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Optimization of process parameters for determination of trace Hazardous dyes from industrial wastewaters based on nanostructures materials under ultrasound energy

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ABSTRACT

In this study, ultrasound-assisted dispersive solid phase micro-extraction based on nanosorbent namely silver-zinc oxide nanoparticles loaded on activated carbon (Ag-ZnO-NP-AC) combined with derivative spectrophotometry method for the simultaneous pre-concentration and determination of Methyl Green (MG) and Rose Bengal (RB) dyes in water and industrial wastewater. Characterized sorbent by field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDX), particle-size distribution (PSD), Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD) and Transmission electron microscopy (TEM) analysis with superior adsorption capacity was applied in ultrasound assisted dispersive-solid-phase micro-extraction (UA-DSPME) methodology. pH, sorbent mass, ultrasonication time, and eluent volume influence and contribution on response correspond to simultaneous pre-concentration and determination of MG and RB were optimized by response surface methodology (RSM) and results were compared with the experimental values. Under the optimal conditions (UA-DSPME), the enrichment factors (EFs) were 93.89 and 97.33 for the MG and RB dyes, respectively. The limits of detection were 2.14 and 2.73 ng mL^{-1} and the limit of quantification were 7.15 and 9.09 ng mL^{-1} for MG and RB, respectively. The analytes can be determined over 10–2000 ng mL^{-1} with recoveries between 90.8% to 97.7% and RSDs less than 3.6%. The developed method due to simplicity and rapidity is able successful for repeatable and accurate monitoring of under study analytes from complicated matrices.

1. Introduction

Wastewater generally contains extensive amount of dyes and organic pollutant which leads procedure [1,2] generate hazards such as mutagen and carcinogenic problem for living organism and reduces the photosynthesis by inhibition of light penetration to deep layer and reduction in oxygen content [3]. Dyes generally have more solubility in water toward other solvent and their appearance even in trace quantity in industrial wastewater cause serious issue and change safety and natural feature of water system [4].

The appropriate control and reduction of these problems attain great important issue [5]. Rose Bengal (RB) applied as sensitizer in wastewater treatment which emerged from its water solubility, absorption in the visible region, good quantum yield of singlet oxygen and cheapness [6]. Methyl Green (MG) is a basic triphenylmethane-type dicationic dye, usually used for staining solutions in medicine and biology [7] and as a photo-chromophore to sensitize gelatinous films [8], while has ability for recognition of deoxyribonucleic acid from ribonucleic acid [9]. MG triphenylmethane class of dye affect thyroid peroxidase-catalyzed oxidation due to the fact that reactions might form various N-de-alkylated primary and secondary aromatic amines with structures similar to aromatic amine carcinogens [10].

Therefore, great effort was necessary to devote on development and design of accurate and precise method for determination of these dyes in various matrices such as organism, atmosphere, water and soil, while their extremely lower content lead to failure in direct determination especially at complicated matrices with very low content of analysis, especially following their treatment and sample dilution. Therefore, conduction of primary separation and/or preconcentration technique is highly recommended [11]. Different pre-concentration methods, including liquid–liquid extraction (LLE) [12,13], solid-phase extraction (SPE) [2], supercritical fluid extraction (SFE) [14], microwave assisted

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extraction (MAE) [15], solid-phase micro-extraction (SPME) [16], liquid-phase micro- extraction (LPME) [17], single drop micro-extraction (SDME) [18] and magnetic solid phase micro-extraction (MSPE) [19] are conventional approaches for pre-concentration and/or determination of analytes from water and wastewater sample prior to their instrumental analysis.

Ultrasound assisted dispersive-solid-phase micro-extraction (UA-DSPME) sample handling technique recognized as real solvent free technique [20,21], while in UA-DSPME selective and efficient extraction simply achieved following best selection of extraction phase and due to elimination of organic solvent is known as green protocol [22]. UA-DSPME allows analytes pre-concentration without requirement to solvent evaporation after the extraction process and accordingly is highly preferred with respect to conventional technique [23]. The total removal of organic solvents for sample preparation avoids or minimizes the waste generation correspond to sample preparation step which extend ability of method for quantification of target analytes in very small samples that is related to convenient dimensions of the UA-DSPME system [24,25]. The amount of extracted analyte depends on the sample volume and concentration of the analyte in the matrix directly may possible in ambient air, water, production stream, etc. [26,27], which leads to increase in the extraction efficiency through at least time [20,28–30].

Nano-structure based sorbents have great interest for the pre-concentration of trace elements and toxic dyes owing to their higher efficiency and more number of reactive atoms [31], especially when combined with their uniform dispersion in the extraction media which supply quick isolation and/or pre-concentration of analytes from the initial solution [32]. Moreover, some nano-sorbents are easily recycled after simple washing stage [33].

In despite of extensive application of separation, preconcentration and extraction protocol for quantification and isolation of compounds, their efficiency significantly affected by various factors such as pH, sorbent mass, sonication time, and eluent volume [34]. Individual screening of these factors is tedious and mostly expensive via conduction of lots of experimental work, while failed to give knowledge about their synergistic or antagonism simultaneous contribution on response. Response-surface methodology (RSM) in despite of one factor at a time is good choice to achieve real optimum point and also to overcome these difficulties, while also give information on factors interaction [35,36].

Multicomponent dyes analysis require development of novel method that be able for their accurate and repeatable determination in the mixtures which limited by their serious peak overlapping that subsequently limit such proposes [12,37]. Derivative spectrophotometry has more appointy to resolve absorption peaks overlap through their separation and correction of background interferences. This method is based on finding wavelengths that possible the accurate and repeatable monitoring of each spices in complex matrices without any interference from other target compounds [38,39].

In this study, Ag-ZnO-NP-AC nanosorbent was synthesized and fully characterized by SEM, XRD and TEM analysis and subsequently was applied for ultrasound assisted dispersive solid phase micro-extraction combined derivative spectrophotometry method for simultaneous pre-concentration and determination of Methyl Green (MG) and Rose Bengal (RB) dyes in binary system. Influence of important variables (pH, sorbent mass, sonication time and eluent volume) on simultaneous determination of MG and RB dyes were optimized by Central Composite Design (CCD) and in later stage their content successfully were determined in binary system from environmental and industrial wastewater samples.

Table 1
Design matrix for the central composite designs.

Factors	Levels				
	−α	Low (−1)	Central (0)	High (+1)	+α
A: pH	4	5	6	7	8
B: sorbent mass (mg)	1	1.5	2	2.5	3
C: ultrasonication time (min)	1	2	3	4	5
D: eluent volume (μL)	100	150	200	250	300

Run Order	Factors				ER% of MG		ER% of RB	
	A	B	C	D	Observed	Predicted	Observed	Predicted
1	5	1.5	2	150	89.10	89.69	90.40	90.26
2	5	2.5	4	250	88.13	88.10	92.05	91.83
3	6	2.0	3	200	98.43	97.99	95.48	95.42
4	7	1.5	2	150	84.01	83.99	92.32	92.61
5	6	2.0	3	200	98.35	97.99	95.27	95.42
6	6	2.5	2	150	77.92	78.27	82.14	82.34
7	6	2.0	1	200	64.36	63.87	71.20	70.72
8	6	1.0	3	200	95.15	94.81	94.91	94.97
9	6	2.0	3	200	97.46	97.99	95.01	95.42
10	5	1.5	2	250	89.07	89.00	83.83	83.97
11	7	2.5	4	150	98.50	98.52	95.98	95.91
12	7	1.5	4	250	97.81	97.80	94.63	94.34
13	6	2.0	3	200	97.87	97.99	95.54	95.42
14	6	2.0	3	200	97.87	97.99	95.72	95.42
15	5	1.5	4	150	92.39	92.46	91.84	91.64
16	6	3.0	3	200	85.04	85.08	86.71	86.62
17	6	2.0	3	200	98.11	97.99	95.77	95.42
18	6	2.0	3	100	93.29	93.08	95.50	95.38
19	7	2.5	2	250	75.74	75.62	75.90	76.17
20	5	2.5	4	150	94.18	94.20	92.84	92.67
21	5	2.5	2	250	78.70	79.15	78.25	78.10
22	7	2.5	4	250	96.45	96.21	94.18	94.30
23	7	1.5	2	250	86.77	87.10	85.40	85.55
24	6	2.0	3	200	97.90	97.99	95.22	95.42
25	6	2.0	5	200	87.03	87.22	89.79	90.23
26	5	1.5	4	250	87.89	88.07	88.48	88.35
27	6	2.0	3	300	90.17	90.08	87.40	87.48
28	4	2.0	3	200	95.63	95.25	88.78	89.09
29	5	2.5	2	150	81.77	81.55	81.69	81.94
30	7	1.5	4	150	98.50	98.40	98.28	98.40
31	8	2.0	3	200	97.49	97.66	94.20	93.91

2. Experimental

2.1. Chemicals and instruments

Ultrapure water (obtained by Milli-Q system, Bedford, MA, USA) was used in all experiments. Stock standard solution of Methyl Green (MG) and Rose Bengal (RB) dyes with a concentration of 100 mg L^{-1} were obtained by dissolving appropriate amounts of MG and RB dyes Merck (Darmstadt, Germany). Working standard solutions were obtained by appropriate dilution of the stock standard solutions. Tetrahydrofuran (THF), methanol, ethanol, acetone, acetonitrile, and N,N-Dimethylformamide (DMF), which were used as eluent solvents, were from Merck (Darmstadt, Germany) were used. X-ray diffraction (XRD, Philips PW 1800) was performed to characterize the phase and structure of the prepared Ag-ZnO nanomaterial using Cu_{ka} radiation (40 kV and 40 mA) at angles ranging from 20 to 80°. The morphology of the Ag-ZnO nanomaterial were observed by field emission scanning electron microscopy (FE-SEM: Hitachi S-4160) under an acceleration voltage of 30 kV. The absorbance was measured by a UV–Vis spectrophotometer (model V-530, Jasco, Japan) at 676 and 467 nm (in first order derivative spectrum) for MG and RB dyes, respectively, using quartz micro cells. A Fourier transform infrared (FTIR) spectrum was recorded using Perkin Elmer-Spectrum RX-IFTIR spectrometer in the