Quantitative Determination of Three Textile Reactive Dyes in Ground Water, Sewage Water and Soil Using Voltammetric and HPLC Techniques

قياس تركيز ثلاثة أصباغ ملابس في المياه الجوفية والمياه العادمة والتربة باستخدام تقنية الانتزاع المهبطي الفولتمتري ذات النبض التفاضلي (DP-Ad CSV) وطريقة الكروموتوغرافيا السائلة عالية الأداء (HPLC)

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Received: (20/9/2003), Accepted: (23/5/2004)

Abstract

Differential-pulse adsorptive cathodic stripping voltammetric (DP-AdCSV) and high performance liquid chromatography (HPLC) techniques were developed for quantitative determination of Reactive Blue 19, Reactive Red 198 and Reactive Orange 107 textile dyes. The calibration curves using the DP-AdCSV method were found to be linear over the ranges 0.05-1.0 ppm, 0.10-1.10 ppm and 0.05-1.0 ppm, respectively. The HPLC method is based on using a mobile phase consisting of acetonitrile:water (60:40, v/v) containing 0.45 M N-Cetyl-N,N,N-trimethylammonium bromide (CTAB) and buffered to pH 7.92. Reverse phase RP C_{18} column was used with a flow rate of 0.6 ml/minute. The retention times for Reactive Blue 19, Reactive Red 198 and Reactive Orange 107 were found to be 5.4 min, 7.8 min and 2.3 min, respectively. The calibration curves were found to be linear over the ranges 0.1-5.0 ppm, 0.1-1.2 ppm and 0.05-1.5 ppm, respectively.

Keywords: Voltammetric, HPLC, Reactive dyes, blue 19, red 198, orange 107,Textile, waste water, ground water, soil.

ملخص

تتضمن هذه المخطوطة تطوير طريقتين لتحليل ثلاثة أنواع من الأصباغ المستعملة من قبل مصانع المنسوجات. وهذه الأصباغ هي الزرقاء (Reactive Blue 19)، والحمراء (Reactive Red198)، والصفراء (Reactive Orange 107). وقد تم في هذا البحث استخدام طريقتين للتحليل، طريقة الانتزاع المهبطي الفولتمتري ذات النبض التفاضلي (DP-Ad CSV)، وطريقة الكروموتوغرافيا السائلة عالية الأداء HPLC.

وقد دلت نتائج البحث، باستعمال طريقةDP-Ad CSV، على أن العلاقة في منحنيات القياس، بين تركيز الأصباغ، وفرق الجهد، كانت خطية في الفترة بين ٠.٠٠٥–١.٠ ملغم/لتر للصبّغ الأزرق، و ٠.١–١.١٠ملغم/لتر للصبّغ الأحمر، و٠.٠٠٥–١.٠ ملغم/لتر للصبّغ الأصفر. أما استعمال طريقة الكروموتوغرافيا السائلة عالية الأداء HPLC فقد اعتمدت على استخدام طور متحرك مكون من acetonitrile:water (60:40, v/v), يحتوي على تركيز ٠.٤٥ جزيئيه من مادة N-cetyl-N, N, N-trimethylammonium bromide (CTAB), وعمود فصل من نوع RP C_{18}. وكان معدل سريان الطور المتحرك في عمود الفصل ٠.٦ مللتر/ دقيقه. وقد دلت نتائج البحث، باستعمال طريقه الكروماتوجرافيا، أن الزمن الذي تستغرقه الأصباغ الثلاثة للانتقال عبر عمود الفصل هي ٥.٤ دقيقه للصبغ الأزرق، و٧.٨ دقيقه للصبغ الأحمر، و٢.٣ دقيقه للصبغ الأصفر. أمّا بالنسبة لمنحنيات القياس، فقد كانت العلاقة بين تركيز الصبّغ ودرجه الامتصاص خطية ومحصورة في الفترات ٠.١٠–٥.٠ ملغم / لتر ، و٠.١٠–١.٢٠ ملغم /لتر، و٠.٠٠٥–١.٥ ملغم / لتر، للأصباغ الأزرق، والأحمر والأصفر, على التوالي.

Introduction

Synthetic dyes and pigments are extensively used for dyeing and printing industries. Over $7.0x10^5$ tons and approximately 10,000 types of dyes are produced annually worldwide[1]. With the increasing use of a wide variety of dyes, pollution by dye-waste water is becoming increasingly alarming. The two major sources of releasing the dyes into the environment are the textile and dyestuff manufacturing industries. Recent estimation indicated that approximately 12% of the synthetic dyes used each year are lost to waste streams during manufacturing and processing operations and that 20% of these losses enters the environment through effluents from waste water treatment facilities [2]. Most of the textile dyes are highly soluble in water; they pass through the water-purification plants without further degradation and are released into the environment. Reactive dyes are typical azo-based chromophores combined with different types of reactive groups. They have been shown to undergo reduction in natural water and the environment. Their degradation products include amines which were found to be carcinogenic. Their presence in effluent and industrial waste-water is of considerable interest because of their potential for contamination of groundwater and drinking water supplies by compounds that may cause health risks [3].

Several methods have been reported for quantitative determination of reactive textile dyes among which are chromatographic [4-8], voltammetric [9-17], spectrophotometric [18], capillary electrophoresis [19-21] and Raman spectroscopy [22].

The aim of the present work is to develop new selective methods for quantitative determination of some textile reactive dyes (Reactive Blue 19, Reactive Red 198 and Reactive Orange 107) and to apply these methods for quantitative determination of these dyes in ground water, sewage water and soil samples.

Materials and Methods

Materials

All chemicals used were of analytical grade and were used as received. Doubly-distilled water was used throughout the work.

Buffer Solutions

Britton-Robinson (BR) buffer solutions were prepared from mixtures of acetic, phosphoric and boric acids, each being 0.04 M as final concentration. Sodium hydroxide solution (0.2 M) was added to adjust the desired pH in the range from 2 to 12.

Standard Dyes Solutions

Dyes were donated from Al-Aqad Textile Factory (Eastern Industrial Zone, Nablus, Palestinian National Authority). Standard solutions were prepared by dissolving 0.010 gm of each dye (Reactive Blue 19, Reactive Red 198 or Reactive Orange 107) in enough distilled water to make 100 mL solution. Working solutions were prepared by serial dilutions from the stock solution.

Metal Ion Solutions

Soluble salts were used to prepare 1.0×10^{-3} M stock solutions for studying metal ions interference effect on dyes determination.

Mobile Phase for HPLC Analysis

HPLC separation was performed as described by Oxspring., et al [23]; the mobile phase consists of acetonitrile:water (60:40, v/v) containing 0.45 M N-Cetyl–N,N,N–trimethylammonium bromide (CTAB). The mobile phase was degassed and filtered through 0.45 micrometer membrane to remove particulate matter which may clog the system.

Instrumentation

All voltammograms were obtained using model 264B EG&G polarographic analyzer/stripping voltammeter, coupled with model 303A stand and model 305 automatic stirrer and RE 0150 x-y recorder. A three-electrode system was employed and potentials were quoted with respect to a Ag/AgCl reference electrode (3M KC1).

pH measurements were carried out using HANNA pH meter, model HI 8424.

A UV-2 Unicam UV-Visible Spectrophotometer was used for all spectrophotometric measurements. All measurements were performed using quartz cells 10-mm and performed at room temperature (20-25 °C).

HPLC analysis were carried out using Shimadzu HPLC chromatograph which consists of one pump (model LC-10 AT vp), manual sample injector (Rheodyne 7725I with 20µl loop), Diode array detector (model SPD-M 10 Avp) with wavelength in the range 190-800 nm, system controller (model SCL-10 Avp) and class-VP 5.0 Software. Analyses were performed on a 125 x 4 mm I.D Merck Lichrospher 100 RP-18 (5µm) column fitted with guard column.

Methods

A. Method using DP-AdCSV Technique

An accurate volume (usually 10.0 ml) of the buffer solution was pipetted into a clean and dry voltammetric cell followed by 0.1 ml of the dye solution under investigation in the range shown in Table 1. The mixture was stirred slowly and degrated with high purity oxygen-free nitrogen for four minutes. After forming a new HMDE, the required accumulation time was affected at the selected accumulation potential while stirring the solution. A negative potential scan was initiated in the negative direction. De–oxygenation with purging nitrogen for 1-4 minutes was carried out between successive measurements depending on the length of the preceding accumulation period. The same steps of accumulation and stripping were followed with the dye solutions in the voltammetric cell. All experiments were carried out at room temperature

(20-25 °C). The concentration of the dyes was calculated from a previously constructed calibration graph of peak current against concentration of dye.

B. Method using HPLC Technique

Prior to HPLC analyses the visible spectra of each standard dye was obtained to establish its maximum absorbance wavelength and each dye was chromatographed individually and detected at the maximum wavelength λ_{max} in order to determine its retention time. The calibration curves were constructed by plotting absorbance in miliabsorbance units (mAU) vs. concentration of dye. The type and concentration of each dye in the real samples were determined from the corresponding retention time and calibration curve (Table 2). All experiments were carried out at room temperature (20-25°C).

Preparation and Analysis of Real Samples

Drinking Water

Water samples were collected in polyethylene bottles from two different places in Al–Badan (Ein Alsebyan and Ein Altebane) which are located in the eastern part of Nablus city under the Palestinian National Authority. The samples were filtrated using 0.45 micrometer membrane and analyzed using the recommended polarographic and HPLC techniques.

Sewage Water

Sewage water samples were collected from the water flow in the eastern area of Nablus at various distances from the beginning of the water flow. The samples were filtrated using 0.45 micrometer membrane, then analyzed using the recommended polarographic and HPLC techniques.

Table (1): Optimum conditions and calibration curves characteristics for voltammetric determination of Reactive Blue 19, Reactive Red 198 and Reactive Orange 107.

Parameters	Reactive Blue 19	Reactive Red 198	Reactive Orange 107
Optimum pH	9.0	4.0	4.0
Accumulation potential (V)	- 0.1	-0.1	0
Accumulation time (sec)	35	55	50
Current range (μA)	1	1	10
Pulse amplitude (mV)	50	100	100
Scan rate (mVs^{-1})	10	10	10
Drop size	Medium	medium	Medium
Linearity range (ppm)	0.05 – 1.00	0.10 - 1.10	0.05 – 1.00
Detection limit (ppm)	0.05	0.1	0.05
RSD (%)	1.79^a 2.11^b	1.98^a 2.43^b	2.10^a 2.62^b

a: average of 5 measurements of 0.3 ppm dye
b: average of 5 measurements of 0.7 ppm dye

Table (2): Details of conditions for HPLC analysis.

Parameter	Reactive Orange 107	Reactive Red 198	Reactive Blue 19
Detection wavelength (nm)	591	519	411
Retention time (min)	5.4	7.8	2.3
Range of linearity (ppm)	0.1-5.0	0.1-1.2	0.05-1.5
Detection limit (ppm)	0.1	0.1	0.05
RSD (%)	5.21	4.75	3.10

Soil Samples

About 1 kg of soil sample was collected at the beginning of the sewage water flow 2 km from the beginning of the water flow at a depth of 20 cm. Dyes were extracted from the soil sample using 800 ml of water, filtrated using 0.45 micrometer membrane and stored in polyethylene bottles. The sample was analyzed using methods A and B.

Results and Discussion

Using method A (Differential-Pulse Adsorptive Cathodic Stripping Voltammetric Technique)

Different experimental parameters that affect the differential-pulse adsorptive cathodic stripping voltammetric (DP–AdCSV) response were studied to optimize the experimental conditions for the determination of dyes. These parameters include the effect of pH, accumulation potential, accumulation time, drop size, pulse amplitude, scan rate and interference from other ions. Quantitative determination of the dyes was based upon the selection of the optimum conditions.

Effect of pH

Following the recommended procedure, the differential-pulse adsorptive cathodic stripping voltammetric (DP-AdCSV) runs of 1 ppm of each of the colors under investigation (Reactive Blue 19, Reactive Red 198 and Reactive Orange 107) were carried out over the pH rang 2.0-12.0 using Britton-Robinson (BR) buffer. The obtained results are presented in (Figure 1). Each of the three dyes showed one peak throughout the whole pH range. Reactive Blue 19 (Fig 1 A) showed that the height of the peak initially increased in the pH range 2.0-9.0, then decreased markedly at pH greater than 9.0 and almost disappeared at pH 12.0. However, for Reactive Red 198 (Fig 1 B) the height of the peak initially increased in the pH range 2.0–3.0, then decreased gradually at pH greater than 3.0 and nearly disappeared at pH 12.0. Finally, for Reactive Orange 107 (Fig 1 C) the height of the peak initially increased in the range 2.0-4.0, then decreased gradually at pH greater than 4.0 and almost disappeared at pH 12.0. The optimums pH with respect to peak height for Reactive Blue 19, Reactive Red 198 and Reactive Orange 107 were found to be 9.0, 3.0, and 4.0, respectively. The results revealed that the position of the peak potential shifts to more negative potential with increasing the pH. This indicates that hydrogen ions are consumed in the reduction process.

Effect of Accumulation Potential

The effect of changing the accumulation potential on the peak current of 1.0 ppm for Reactive Blue 19, Reactive Red 198, and Reactive

Orange 107 dyes from 0 to -1.2 V was studied. A gradual decrease in the peak current was observed upon changing the accumulation potential from 0 to – 1.2 V for the three dyes. The optimum accumulation potentials were at – 0.1, – 0.1, and 0 V, for Reactive Blue 19, Reactive Red 198 and Reactive Orange 107, respectively, as shown in Table 1. The obtained accumulation potentials were found to be suitable for reasonable sensitive and reproducible peak current because at these accumulation potentials there is a large amount of oxidized dye.

Effect of Accumulation Time

Differential pulse adsorptive cathodic stripping voltammograms (DP-AdCSV) for 1.0 ppm of Reactive Blue 19, Reactive Red 198 and Reactive Orange 107 dyes after different accumulation times were studied. The peak potentials were – 0.82, – 0.35 and – 0.31 V, for Reactive Blue 19, Reactive Red 198 and Reactive Orange 107, respectively. No change with accumulation time was observed. The obtained results showed that there is a significant increase in the peak current as the accumulation time increases. The optimum accumulation times for the maximum peak current were found to be 35, 55 and 50 seconds for Reactive Blue 19, Reactive Red 198 and Reactive Orange 107, respectively (Table 1). The amount of adsorbed dye at the electrode surface increases with increasing the accumulation time. At larger accumulation times adsorption phenomenon is probably causing a steady current value.

Effect of Drop Size

The effect of drop size on peak current height was investigated at 1 ppm level for Reactive Blue 19, Reactive Red 198 and Reactive Orange 107 dyes. The solutions were prepared as described in the recommended procedure. It was found that the peak current increases by increasing the surface area of the mercury drop HMDE due to the increase in the accumulation of the dye which causes a peak current enhancement. However, in the present work a medium drop size (Table 1) was selected since it gave reasonable reproducibility and sensitivity.

Effect of Pulse Amplitude

The effect of pulse amplitude on the peak current of 1 ppm of Reactive Blue 19, Reactive Red 198 or Reactive Orange 107 dye was investigated following the recommended procedure. It was found that the peak current increases as the pulse amplitude increases. The peak potential of Reactive Blue 19 and Reactive Red 198 stayed constant as pulse amplitude increases in the cathodic scan, while Reactive Orange 107 showed a positive shift in the peak potential as pulse amplitude increases in the cathodic scan. In the present work, medium pulse amplitude of 50 mV was selected for Reactive Blue 19, while large pulse amplitudes of 100 mV was selected for Reactive Red 198 and Reactive Orange 107 (Table 1).

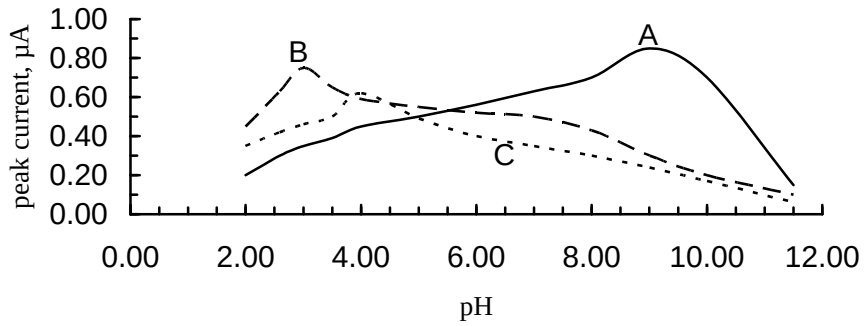

Figure (1): Effect of pH on the DP-AdCSV of
A- 1 ppm Reactive Blue 19 (pulse amplitude 50 mV)
B- 1 ppm Reactive Red 198 (pulse amplitude 100 mV)
C- 1 ppm Reactive Orange 107 (pulse amplitude 100 mV) accumulated at 0.0 V for 30 sec, scanned from 0.0 to-1.2 V, medium drop size, scan rate 10 mVs-1 and at 25 °C.

Cyclic Voltammetric Measurement

The cyclic voltammetric measurement of Reactive Blue 19, Reactive Red 198 and Reactive Orange 107 dyes showed a single reduction peak at HMDE. The repetitive cyclic voltammograms of 3 ppm of any dye

indicated the rapid desorption of the adsorbed species from the electrode surface as peak current decreases sharply in the second cycle. No anodic peaks were observed which indicates an irreversible reduction process. The shift of peak potential is attributed to the adsorption phenomenon. Linear sweep (DC) voltammetric technique with scan rates of 500, 500 and 1000 mVs^{-1} (Table 1) was selected for Reactive Blue 19, Reactive Red 198 and Reactive Orange 107, respectively. Typical results of repetitive cyclic voltammogram of 3 ppm Reactive Red 198 are presented in (Figure 2).

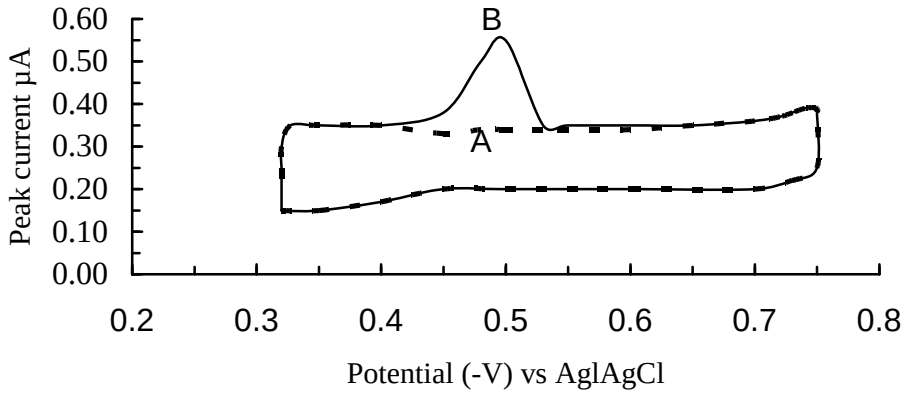

Figure (2): Cyclic voltammogram for reduction of 3 ppm Reactive Red 198 at HMDE, recorded at a scan rate of 500 mVs^{-1}.
A- first cycle.
B- second cycle. Other conditions as listed in Table 1.

Effect of Scan Rate

The effect of scan rate on the peak current of 3 ppm of Reactive Blue 19, Reactive Red 198 and Reactive Orange 107 dyes has been investigated using both DP-AdCSV and DC-AdCSV. In DP mode, it was found that increasing the scan rate has no significant effect on the peak

current. On the other hand, a gradual increase in the peak current was associated with the increase in the scan rate on DC mode, with a little shift in the peak potential to more negative values which indicates slow kinetics character of the dissolution and a degree of irreversibility in the electrode process of these dyes.

Effect of Metal Ions on Dye Determination

The effect of metal ions on the determination of the three dyes under investigation (Reactive Blue 19, Reactive Red 198 and Reactive Orange 107) using the proposed voltammetric method was studied for solutions of dyes prepared as described in the recommended procedure. The obtained results are presented in (Table 3). Cd^{2+} was found to interfere seriously in the determination of Reactive Blue 19, and more than 5 ppm of Cd^{2+} could not be tolerated. The interference of Cd^{2+} might be due to the formation of a complex with the dye. Cr^{3+}, on the other hand, showed negative interference and more than 10 ppm of Cr^{3+} could not be tolerated. The negative interference might be due to the hydrolysis of the dye in the presence of Cr^{3+}. In the determination of Reactive Red 198, Pb^{2+} showed a peak at – 0.36 V. The peak height was found to increase gradually by increasing the concentration of Pb^{2+} until it overlaped with the peak of Reactive Red 198 at a potential of –0.35 V. Pb^{2+} at 15 ppm caused interference of +14.3 % and above this concentration could not be tolerated. Similar results were obtained for the effect of Fe^{3+}, which showed peak potential at – 0.53 V. Fe^{3+}, at a concentration of 50 ppm caused interference with an error of +5.7 % in the determination. The positive interference of Fe^{3+} might be due to the formation of a complex with the dye. Finally, in the determination of Reactive Orange 107, Fe^{2+} was found to interfere with a concentration above 10 ppm. Under the same conditions, Fe^{2+} showed a peak potential at – 0.26 V. The peak height was found to decrease gradually by increasing the concentration of Fe^{2+} until it overlaped with the peak of Reactive Orange 107 Peak at a potential of – 0.30 V. The negative interference might be due to the hydrolysis of the dye in the presence of Fe^{2+}.

Using Method B (HPLC Technique)

Absorption Spectra

The absorption spectra of each dye (Reactive Blue 19, Reactive Red 198 and Reactive Orange 107) were studied in the wavelength range 400 – 800 nm. The standard solution of each dye (20 ppm) was prepared in distilled water at pH = 7.9. From each spectrum, the maximum absorbance for the HPLC analysis was selected. These were 591 nm, 519 nm and 411nm for Reactive Blue 19, Reactive Red 198 and Reactive Orange 107, respectively (Table 2).

Retention Time

The conditions recommended for HPLC analysis [16] were applied to determine the retention time of each dye. The obtained results (Table 2) showed retention times of 5.4 min, 7.8 min and 2.3 min for Reactive Blue 19, Reactive Red 198 and Reactive Orange 107, respectively. All measurements were taken at room temperature (22-25°C). Comparison between the polarity of the three dyes showed that Reactive Orange 107 has the highest polarity (shortest retention time) followed by Reactive Blue 19 and Reactive Red 198 in that order.

Calibration Curves Using Method A

According to the obtained results, the optimum conditions for the analytical determination of Reactive Blue 19, Reactive Red 198 and Reactive Orange 107 dyes using DP-AdCSV at HMDE were selected and presented in Table 1. Typical voltammograms showing successive enhancements of peak current with increasing the concentration of the Reactive Blue 19 dye are shown in Figure 3. The calibration graphs were constructed by plotting the peak current vs. concentration of dye. The ranges of linearity were found to be 0.05 - 1.0 ppm, 0.10 - 1.10 ppm and 0.05 - 1.00 ppm with detection limits of 0.05, 0.10 and 0.05 ppm for Reactive Blue 19, Reactive Red 198 and Reactive Orange 107, respectively. Table 1 summarizes the optimum conditions for the determination of these dyes as well as the characteristics of the calibration curves. Comparison between the three dyes shows that Reactive Blue 19 and Reactive Orange 107 have similar detection limits

Table (3): Effect of metal ions on the polarographic determination of textile dyes. Other conditions are listed in Table 1.

Metal ions added	Concentration of metal ion added (ppm)	Reactive Orange 107 (0.4 ppm)		Reactive Red 198 (0.4 ppm)		Reactive Blue 19 (0.4 ppm)	
		Peak current (µA)	Error (%)	Peak current (µA)	Error (%)	Peak current (µA)	Error (%)
None	-	3.30	N	0.350	N	0.33	N
Ba^{2+}	100	3.30	N	0.35	N	0.33	N
Sr^{2+}	100	3.30	N	0.35	N	0.33	N
Al^{3+}	100	3.30	N	0.35	N	0.33	N
Mg^{2+}	100	3.30	N	0.35	N	0.33	N
Cr^{3+}	15	3.30	N	0.35	N	0.31	-6.1
Cr^{3+}	100	3.30	N	0.35	N	A	a
Pb^{2+}	10	3.30	N	0.35	N	0.33	N
Pb^{2+}	15	3.30	N	0.40	+14.3	0.33	N
Pb^{2+}	100	3.30	N	0.40	+14.3	0.33	N
Cu^{2+}	100	3.30	N	0.35	N	0.33	N
Zn^{2+}	100	3.30	N	0.35	N	0.33	N
Co^{2+}	100	3.30	N	0.35	N	0.33	N
Cd^{2+}	5	3.30	N	0.35	N	0.33	N
Cd^{2+}	10	3.30	N	0.35	N	0.39	+18.2
Cd^{2+}	100	3.30	N	0.35	N	A	a
Ni^{2+}	100	3.30	N	0.35	N	0.33	N
Mn^{2+}	100	3.30	N	0.35	N	0.33	N
Hg^{2+}	100	3.30	N	0.35	N	0.33	N
Fe^{3+}	10	3.30	N	0.35	N	0.33	N
Fe^{3+}	50	3.30	N	0.37	+5.7	0.33	N
Fe^{3+}	100	3.30	N	a	A	0.33	N
Fe^{2+}	10	3.30	N	0.35	N	0.33	N
Fe^{2+}	15	2.40	-27.3	0.35	N	0.33	N
Fe^{2+}	100	a	a	0.35	N	0.33	N

Note: (+): increasing the peak height. (-): decreasing the peak height.
(N): no effect. (a): not measured

and range of linearity, while Reactive Red 198 has a lower detection limit. The relative standard deviations were calculated for the three dyes and the results are presented in Table 1.

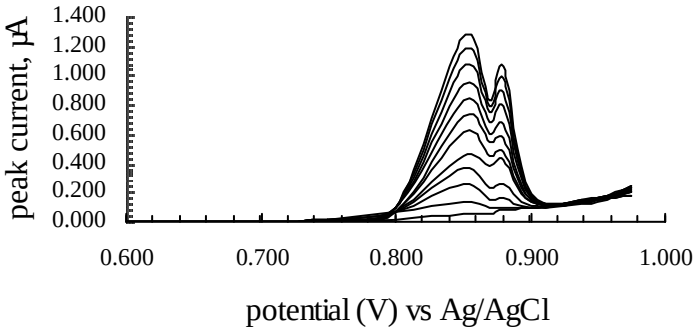

Figure (3): Typical DP-AdCSV voltammograms of Reactive Blue 19 at concentrations of 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 and 1.1 ppm, respectively, under the conditions recommended for Reactive Blue 19 are presented in Table 1.

Calibration Curves Using Method B

The calibration curves using HPLC technique were constructed by plotting peak height vs. concentration of each dye. The obtained results showed linearity in the ranges 0.10-5.00 ppm, 0.10-1.20 ppm and 0.05-1.50 ppm for Reactive Blue 19, Reactive Red 198 and Reactive Orange 107, respectively, with detection limits of 0.10, 0.10 and 0.05 ppm and relative standard deviations of 5.21 %, 4.75 % and 3.10 %, respectively. The optimum conditions for the determination of the dyes as well as the characteristics of the calibration curves are shown in Table 2.

Quantitative Determination of Reactive Blue 19, Reactive Red 198 and Reactive Orange 107 Dyes in a Mixture Using Method A

It can be seen from Table 1 that the conditions for determination of each dye differ from those of the other two dyes. In order to determine

each dye in the presence of the other two dyes, the conditions of analysis should be made according to the recommended conditions of the corresponding dye. Figure 4 I, shows typical results for the determination of the three dyes in a mixture at the conditions recommended for Reactive Blue 19. Figure 4 II, shows typical results for the determination of the three dyes in a mixture at the conditions recommended for Reactive Red 198. While Figure 4 III, shows typical results for the determination of the three dyes in a mixture at the conditions recommended for Reactive Orange 107.

Comparison between the three Figures (4 I, 4 II and 4 III) shows that it is possible to identify and determine each dye in the presence of the other two dyes. The reduction in the peak current of Reactive Orange 107 in the presence of the other two dyes has not been studied yet.

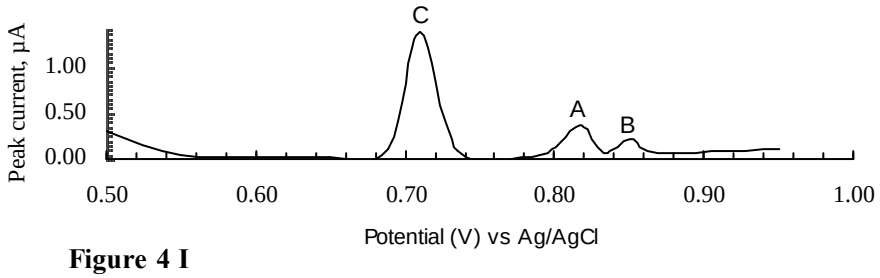

Figure 4 I

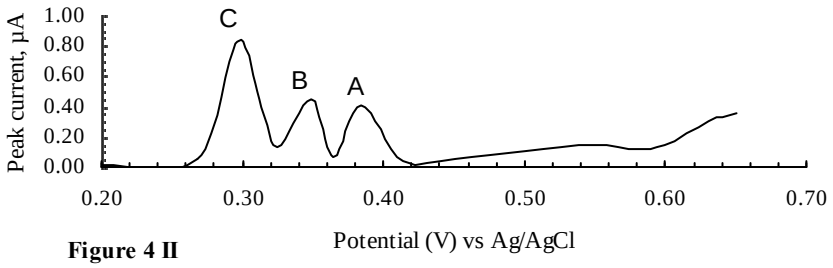

Figure 4 II

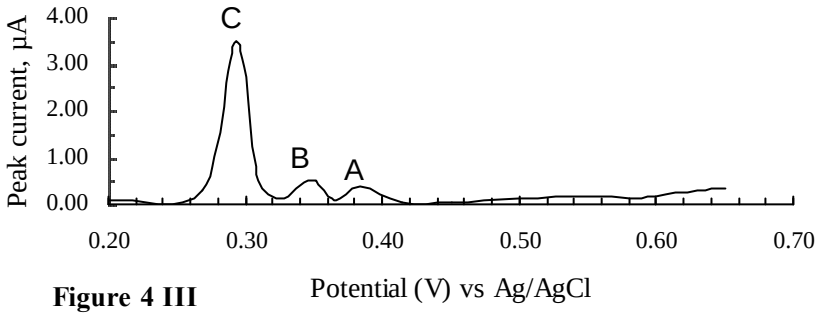

Figure 4 III

Figure (4): Typical results for DP-polarographic quantitative determination of 0.4 ppm Reactive Blue 19, 0.4 ppm Reactive Red 198 and 0.4 ppm Reactive Orange 107 in a mixture, under the conditions recommended for:

I. Reactive Blue 19
II. Reactive Red 198
III. Reactive Orange 107.

A represents the peak for Reactive Blue 19
B represents the peak for Reactive Red 198
C represents the peak for Reactive Orange 107

Quantitative determination of Reactive Blue 19, Reactive Red 198 and Reactive Orange 107 Dyes in a Mixture Using Method B

The conditions for determination of each dye (Reactive Blue 19, Reactive Red 98 and Reactive Orange 107) (Table 2) were used to determine each dye in a mixture with the other two dyes. The conditions of analysis should be made according to the recommended conditions of the corresponding dye. Typical results for the determination of Reactive Blue 19, Reactive Red 198 and Reactive Orange 107 in presence of each other are presented in Figures (5 I, 5 II and 5 III). Comparison between the three Figures showed that it is possible to identify and determine each dye in the presence of the other two dyes without any interference.

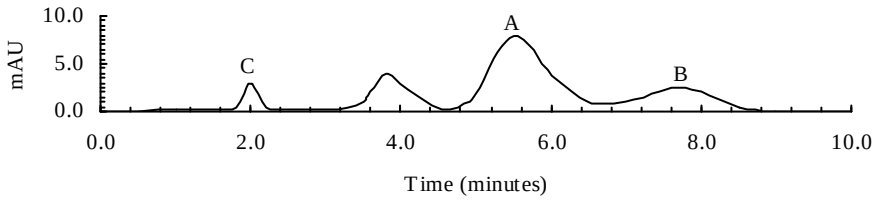

Figure 5 I

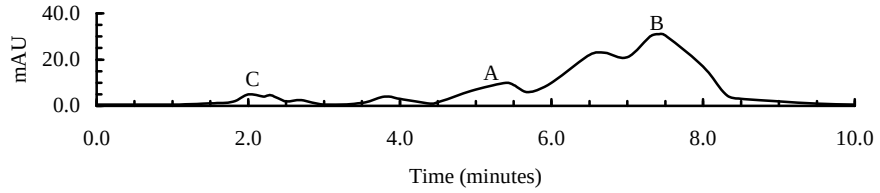

Figure 5 II

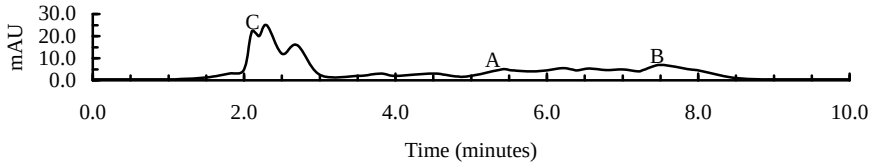

Figure 5 III

Figure (5): Typical HPLC quantitative determination of 20 ppm Reactive Blue 19, 20 ppm Reactive Red 198 and 20 ppm Reactive Orange 107 in a mixture, under the conditions recommended for

I. Reactive Blue 19
II. Reactive Red 198
III. Reactive Orange 107.

A represents the peak for Reactive Blue 19
B represents the peak for Reactive Red 198
C represents the peak for Reactive Orange 107

Analysis of real samples of ground water, sewage water and soil using methods A and B

The two proposed methods of analysis were applied for quantitative determination of Reactive Blue 19, Reactive Red 198 and Reactive Orange 107 in real samples of ground water, sewage water and soil. Three different samples of sewage water were collected from the water flow in the eastern area of Nablus city at various distances from the beginning of the water flow, and two samples of ground water collected from two different places in Al-Badan (Ein–Alsebyan and Ein–Altebane), while the soil sample was collected one meter away from the beginning of the sewage water flow. The samples were analyzed using Methods A and B. The obtained results are presented in (Table 4). Reactive Red 198 was not detected in any of the analyzed samples.

Table (4): Typical results of determination of textile dyes in real samples using methods A and B

Sample	Concentration of Dyes Present (ppm)			
	Using Method A		Using Method B	
	Reactive Orange 107	Reactive Blue 19	Reactive Orange 107	Reactive Blue 19
Sewage water at the beginning of the water flow	1.00	1.45	0.82	1.60
Sewage water 2 Km away from the water flow	0.05	Present below range of linearity	Present below range of linearity	Not detected
Sewage water 10 Km away from the water flow	Not detected	Not detected	Not detected	Not detected
Ground water collected from Ein–Alsebyan	Not detected	Not detected	Not detected	Not detected
Ground water collected from Ein–Altebane	Not detected	Not detected	Not detected	Not detected
soil sample near the sewage water flow	Present below range of linearity	Present below range of linearity	Present below range of linearity	Not detected

Conclusion

The two proposed methods for quantitative determination of textile dyes in water and soil are simple, cheap and fast. The determination of the three dyes is possible by selecting the optimum conditions for each dye. The detection limit of both methods is relatively low, which makes them suitable for determination of degree of pollution of drinking water and soil with textile dyes.

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