwitter ionic acid for simultaneous sorption of Eriochrome Black T and chromium ions from binary hazardous waters, J. Colloid Interf. Sci., 468 (2016) 324–333.

[14] K. Dong, F. Qiu, X. Guo, J. Xu, D. Yang, K. He, Adsorption behavior of azo dye Eriochrome Black T from aqueous solution by β-cyclodextrins/polyurethane foam material, Polym. Plast. Technol. Eng., 52 (2013) 452–460.

[15] O.A. Attallah, M.A. Al-Ghobashy, M. Nebsen, M.Y. Salem, Removal of cationic and anionic dyes from aqueous solution with magnetite/pectin and magnetite/silica/pectin hybrid nanocomposites: kinetic, isotherm and mechanism analysis, RSC Adv., (2016) 11461–11480.

[16] A. Mittal, V.K. Gupta, Adsorptive removal and recovery of the azo dye Eriochrome Black T, Toxicol. Environ. Chem., 92 (2010) 1813–1823.

[17] M. Zubair, N. Jarrah, M.S. Manzar, M. Al-Harthi, M. Daud, N.D. Mu'azu, S.A. Haladu, Adsorption of Eriochrome Black T from aqueous phase on MgAl-, CoAl- and NiFe- calcined layered double hydroxides: kinetic, equilibrium and thermodynamic studies, J. Mol. Liq., 230 (2017) 344–352.

[18] M.D.G.D. Luna, E.D. Flores, D.A.D. Genuino, C.M. Futalan, M.W. Wan, Adsorption of Eriochrome Black T (EBT) dye using activated carbon prepared from waste rice hulls—optimization, isotherm and kinetic studies, J. Taiwan Inst. Chem. Eng., 44 (2013) 646–653.

[19] V.M. Vŭcurovíc, R.N. Razmovski, U.D. Miljíc, V.S. Puškaš, Removal of cationic and anionic azo dyes from aqueous solutions by adsorption on maize stem tissue, J. Taiwan Inst. Chem. Eng., 45 (2014) 1700–1708.

[20] P. Kaur, N. Rajani, P. Kumawat, N. Singh, J.P. Kushwaha,Performance and mechanism of dye extraction from aqueous solution using synthesized deep eutectic solvents, Colloid Surf., A539 (2018) 85–91.

[21] M. Kaykhaii, E. Ghasemi, Micro-cloud point extraction for preconcentration of aspirin in commercial tablets prior to spectrophotometric determination, J. Anal. Chem., 71 (2016) 844–848.

[22] M.J. Anderson, P.J. Whitcomb, Design of experiments, John Wiley & Sons, 2000.

[23] R.F. Gunst, R.L. Mason, Fractional factorial design, Wiley Interdiscip. Rev. Comput. Stat., 1 (2009) 234–244.

[24] M. Rahmani, E. Ghasemi, M. Sasani, Application of response surface methodology for air assisted-dispersive liquid-liquid microextraction of deoxynivalenol in rice samples prior to HPLC-DAD analysis and comparison with solid phase extraction cleanup, Talanta, 165 (2017) 27–32.

[25] M. Rahmani, M. Kaykhaii, M. Sasani, Application of Taguchi L16 design method for comparative study of ability of 3A zeolite in removal of Rhodamine B and Malachite green from environmental water samples, Spectrochim. Acta Part A, 188 (2018) 164–169.

[26] Anıl, N. Öztürk, O. Alagha, P. Ergenekon, Optimization of solid-phase microextraction using Taguchi design to quantify trace level polycyclic aromatic hydrocarbons in water, J. Sep. Sci., 35 (2012) 3561–3568.

[27] M. Nalbant, H. Gökkaya, G. Sur, Application of Taguchi method in the optimization of cutting parameters for surface roughness in turning, Mater. Des., 28 (2007) 1379–1385.

[28] S. Xie, M.C. Paau, C.F. Li, D. Xiao, M.M. Choi, Separation and preconcentration of persistent organic pollutants by cloud point extraction, J. Chromatogr. A, 1217 (2010) 2306–2317.