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Magnetic solid phase extraction based on fullerene and activated carbon adsorbents for determination of azo dyes in water samples by capillary electrophoresis

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A magnetic solid phase extraction method coupled to capillary electrophoresis for the simultaneous determination of three azo dyes (sunset yellow, allura red and tartrazine) in wastewater samples was proposed. The method employs the dispersion of magnetic adsorbents in the sample. Variables involved in the retention–elution procedures were optimized using a simplex centroid design. The optimal conditions were: an adsorbent composition of magnetite–activated carbon–fullerene (10 : 0.59 : 0.41), a sample pH of 4.0, and a sample volume (μl) : weight of adsorbent (mg) ratio of 0.01. Under optimal conditions, a linear range was obtained from 3.0–40.0 mg l^{-1} with limits of detection ranging from 1.0–2.0 mg l^{-1} . The average recoveries of each dye at two spiked levels (10 and 25 mg l^{-1}) ranged from 95–106% with relative standard deviations of less than 10% in all cases. The proposed method was applied to analyze wastewater samples from different locations. Two samples gave positive responses to the presence of tartrazine residues. The method proposed offers advantages in terms of simplicity, sensitivity, high efficiency, low cost, and short analysis time, making it an alternative for the analysis of azo dyes in water samples and other complex matrices.

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Introduction

In recent decades, environmental pollution has represented a problem throughout society. Some organic additives such as synthetic dyes are considered potentially dangerous, associated with neurotoxic, mutagenic, genotoxic and carcinogenic diseases. Nearly 40 000 dyes and pigments are employed in the manufacturing industry, and the removal of these compounds from water samples represents a matter of special interest.^{1,2} Among these environmental pollutants, azo dyes are synthetic organic compounds, characterized by azo groups ($-\text{N}=\text{N}-$) and aromatic groups as part of their structure, resulting in a substance with high electron conjugation and a high molar adsorption coefficient, making them useful at low concentrations. They have a higher stability to chemical treatments, and additionally most of them are completely resistant to the biodegradation process compared with dyes of natural origin.^{3,4}

Their uncontrolled application in different industries makes the residues of these compounds or their degradation products form a part of industrial waste equivalent to 10–15% of dyes produced annually. The interaction of these compounds with the aquatic ecosystem can produce serious ecological and sanitary problems, such as: the reduction of light adsorption, changes in hydric resources, soil and atmosphere and the secondary production of different aromatic amines under anaerobic conditions, compounds that are considered as carcinogenic, in detectable concentrations above 30 mg l^{-1} .^{5–7} Azo dyes represent 65% of commercial dyestuffs used in the market.^{8,9} The most common azo dyes employed in the industry are allura red (AR), sunset yellow (SY) and tartrazine (TAR). These compounds are widely used in several industrial applications in textiles, rubber products, plastics, pharmaceutical formulations, cosmetics and foods.^{10,11} Several analytical methodologies have been described for the determination and quantification of azo dyes, such as high performance liquid chromatography (HPLC),^{12–14} spectrophotometry,^{15–17} and capillary electrophoresis (CE).^{18–20} Capillary electrophoresis has become a useful technique for the analysis of dyes, because it offers high separation efficiency, short analysis time, low sample and solvent consumption, and is considered a low-cost technique compared with other separation techniques.

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However, one of the most difficult steps in the analysis of dyes is the extraction and clean-up of the samples before instrumental determination.²¹ The most commonly employed technique for the extraction and clean-up of target metabolites from water samples is solid-phase extraction (SPE). However, selection of the sorbent in SPE depends on the sample composition, selectivity and affinity required.¹⁹ During azo dye extraction by SPE, solid phases containing amine groups have been used as adsorbents. In recent years, several chemical compounds have been considered as adsorbents in the removal of azo dyes from several matrices, and adsorption processes have been considered as an attractive method to remove dyes from several matrices due to their low cost and simplicity of operation. Several adsorbents, consisting of alumina,²² zeolites,²³ polymer based silica gels,²⁴ membranes,²⁵ and carbonaceous materials have been applied as adsorbents of several organic and inorganic pollutants from aqueous solutions for water treatment.^{26–28} Electrostatic properties provide strong interactions with the analytes *via* non-covalent forces, such as hydrogen bonding, π - π interactions, electrostatic forces, van der Waals forces and hydrophobic interactions.²⁹ The principal advantage that carbonaceous nanomaterials offer depends on the nature of the analyte, functional groups present, polarity, size and the system conditions such as pH, ionic strength and the adsorbate concentration.³⁰ These materials offer high adsorption activities, selectivity and effectiveness. Carbonaceous nanomaterials, such as activated carbon, carbon nanotubes and fullerene have been demonstrated to be effective alternatives in the removal, extraction and clean-up of dyes in several matrices in comparison to traditional adsorbents.³⁰

In recent years, magnetic solid phase extraction (MSPE) has received considerable attention for its versatility and robustness in its application in extraction, pre-concentration and the clean-up process for several compounds, as well as its coupling with several analytical methodologies, such as high performance liquid chromatography (HPLC), spectrophotometry, and capillary electrophoresis (CE).^{31,32} The adsorbents used in this technique are magnetic solids chemically modified to obtain high superficial areas, affinity and selectivity in the system according to the needs required for each analyte.^{31–33} MSPE is based on the addition and dispersion of a magnetic adsorbent in a liquid sample allowing major contact and interaction between the adsorbent and the analyte to ensure the maximal retention of some components of interest. The advantage of MSPE in comparison with classic techniques is the minimal manipulation of the sample; once the magnetic adsorbents have adsorbed the analytes on the surface, they can be isolated through the influence of an external magnetic field, and then the adsorbed analytes can be eluted in an appropriate solvent. The most attractive property of MSPE is the easy isolation of the magnetic adsorbents from sample solutions by the application of an external magnetic field, additionally this technique is considered low cost with simplicity of operation.³³ This technique has been employed in potential applications, such as isolation, immobilization, separation, and pre-

concentration of several analytes, such as cells, enzymes, proteins, and organic compounds from large volume samples. In recent years, several chemical compounds have been considered as adsorbents coupled with MSPE for the removal of azo dyes from several matrices.

In accordance with the potential applications, in recent years new chemical compounds have been studied for their application as adsorbents. Recently carbonaceous nanomaterials, such as graphene oxide,³⁴ fullerene,³⁰ multi-walled carbon nanotubes,³⁵ and activated carbon,^{6,36} have been studied and applied individually in the determination or removal of several organic and inorganic pollutants for water treatment.

In this work a new method for the removal and analysis of azo dyes in wastewater samples is developed and applied in the determination of three azo dyes. The method describes the adsorption behavior between the azo dyes and a mixed adsorbent of carbonaceous materials (activated carbon and fullerene) based on adsorption capacity, pH effect, composition and adsorbent proportion. The method involves the preparation of a new adsorbent compound from a mixture of magnetite and carbonaceous materials. A magnetic adsorbent is synthesized in order to improve the removal, retention and re-extraction properties during azo dye analysis in water samples by CE.

Experimental

Reagents and chemicals

All solutions were prepared by dissolving the respective analytical grade reagent in deionized water, with resistivity not less than 18.0 M Ω cm, provided by a Milli-Q system (Millipore, Bedford, MA, USA). Sodium tetraborate, sodium hydroxide and hydrochloric acid were obtained from J.T. Baker (Phillipsburg, NJ, USA). Methanol was obtained from Mallinckrodt Baker (Xalostoc, Mexico).

Allura red, sunset yellow, tartrazine, and picric acid were obtained from Sigma (St, Lois, MO, USA). The different standard solutions were prepared by a daily dilution of a stock solution of dye at a concentration of 1.0 g l⁻¹ of each component. This solution was stored in the dark at 4 °C and refreshed weekly. A picric acid solution at a concentration of 50 mg l⁻¹ was used as an internal standard.

The magnetic adsorbents were prepared from ferrous sulfate heptahydrate, activated carbon and fullerene, obtained from Sigma.

Apparatus

Morphological analysis of the magnetic adsorbents was performed using a JEOL JSM-6360LV scanning electron microscope (SEM; JEOL (Europe) B.V. Belgium).

Electrophoresis was performed using a Beckman Coulter P/ACE 5500 (Fullerton, CA, USA) with a photo diode array detector. Data were collected and analyzed with Beckman P/ACE system MDQ version 2.3 software. Separations of the dyes were performed in a fused-silica capillary (75 μ m I.D.). A pH/ion analyzer model 450 from Corning (Corning Science Products,

NY, USA) was used to accurately adjust the pH of the electrolyte solution to 0.01 pH units. A Branson Ultrasonic system (Danbury, CT, USA) model 3510 was employed in the dispersion of the magnetic adsorbent and elution of the analytes. Finally, a Maxi-Mix I (Barnstead/ThermoFisher, IA, USA) was used as a vortex mixer.

Preparation of the adsorbent

The preparation of the adsorbents was carried out in one step. Magnetite was obtained through the co-precipitation method and partial oxidation of Fe(II) by bubbling oxygen through basic media.³¹ 25 ml of a 41 mM FeSO₄·7H₂O solution was stirred at 60 °C. The solution was adjusted to pH 10 with NaOH solution 6 M for 1 h, followed by the addition of carbon derivatives in different proportions. Preparation ratios were selected to be 0.0–1.0; 0.0 for activated carbon and 1.0 for fullerenes. Compositions of 0.17, 0.33, 0.50 and 0.67 were obtained by the experimental design selected, and the compositions of the weight ratios for activated carbon : fullerene were (0.17 : 0.83), (0.33 : 0.67), (0.5 : 0.5), (0.67 : 0.33) respectively. The reaction process was concluded after 1 h, and the magnetic particles were isolated by an external magnetic field and washed with deionized water.

Sample treatment

The MSPE methodology proposed was performed using the following sequence: initially, 5 mg of the magnetic adsorbent material was added into a 1.5 ml polypropylene tube. The particles were conditioned with 500 µl of methanol in an ultrasonic bath for 5 min. Then, the adsorbent was isolated magnetically, and washed three times with 1 ml of deionized water. A sample volume of 500 µl was added to the pre-activated magnetic adsorbent and mixed in an ultrasonic bath for 15 min. After sonication, an external magnetic field was applied to isolate the magnetic solid with the adsorbed analytes. The remaining solution was decanted, and the solid phase was washed three times with 2 ml of deionized water. The retained dyes were eluted from the magnetic solid by dispersion in 500 µl of methanol solution containing NaOH 1×10^{-3} M for 5 min.^{37–39} The resulting solution was evaporated to dryness under an air stream, and the residue was reconstituted in 300 µl of electrolyte solution containing 50 mg l⁻¹ of an internal standard. Finally, the solution was analyzed by CE and the solid phase was washed three times with 2 ml of methanol and deionized water, and dried at 60 °C for 24 h, for their reuse twice more by the MSPE procedure.

Electrophoretic procedure

Daily, the capillary was activated with 1.0 M NaOH at 25 °C for 15 min, followed by 0.1 M NaOH for 10 min, deionized water at 25 °C for 10 min, and then electrolyte solution at 25 °C for 10 min. The capillary was washed out between successive analyses using: 1.0 M NaOH for 2 min, 0.1 M NaOH for 1 min, deionized water for 1 min and electrolyte solution for 1 min. All flushing procedures were performed at a pressure of 20 psi. The electrolyte solution consisted of a borate buffer (30 mM, pH 10)

with β-cyclodextrine (2 mM) employed as a chiral selector in the separation of compounds such as optical, positional, and structural isomers.⁴⁰

The wavelength detector (λ) was set at 214 nm. Samples were injected in a hydrodynamic mode under a pressure of 0.5 psi for 5 s. The capillary was kept at 25 °C, and a voltage of 15 kV was applied to separate the analytes. Different peaks were identified by migration times and the co-injection of standard solutions.

Results and discussion

Optimization of the system by MSPE

In order to evaluate the retention of azo dyes on the magnetic solids, three magnetic adsorbents composed of magnetite and activated carbon or fullerene were used. The solids were synthesized and characterized individually; they were synthesized using a 10 : 1 weight ratio (magnetite : carbon phase). Retention experiments were carried out in the pH interval of 4.0 to 10.0. All of the experiments were performed using 500 µl of a 10 mg l⁻¹ standard solution of each analyte and 5 mg of the solid phase. Once the extraction was completed, the azo dyes remaining in the solution were determined by CE. Retention (%) was calculated as a function of the concentration added and concentration found after extraction. Fig. 1 shows the percent retention obtained using different carbon derivatives.

According to the results obtained, the analytes showed a dependence on the composition of the carbon phase contained in the magnetic adsorbent. The adsorbent synthesized with activated carbon was employed in the extraction of azo dyes by MSPE. Retention of the analytes depends on porosity and the superficial area of the activated carbon. On the other hand, the pH value was not shown to be a critical factor in the retention of azo dyes. The results show that, in the pH interval tested, a similar % of retention was obtained. A higher retention was observed for SY and AR, with retentions around 100%. This behavior can be explained as a consequence of non-electrostatic interactions, such as π - π interactions between the π bonds of activated carbon and the aromatic rings in SY and AR. Additionally, retention is maximised by hydrophobic or donor-acceptor interactions between the surface of the adsorbent and the aromatic rings of azo dyes acting as acceptors.^{1,30,31}

The adsorbent containing fullerene shows higher selectivity in the retention of AR and TAR, with percent retention values of 84.29, 87.02 and 100 at pH values ranging from 4.0–6.0. The adsorptive activity of fullerenes for azo dyes shows high selectivity in the adsorption of TAR, obtaining a percent retention close to 100%. This tendency is associated with adsorption of the azo dyes on the surface by physical adsorption through dispersive interaction forces and *via* π electron interactions and the spatial distribution of TAR compared with SY and AR, which presents a higher steric effect than the naphthalene structures.^{37,41}

According to the results, the percent retention depends, for selectivity, on the analyte and carbon derivative employed in the

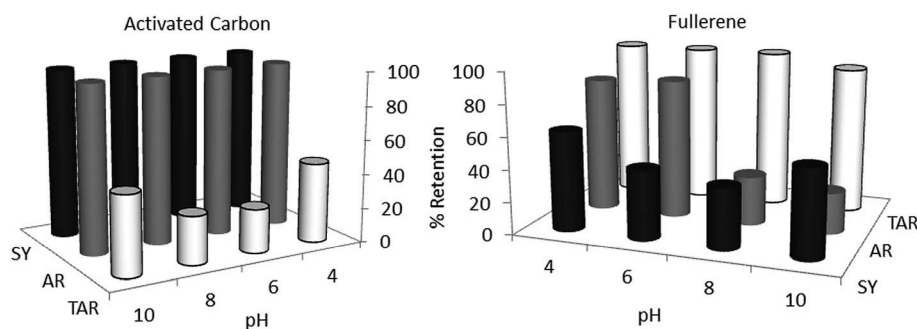


Fig. 1 % retention (mean, $n = 3$) at different pH values using magnetic adsorbents modified by carbon derivatives.

preparation of the magnetic adsorbents and the pH of the solution. Preparation of a new adsorbent containing magnetite–fullerene–activated carbon is required to improve retention of the analytes. A Simplex Centroid Design (SCD) was selected as the optimization method, since it provides the optimal working conditions with minimal experimentation.³⁸ SCD allows the evaluation of control factors that have a significant influence on the extraction and elution of azo dyes with the adsorbent mixture. The experimental design matrix indicates the combination of factors in each experiment and allows for the simultaneous evaluation of several variables with the minimum number of trials.

Optimization of the system with SCD involves 5 steps: (I) identifying the output variable to optimize, (II) identifying and selecting factors that affect the system, (III) selecting the restrictions of each factor, (IV) analyzing the data and determining the optimal conditions, and (V) conducting a confirmatory experiment under the optimal conditions obtained.

In MSPE, the desired response is the maximum adsorption of azo dyes with less dispersion (sum of retention/standard deviation). The variable optimized in the procedure is the pH value (4.0–6.0) of the initial solution; the values were selected in order to evaluate the pH dependence on the maximal retention of azo dyes. The amount of fullerene : activated carbon in the weight ratio (0.0–1.0), 0.0 for activated carbon and 1.0 for fullerenes, was selected to estimate the affinity of the analytes according to the adsorbent employed during the retention–elution process. In order to estimate the % retention conditions, the amount of magnetic adsorbent (mg) in a sample volume (μl) was evaluated (0.002–0.020) and these proportions had to be enough to ensure maximal analyte adsorption onto the solid.

Table 1 shows the results obtained during optimization. All of the experiments were performed using 500 μl of the standard solution of azo dyes at a concentration of 10.0 mg l^{-1} . Once the extraction was completed, the azo dyes retained were eluted, dried, reconstituted and analyzed under the conditions previously described in the Experimental section. The percent retention was calculated as a function of the concentration added and concentration found in the eluted solution after MSPE treatment.

Using the results obtained, the data were analyzed using MINITAB® V 17 software. The data were adjusted to the quadratic model, according to the ANOVA test. The equation for the surface response for each analyte was:

$$Y_1 = 3.51X_1 + 6.34X_2 + 4.86X_3 - 0.249X_1X_2 - 1.45X_1X_3 + 20.51X_2X_3$$

where Y_1 is the sum/standard deviation, X_1 is the pH value, X_2 is the composition adsorbent, and X_3 is the ratio of the weight of magnetic adsorbent (g) : volume : sample: (ml). The critical variable during MSPE treatment is the composition of the magnetic adsorbent. Fig. 2 shows a graphical representation of the experimental design in the adsorption and elution of azo dyes.

The mixed adsorbent (activated carbon : fullerene) provided diverse interactions between the analytes and the adsorbent. The experiments performed showed that the principal factor for retention is the interaction mode between the analytes, followed by the solution pH. According to the composition of the adsorbent this can provide non-electrostatic interactions (π – π interactions), such as hydrophobic interactions, obtaining the maximal adsorption of azo dyes with aromatic rings present in the structure, as is observed for naphthalene (SY and AR). Additionally, their spatial distribution, physical adsorption, and dispersive interaction forces permit homogenous adsorption

Table 1 Results obtained with the central composite design in the determination of optimal conditions

Exp	Control factors			% retention			Output variable Sum/standard deviation
	pH	Composition	V : w ratio	SY	AR	TAR	
1	4.30	0.67	0.005	65.69	98.00	98.00	14.02
2	4.60	0.33	0.008	31.81	57.28	10.84	4.30
3	5.30	0.17	0.005	20.32	31.88	10.31	5.79
4	4.00	0.00	0.020	29.21	78.68	98.00	5.80
5	4.00	0.50	0.011	51.39	93.20	68.49	10.14
6	5.00	0.50	0.002	26.57	49.34	1.73	3.26
7	4.30	0.17	0.014	27.65	59.64	98.00	5.26
8	6.00	0.00	0.002	14.78	25.45	1.02	3.37
9	5.00	0.00	0.011	18.73	20.20	3.75	4.69
10	4.00	1.00	0.002	26.69	50.36	98.00	4.81

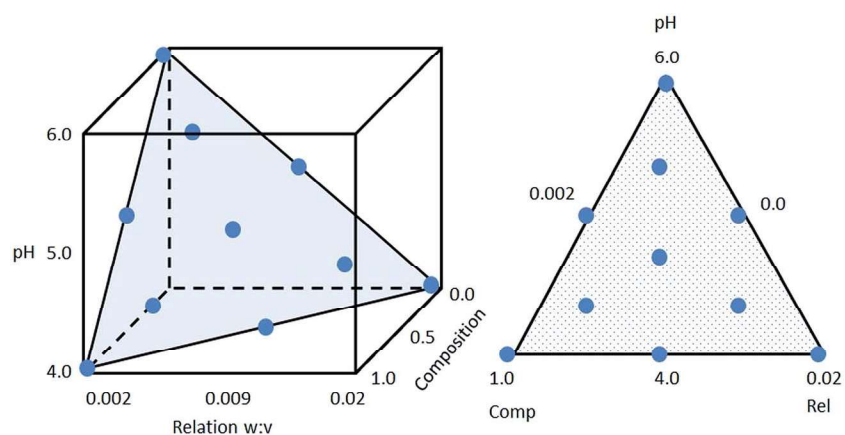


Fig. 2 Experimental design (simplex centroid design).

of the analytes in comparison to the individual forms of the adsorbents.

According to the results obtained by SCD, the optimal conditions for sample treatment were: pH 4.0, a proportion of adsorbent of 0.59 (magnetite 80 mg, activated carbon 4.8 mg, fullerene 3.2 mg), and a ratio of sample : volume (μl) : weight of magnetic adsorbent (mg) of 0.01 (500 μl : 5 mg).

Characterization of the optimum magnetic adsorbent

The overall morphology of the magnetic adsorbents was studied by scanning electron microscopy. SEM images of (a) Fe_3O_4 -activated carbon, (b) Fe_3O_4 -fullerene (c) and (d) Fe_3O_4 -activated carbon-fullerene, Fig. 3, show that according to the preparation methodology the adsorbents present physical interactions between the carbonaceous material and the magnetite. According to the SEM images there is clearly the presence of activated carbon sites, and a covering of fullerene and Fe_3O_4 particles attached to the surface of the derivative carbon. The composition of the optimal adsorbent on the surface provides enhanced adsorption of azo dyes, increasing the active sites and providing a selective condition for the retention of the analytes presents in the analytical matrix.

To describe the behavior of the surface area, it was determined according to the ASTM D4607-94 method, whereby three replicates of each adsorbent were employed. The surface area in the optimal adsorbent presented a value of $654 \text{ m}^2 \text{ g}^{-1}$, while the surface area of the adsorbent after the MSPE methodology was $598 \text{ m}^2 \text{ g}^{-1}$. Additionally, under the optimal conditions of preparation the contributions of Fe_3O_4 , activated carbon and fullerene were evaluated three times, individually, and respectively for the adsorption of each azo dye. According to the results obtained, the average contributions for AR are Fe_3O_4 : 27%; activated carbon: 66% and fullerene: 5%, for SY are Fe_3O_4 : 16%; activated carbon: 78% and fullerene: 2% and for TAR are Fe_3O_4 : 13%; activated carbon: 59% and fullerene: 23% with % RSD less than 10% in all cases. The adsorption capacity and the affinity of the magnetic adsorbent for the analytes of interest were determined using an adsorption isotherm and the corresponding Scatchard

analysis. Adsorption isotherms were constructed with 500 μl of azo dye solution at concentrations ranging from 0.0007 to 0.11 mM, and each solution was subjected to the proposed methodology with 5 mg of magnetic adsorbent. After the dispersion, the initial solution was analyzed by CE, evaluating the azo dyes present in the solution by the difference in the concentration added and the concentration found. In the Scatchard analysis, the amount of azo dye bound to the magnetic adsorbent was obtained by subtracting the free concentration from the initial concentration of each analyte at a binding equilibrium increased to a concentration around of 0.055 mM.^{42–46}

When the azo dyes' concentrations were varied, a Scatchard plot was obtained according to the following equation:

$$\frac{Q}{[\text{azo dyes}]} = \frac{(Q_{\text{max}} - Q)}{K_d}$$

where Q (mmol g^{-1}) is the amount of each azo dye bound to the magnetic adsorbent at equilibrium, $[\text{azo dyes}]$ (mM) is the free azo dye concentration at equilibrium, K_d is the dissociation

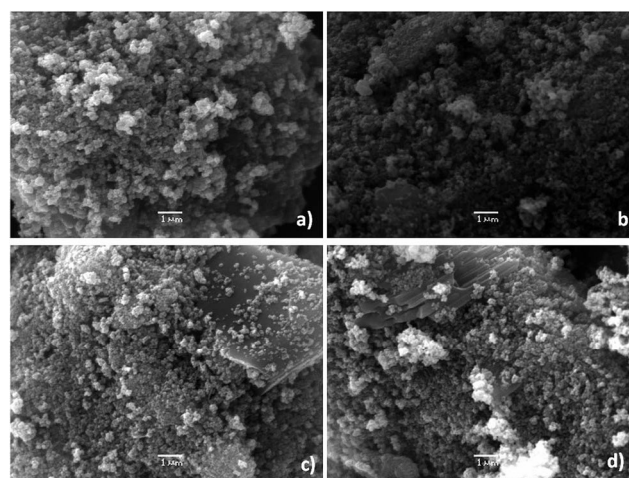


Fig. 3 Scanning electron microscopy images of magnetic adsorbents (a) Fe_3O_4 -activated carbon, (b) Fe_3O_4 -fullerene, (c) and (d) Fe_3O_4 -activated carbon-fullerene (10 : 0.59 : 0.41).

constant (the affinity of the magnetic adsorbent for the azo dye), and Q_{\max} (mmol g^{-1}) is the maximum binding amount.

Table 2 shows the values obtained, corresponding to a low interaction between the adsorbent and azo dyes, which is desired in retention–elution processes.⁴⁵ The linearity in the Scatchard plot indicates the presence of homogeneous active sites on the magnetic adsorbent. Retention, elution and affinity experiments demonstrate the usefulness of the developed magnetic adsorbent for azo dye determination in water matrices by magnetic solid phase extraction.

Method validation

Under optimal conditions, the analytical parameters of the magnetic solid-phase extraction coupled to capillary electrophoresis (MSPE-CE) method were evaluated using an initial water sample volume of 1.0 ml spiked with azo dyes in the concentration range of 0–40 mg l^{-1} and diluted to 3 ml with deionized water. Each standard was prepared and analyzed in triplicate. The resulting standards were thoroughly homogenized. The analytes were pre-concentrated using the proposed methodology as described in the Experimental section. The peak heights obtained (AU) were measured and the calibration line was constructed from the average signal area. The calibration line showed a linear dependence between signal area and the concentration of azo dyes in the spiked water sample. Regression parameters of the calibration lines are shown in Table 3. LODs were calculated for a signal-to-noise ratio (S/N) = 3.29.

The accuracy of the method was investigated by determining the recoveries of the azo dyes added to wastewater samples at two concentration levels with three replicates at each concentration (10 and 25 mg l^{-1}). The mean recoveries obtained for the three analytes were found in the range of 95–106%, with a relative standard deviation (RSD) less than 10% in all cases. Based on the results, the method was determined as adequate for the analysis of azo dyes in wastewater samples. At pH values above 10 a decrease in adsorption was observed because the magnetite particles acquired a negative charge due to the binding of hydroxide groups, thus causing electrostatic repulsion between the adsorbent and the analytes.⁴⁶

To determine the effect of successive extraction on the magnetic adsorbent by MSPE, a spiked sample (10 mg l^{-1}) was employed and analyzed under optimal conditions. According to the results, the recoveries decreased gradually with reuse, despite the analytical signal height showing repeatability after

Table 3 Regression parameters of the calibration lines (mUA) vs. the concentration of azo dyes (mg l^{-1}) in 500 μl of water

Analyte	Regression parameters			
	Intercept, $b_0 \pm t_s(b_0)$	Slope, $b_1 \pm t_s(b_1)$	Correlation coefficient, r^2	
SY	-0.0623 ± 0.0345	8.276 ± 0.091	0.999	
AR	-0.0432 ± 0.0684	5.969 ± 0.046	0.998	
TAR	-0.0201 ± 0.0437	6.521 ± 0.043	0.998	
	Linearity range (mg l^{-1})	Limit of detection (mg l^{-1})	Limit of quantification (mg l^{-1})	
SY	3.0–40.0	1.0	3.0	
AR	6.0–40.0	2.0	6.0	
TAR	6.0–40.0	2.0	6.0	
	Repeatability inter-day (% RSD, $n = 3$)		Repeatability intra-day (% RSD, $n = 3$)	
	10 mg l^{-1}	25 mg l^{-1}	10 mg l^{-1}	25 mg l^{-1}
SY	9.55 (7.93)	24.51 (2.53)	9.93 (2.02)	24.68 (4.08)
AR	9.70 (6.18)	25.78 (3.34)	10.23 (6.14)	25.19 (3.94)
TAR	10.62 (4.92)	25.09 (5.24)	9.84 (3.46)	26.06 (8.27)

3 determinations, with recovery of approximately 95% for each analyte with a % RSD of 6.8.

The proposed methodology was applied to the determination of azo dyes in three wastewater samples from different industrial locations. Three replicate determinations of each analyte present in the selected samples were performed. According to the results obtained by analysis of the azo dyes in water, two samples were positive for the presence of TAR with concentrations of 6.42 and 20.01 mg l^{-1} , which was identified from its migration time. The relative standard deviation (RSD) was less than 10% in the analysis.

The obtained electropherograms of the water sample analysis after extraction are shown in Fig. 4. No interference from the matrix was observed after the MSPE-CE of a blank sample (A), or a spiked water sample containing 10 mg l^{-1} of each analyte, 50 mg l^{-1} of internal standard, IS (B), demonstrating the selectivity of the magnetic adsorbent for azo dyes. A real water sample analyzed by MSPE-CE (C) and a real water sample analyzed by CE without MSPE (D) are also shown in Fig. 4.

Table 2 The results of Scatchard analysis

Azo dyes	Linear equation	K_d (mM)	Q_{\max} ($\mu\text{mol g}^{-1}$)
SY	$0.8496 \pm 0.0032 - 0.5620 \pm 0.0608Q$	1.779 ± 0.1924	1.51 ± 0.1634
AR	$0.9421 \pm 0.0037 - 0.4645 \pm 0.0671Q$	2.15 ± 0.3105	2.025 ± 0.2926
TAR	$0.9603 \pm 0.0047 - 0.5846 \pm 0.0859Q$	1.71 ± 0.2512	1.642 ± 0.2414

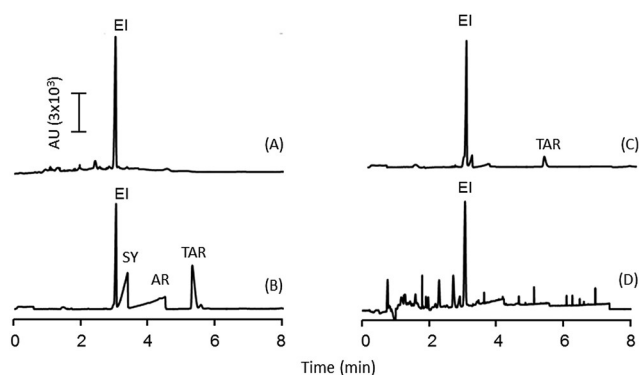


Fig. 4 Electropherograms obtained from the analysis of azo dyes: (A) a blank water sample, (B), a spiked water sample (10 mg l^{-1}) analyzed by MSPE-CE, (C), a real water sample and (D) a real water sample without MSPE. Sunset Yellow (SY), Allura Red (AR), tartrazine (TAR), internal standard (IS). CE conditions: a fused-silica capillary ($41.7 \text{ cm} \times 50 \mu\text{m}$ I.D.); a running buffer composition of 30 mM borates with 2 mM β -cyclodextrin at pH 10.0; a running voltage of 15 kV; injection at 0.5 psi for 5 s.

Conclusions

The proposed MSPE technique, based on the synthesized magnetic adsorbents of mixed composition (Fe_3O_4 -fullerene-activated carbon), proved to be an efficient strategy in the adsorption of azo dyes in complex matrices such as wastewater, with a % recovery ranging between 95% and 106% for each azo dye. The methodology described is faster, with minimum sample manipulation, and provides better selectivity, lower solvent consumption and consequently a lower cost with respect to traditional SPE.

The homogeneous adsorption of sunset yellow, allura red and tartrazine on the magnetic adsorbent is governed by the composition of the carbon derivatives in the preparation process as well as the spatial distribution of each analyte.

The adsorption phenomenon is due to three different types of interactions: non-electrostatic interactions (π - π interactions) and hydrophobic interactions between the π electrons of the activated carbon and the fullerene and the aromatic rings present in sunset yellow and allura red; additionally, the adsorbent permits physical adsorption and therefore dispersive interactions, and their spatial distribution permits homogeneous retention of all the azo dyes studied.

The technique developed presents advantages for the application of CE as a separation technique, such as simplicity, low cost, and analysis time. Additionally, this technique provides satisfactory results in terms of sensitivity and accuracy, despite the enrichment factor obtained of 500/300. The MSPE method achieves appropriate LODs for the identification and quantification of azo dyes.

The developed method was satisfactorily applied as a routine procedure to identify and quantify azo dyes in real wastewater samples. The MSPE technique is an excellent strategy in the removal and selective adsorption of several analytes, and additionally is also a good alternative for coupling to other analytical methodologies.

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