An-Najah National University
Faculty of Graduate Studies

Voltammetric and HPLC Determination of Some Textile Dyes

By
Amani L.N. Zu'bi

Supervisor
Prof. Ali Z. Abu Zuhri

Co-Supervisor
Dr.Nidal Za'tar

**Submitted in Partial Fulfillment of the Requirements for the Degree
of Master of Science in Chemistry, Faculty of Graduate Studies
An- Najah National University, Nablus, Palestine**

Voltammetric and HPLC Determination of
Some Textile Dyes

By
Amani L.N. Zu'bi

This thesis was defended successfully on

Committee Members   **Signature**

1. **Prof. Ali Z.Abu Zuhri**
   Prof. of Analytical Chemistry   **.........................**
   An-Najah National University

2. **Dr. Nidal A. Za'tar**
   Associate Prof. of Analytical Chemistry   **.........................**
   An- Najah National University

3. **Dr. Raqi M. Shubietah**
   Associate Prof. of Analytical Chemistry   **.........................**
   An- Najah National University

4. **Dr. Ziyad Al- Shakhshir**
   Assistant Prof. of Analytical Chemistry   **.........................**
   Al- Quds University

DEDICATION

To: My Mother

My Husband

My Sons

My Brother and Sisters

With great Love

And with great respect to the spirit of my father

ACKNOWLEDGMENT

List of contents

Chapter One

Introduction

Chapter Two

Experimental

Chapter Three

Results and discussion

Voltammetric analysis

Chapter Four

Results and discussions

HPLC Analysis

Chapter Five

Reducing degradation of azo dyes by zero –valent iron in aqueous

Chapter Six

Comparative study

Comparison of the voltammetric and HPLC methods with other

List of Tables

IX

List of Figures

Title   **Page**

Abstract

Simple and sensitive voltammetric and HPLC methods were developed for the determination of the three azo dyes (Acid Orange7, Acid Orange10 and Acid Orange12). Optimization of various experimental conditions for quantitative determination of dyes is described.

The voltammetric method for determination of trace amounts of dyes is carried out by differential pulse-adsorptive cathodic stripping voltammetry (DP-AdCSV) technique at a hanging mercury drop electrode (HMDE). The effects of different parameters that influence the (DP-AdCSV) response are described. These parameters include pH, accumulation potential, accumulation time, pulse amplitude, scan rate, drop size and interference by other ions.

The calibration graphs for the determination of the studied dyes were linear in the range 0.004-0.105 ppm, 0.009-0.180 ppm and 0.007-0.140 ppm with detection limit of 0.002 ppm, 0.005 ppm and 0.004 ppm and relative standard deviation of 1.96%, 2.10% and 2.15% for Acid Orange7, Acid Orange10 and Acid Orange12 respectively.

The HPLC method for the determination of dyes using optimum conditions is carried out. The wavelengths of maximum absorbance were 477nm for Acid Orange 10, 485nm for Acid Orange 7 and Acid Orange 12. Retention times were found to be 2.8 min, 4.8 min, and 3.1min for Acid Orange7, Acid Orange10 and Acid Orange12 respectively. Calibration graphs for the determination of the studied dyes were linear in the range 0.05-4.0 ppm, 0.10-4.0 ppm and 0.10-4.0 ppm with relative standard deviation of 3.8%, 4.1% and 4.2% and detection limit of 0.03, 0.05 and 0.05 ppm for Acid Orange7, Acid Orange10 and Acid Orange12 respectively.

The Reducing degradation kinetics of the studied dyes by zero-valent iron in aqueous-solutions were studied. Effective degradation was achieved with rate constants of 0.004, 0.002 and 0.003 mmol/L.min, and half-lives of 10 min 22 min and 17min for Acid Orange7, Acid Orange10 and Acid Orange12 respectively.

CHAPTER ONE

INTRODUCTION

Chapter One
Introduction

1.1 Textile dyes

Dyes are intensely colored substances that can be used to produce a significant degree of coloration when dispersed or reacted with other materials .The dye molecule can be considered to be structured from two components, the dye chromophore and the dye functional group. The dye chromophore includes the double bonds and is responsible for the color of the dye while the functional group is responsible for the bond between the fiber and the dye [10].

In the nomenclature of dye, its classification is based on the major functionality of the dye. The main classes being azo dyes (including sulphonated azo dyes), anthraquinone, polymethine, phthalocyanine, xanthenes, sulphur, aryl-methane and coumarine dyes. The use of dye generally refers to the manner in which it is applied. Some of most common applications are in acidic or basic media as mordants, lakes, pigments, solvents, or dispersants [30].

Organic dye industry has been developing rapidly today, approximately 10,000 types of dyes are produced annually and used in diverse applications, the annual world production amounts to nearly one million tons, more than half of them are azo dyes [22,35].

Azo compounds constitute the largest and most diverse group of dyes and pigments used in commercial applications. Over 3000 different azo dyes are used to satisfy the consumer demand for color appeal in textiles, paper, gasoline, food stuffs, leather and printing applications [12,39].

Dyes make our world beautiful but it brings pollution, they are released into the environment as industrial effluents from food, cosmetic, drug, textile and dyestuff factories. Recent estimation indicates that approximately 12% of the synthetic dyes used in textile processes each year are lost to waste streams during manufacturing and processing operations, and that 20% of these losses are released into the environment through effluents from waste water treatment plants. These compounds are quite difficult to be removed in water treatment procedures, and can be transported from municipal sewage water to rivers because of their high water solubility [43, 44].

Interest in the environmental behavior of dyes arise largely from concerns about toxicity. Some synthetic dyes may be pathogenic if they are consumed in excess. It has also been shown that synthetic precursors, intermediates and degradation products of these dyes could be potential health hazards owing to both their toxicity and carcinogenicity [40]. Dyes of aromatic structures [11], dyes with azo bonds, nitro- or amino-groups are carcinogenic [13], metal-based complex dyes, such as chromium-based dyes, can lead to the release of chromium (that is carcinogenic) into water supplies [3,7]. The majority of dyes may cause allergic responses, skin dermatoses, eczema [27,37], affect the liver [21,27], the lungs [4], the vasco-circulatory system [28], the immune system [26], and the reproductive system [14, 27] of experimental animals as well as humans.

Sulphonated azo dyes (that are our interest in this work) possess acidic groups in their chemical structure, the sulphonic acid groups in particular are often present as sulphonate anions and provide very good water solubility. In addition, azo dyes have been shown to undergo reduction in natural water ways and the environment, the degradation products include amines, and some of them are known to

be carcinogenic. Their presence in effluent and industrial waste-water is of considerable interest because of the potential for contamination of ground and drinking water supplies by compounds that may cause health risks. Therefore the detection, identification, and quantification of azo dyes in waste water at low levels is important for the protection of natural waters [29,30].

Stained waste water has to be treated to reduce ecological consequences [23]. Dyes in waste water can be eliminated by various methods, including flocculation, precipitation, reverse osmosis, adsorption [25], and also oxidative-reductivechemical and photo chemical [24] processes, other techniques comprise radiation and decolorization with ozone in combination with H_2O_2. At present, the major techniques in treating dye waste water [22] are biological treatment, activated carbon method and light degradation. However, there are shortcomings in these techniques, for example, activated carbon method results in transferring the dyes to another place, light-degradation treatment is energy consuming and limited in treating amount, and the conditions of biological process in microorganism treatment are difficult to control to reach a satisfactory level [41].

Zero- valent iron, $Fe°$, in the form of powder, is a strong reducer, and it is cheap and easy to get. The practical application of zero-valent iron in treating ground waste [15] has been made. Treated by $Fe°$, dye waste waters can be decoloured, and the products (aromatic amine) are easily degraded by microorganisms [15].

1.2 Quantitative determination of textile dyes:

Some voltammetric, chromatographic, capillary electrophoresis, and spectrophotometric methods have been reported for determination of textile dyes.

1.2.1 Polarographic and voltammetric determination of textile dyes.

Fogg, et al [18] used polarographic and voltammetric methods for determination of two reactive triazine-based azo dyes containing 4-carboxypyriyl and 1,4-diazabicyclo [2,2,2] octanyl [DABCO] leaving groups. The direct current and differential pulse polarograms show one peak corresponding to the reduction of the azo group and other peaks at more negative potentials corresponding to the reduction of reactive groups. Optimum conditions were found for polarographic and voltammetric determination at submicromolar concentration of the tested dyes. Based on the reduction of azo group the calibration graphs were linear in the range 1.0×10^{-7}-1.0×10^{-5}M and 5.0×10^{-8}-1.0×10^{-7}M for polarographic and voltammetric methods, respectively. The peaks corresponding to the reduction of the reactive group can be used for monitoring the hydrolysis of the tested dyes.

Fogg, et al [17] used cathodic stripping voltammetry for determination of reactive Violet 5 and its hydrolysis product (that is produced as a side product in the dyeing process) in a mixture at sub-ppb levels by cathodic stripping voltammetry because the potentials of their azo reduction peaks are separated sufficiently. The calibration graphs of reactive Violet 5 and its hydrolysis product were linear in the range 1.0×10^{-7}-5.0×10^{-7}M.

Barek, et al [5] used polarographic and voltammetric method for determination of five triazine–based azo dyes differing only in their potentially reactive groups. One peak was found for each of the five dyes corresponding to the reduction of the azo group, other peaks at more negative potentials corresponding to the reduction of reactive groups. Optimum conditions were found for polarographic and voltammetric determination at submicromolar concentration of the tested dyes. Based on the reduction of azo group, using a static mercury drop electrode, the detection limit was 2.0×10^{-8}M for differential pulse polarography, using a hanging mercury drop electrode detection limits were around 1.0×10^{-8}M for differential pulse voltammetry and 2.0×10^{-10}M for adsorptive stripping voltammetry.

Other peaks at more negative potentials corresponding to the reduction of reactive groups can be used for monitoring the hydrolysis of the tested dyes.

Barros, et al [6] used polarography to differentiate between Food Yellow 3 and Acid Orange 7 in cork, which exhibit similar polarographic behavior. In the presence of tetraphenylphosphonium chloride (I), the addition of NaOH separated the polarographic peaks of the two dyes. A dropping mercury electrode, a vitreous-carbon counter electrode and an Ag-AgCl (Satd.KCl) reference electrode were used. Detection limits of 100 ppb were obtained corresponding to an amount of colouring matter of 2μg/cork.

Abollino, et al [2] studied the electrochemical behaviour of the Cd(II), Mn (II), Ni (II) and Pb (II) complexes of seven sulphonated azo dyes and four quinolines, in the pH range (4-8) using adsorptive cathodic-stripping voltammetry. A hanging mercury drop electrode, an Ag/AgCl electrode and a Pt electrode served as the working, reference and counter electrodes, respectively.

1.2.2 Chromatographic determination of textile dye

Urquiza, et al [40] used ion-interaction high-performance liquid chromatography method for quick separation and determination of the sulphonated dye Acid Yellow 1, and the sulphonated azo dyes Acid Orange 7, Acid Orange12, Acid Orange 52, Acid Red 2, Acid Red 26, Acid Red 27 and Acid Red 88. A RP-ODS stationary phase is used, and the mobile phase contains an acetonitrile–phosphate buffer (27:73, v/v) mixture at pH 6.7, containing 2.4 mM butylamine as ion-interaction reagent. Good separations were obtained using isocratic elution and spectrophotometric detection at 460 nm. The detection limits for the eight dyes ranged from 7 to 28μg/l for an injection volume of 100μl. Spiked tap water samples (100ml) containing different concentration levels (0.3-1.2μg/l) of the dyes were analyzed after acidification to pH 3 and preconcentration in disposable solid-phase extraction C_{18} cartridges.

Jiménez, et al [23] studied the chromaticity variation and the formation of degradation products of several textile dyes using a UV spectrophotometer and HPLC with diode array detection. Dyes studied belong to the azo, methine, indigo, natural and arylmethane

classes. Aliquots of the solutions treated at constant potential were analyzed and compared with control dye solutions. The final electrolysis solutions obtained by using different electrode materials: Pt, Ti and diamond presented different chromatograms. It was found that the novel diamond electrode is efficient in studying the degradation of various dyes. Possible fragmentation and molecule moiety rearrangement are proposed as a result of the electrochemical treatment.

Weatheral, et al [42] tested the purity of eight commercial sulphonated azo dyes used as acid dyes for wool by HPLC with use of a stainless-steel Alltech Mixed Mode RP-C8/Anion cartridge (15cm x 4.6mm), five isocratic mobile phases, and 254-nm detection. Impurities in dyes ranged from 0.04% in Acid Orange 18 to 5.5% in Acid Red 151. Other dyes studied were Acid Orange 7, Acid Orange 10 and Acid Orange 12, Acid Red 66, Acid Red 73 and Acid Red 88.

Straub, et al [36] compared the technique of HPLC coupled with thermospray MS and particle beam MS for the identification of 14 azo dyes and their synthetic intermediates, byproducts, additives or degradation products. Detection limits in the range 500ng to 50μg

were obtained from particle beam MS while thermospray MS was two to three orders of magnitude more sensitive. Only through the application of both detection techniques, could the dyes be satisfactorily characterized.

1.2.3 Capillary electrophoresis determination of textile dyes

Urquiza, et al [38] determined the dissociation constants of 10 sulfonated azo dyes, six of the dyes studied are most common food colours used as additives, and four commonly used as textile dyes (Acid Orange7, Acid Orange 12, Acid Red 26 and Acid Red 88),was done by two different systems, one by using capillary electrophoresis (CE) with diode array detection and the other by using UV-visible absorption spectrophotometry. Capillary electrophoresis methods allow calculation independent of solute purity due to the possibility of working with small amounts of sample compared with the spectrophotometric method.

Urquiza,et al [39] used a method based on capillary zone electrophoresis coupled with photodiode-array detection to determine several sulfonated dyes, including a sulfonated dye (acid yellow 1) , and the sulfonated azo dyes acid orange7, acid orange 12, acid orange

52 , acid red 26, acid red 27 and acid red 88.. The detection limits for the seven dyes ranged from 0.1 to 4.53 μg/ml. Spiked river water samples (100 ml), containing different concentration levels (0.025-0.150) μg/ml of the dyes were analyzed after acidification (pH 3) and pre–concentration in disposable 1 ml cartridges.

Blatny, et al [9] used capillary zone electrophoresis for separation of nine synthetic organic dyes including seven azo compounds, as anions. As most of the solutes are sulfonic acids, the separation could not be effected by varying the pH of the buffer solution. Therefore two methods were applied to adjust the electrophoretic mobility in a specific way: complexation by bis-tris-propane and interaction with linear polymers added to the buffer and acting as pseudo-phases. A buffer system containing polyethylene glycol and polyvinylpyrrolidone permits the separation of all analytes. Retention of the dyes caused by the polymeric additives was related to the solutes structure. It was demonstrated by cluster analysis that the relative decrease in the electrophoretic mobility of the dyes correlates with the number of benzoaromatic rings in the solute molecules.

Riu., et al [31] determined several sulfonated dyes in spiked groundwater samples and industrial effluents by automated solid-phase extraction followed by capillary electrophoresis with UV detection, and by capillary electrophoresis/mass spectrometry (CE/MS). Studied dyes include one monosulfonated (Mordant Yellow 8) and seven disulfonated azo dyes (Acid Red 1, Mordant Red 13, Acid Red 14, Acid Red 7, Acid Yellow 23 and Acid Blue 113). The method detection limit ranged from 10 to 150μg /L using CE/UV, and from 100 to 800μg /L using CE/MS.

1.2.4 Spectrophotometric determination of textile dyes

Zamora, et al [45] used spectrophotometric method and multivariate calibration technique for determination of a set of 16 different dye mixtures containing Reactive Red 195, Reactive Yellow 145 and Reactive Orange 122. In this study, the calibration model is based on absorption spectra in the range of 350-650-nm range, and made the determination of the dye concentrations possible in a validation set with significantly greater accuracy than the conventional univariate calibration method.

Fan, et al [16] used spectrophotometric method to measure the dissociation constants of Acid Orange45 in water and aqueous alcohol solvents consisting of 10-90% methanol, 10-70% ethanol, 10-60% propan-2-ol and 10-50% t-butanol. The measurements were made at 25ºC and ionic strength 0.1M. The alcohol co-solvents were found to affect the acid-base equilibria, the visible absorption spectra and the colour transition range. The pKa values decreased with increasing alcohol co-solvent concentration in the order t-butanol > propan -2-ol > ethanol > methanol > H_2O. For each solvent system a linear relationship existed between the pKa value and the mole fraction of the co-solvent over a limited concentration range.

Sankar, et al [32] determined some adrenergic drugs using Acid Orange7 by dissolving tablets or injection solution, equivalent to 10 mg in 50 ml of water and the solution was filtered and diluted to 100 ml. A portion of sample solution (10 to 200 µg/ml) was treated with 2 ml of 0.1M HCl and 1 ml of aqueous 0.5% Acid Orange 7 and then diluted to 10 ml with water. The solution was extracted with 10 ml of $CHCl_3$ and the absorbance was measured at 495 nm. Beer's law was obeyed from 1 to 20µg/ml.

Bhongade, et al [8] determined some phenothiazine derivatives using Acid Orange 7 by dissolving tablets, syrups and injection solution in water to produce a final concentration of 50 µg/m1. A 2-ml portion of sample solution was treated with 2 ml each of 0.1M HCL and Acid orange7, and diluted to 10 ml with water. The solution was extracted with 15 ml of CHC1$_3$ and the absorbance was measured at 495 nm. Beer's law was obeyed from 3 to 25 µg/m1 with RSD in the range of 1-2%.

1.3 Aim of this work

The main aim of this work is to develop new voltammetric and HPLC methods for determination of the three azo dyes (Acid Orange 7, Acid Orange 10 and Acid Orange 12) and investigate the optimum conditions for their determination. A comparative study between the suggested methods and previously reported methods will be investigated. on the other hand the reducing degradation of the azo dyes by zero–valent iron in aqueous solution will be studied in order to find a safe, cheap and practical technique for degradation of azo dyes.

CHAPTER TWO

EXPERIMENTAL

Chapter two
Experimental

Part 1: Voltammetric Analysis

2.1 Chemicals and Reagents

All chemicals used were of analytical grade. The three studied dyes (Acid Orange7, Acid Orange10 and Acid Orange12) were manufactured by Sigma. Other chemicals used were manufactured by (Aldrich, Merck or Riedel-delhaen). Doubly-distilled water was used throughout this work.

2.2 Preparation of solutions

A- Buffer Solution

Britton-Robinson (BR) buffer solutions were prepared according to the procedure recommended by Rahim A, et al (1) from acid mixture of acetic, phosphoric and boric acids, (final conc. 0.04M of each), then adding sodium hydroxide solution (0.2M) to set the desired pH in the range 2.6-11.

B- Standard Dyes Solution

Dyes Standard solutions of 1.0×10^{-3}M were prepared by dissolving an appropriate amount of each dye in doubly distilled water. Working

solutions were prepared by serial dilutions from the stock solution.

C- Metal Ion Solutions

Soluble salts were used to prepare $1.0 \times 10^{-3} M$ metal ion stock solutions, by dissolving an appropriate amount of each metal salt in doubly distilled water, further dilutions from stock solution were done to prepare working solutions.

2.3 Instrumentation

Differential pulse adsorptive cathodic stripping voltammetry (DP-AdCSV) were carried out using EG&G voltammetric analyzer, model 264-B with a 303A static mercury dropping electrode, operated in the hanging mercury drop electrode (HMDE). The three-electrode system was completed by means of a platinum wire auxiliary electrode and an Ag/AgCl reference electrode. The pH measurements were carried out using HANNA pH- meter, model HI 8424.

2.4 Recommended Voltammetric Procedure

The voltammetric peaks were obtained using the differential pulse - adsorptive cathodic stripping voltammetric technique. Hence the technique is called differential-pulse adsorptive cathodic stripping

voltammetry (DP-AdCSV). The general procedure for obtaining voltammetric peaks was as follows:

10 ml of Britton - Robinson (BR) buffer solution (pH 3) was placed in the cell and purged with highly pure nitrogen for 4 minutes with stirring (to remove the dissolved oxygen that may interfere). A precocentration accumulation potential of 0.0V was applied to a fresh mercury drop for the required accumulation time while the solution was stirred. On the completion of accumulation time, the stirrer was switched off automatically. A negative potential scanning was initiated between 0.0 and -1.0V using a differential–pulse mode. After the blank voltammogram had been obtained, the adsorptive stripping was repeated with a new mercury drop after the addition of 0.1 ml dye sample containing an amount of dye in the range 0.2-10.5 ppm for Acid Orange7, 0.5-18.0 ppm for Acid Orange10 and 0.4-14.0 ppm for Acid Orange12, using the optimum conditions. For each dye a calibration plot of peak current against concentration was constructed and used for subsequent determination.

Part II: HPLC Analysis

2.5 Chemicals and Reagents

All solvents used are of HPLC grade.

2.6 Preparation of Solutions

A- Standard Dyes Solutions

Dyes standard solutions of 1000 ppm were prepared by dissolving proper amount of each dye in HPLC water. Working solutions were prepared by serial dilutions from the stock solution and buffered at pH 7.4.

B- Mobile Phase

Mobile phase consists of acetonitrile: water (60:40,V/V) containing 0.45 M N-Cetyl-N,N,N- trimethylammonium bromides (CTAB).

The mobile phase was prepared by dissolving proper amount of CTAB in acetonitrile : water (60:40, V/V). It was buffered at pH 7.2, degassed using JENCONS Scientific LTD sonicater, and filtered through 0.45 micrometer membrane to remove any particulate matter that might clog the system.

C- Simulated samples

Simulated samples were prepared by dissolving proper amounts of each dye in sewage water that was collected from the beginning of water flow in the east area of Nablus, and then filtered using 0.45 micrometer membrane to remove any particles that might clog the system.

2.7 Instrumentation

A. UV-2 UNICAM UV–Visible spectrophotometer was used for all spectrophotometric measurements. All measurements were carried out using quartz cells 10-mm at room temperature (20-25∘C).

B. SHIMADZU HPLC chromatograph that consists of one pump (model LC-10AT vp), manual sample injector (Rheodyne 7725i 20μL), 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 125 x 4 mm I.D Merck Lichrospher 100 RP C-18 (5μm) column fitted with guard column, flow rate of 0.5 ml min^{-1}and injection volume 20μL.

2.8 Recommended HPLC procedure

Prior to HPLC analyses the visible spectra of each standard dye was obtained to establish its maximum absorbance wavelength. Each dye was chromatographed individually, by injecting 20µL of 10 ppm of each dye at pH 7.4, to SHIMADZU HPLC chromatograph, and detected at its maximum wavelength, in order to determine the retention time. The calibration curves were constructed by plotting absorbance against concentration of dye and used for subsequent determination.

CHAPTER THREE

RESULTS and DISCUSSION USING

VOLTAMMETRIC METHODS

Chapter three
Results and Discussion Using
Voltammetric Method

Voltammetric analysis

Systematic studies of various experimental parameters that influence the differential pulse-adsorptive cathodic stripping voltammetric response were carried out in order to optimize the experimental conditions for the determination of dyes. These parameters include the effect of pH, accumulation potential, accumulation time, pulse amplitude, scan rate, current range, drop size, and interference by other ions.

3.1 Effect of pH

Following the voltammetric procedure (2.4) the differential pulse-adsorptive cathodic stripping voltammetric (DP-AdCSV) runs of 5.0×10^{-6}M of each of the colors under investigation (Acid Orange7, Acid Orange 10, and Acid Orange 12) were carried out over the pH range 2.6-11 using Britton–Robinson (BR) buffer.

It was found that for each dye the voltammograms consist of one peak through out the whole pH range studied.

Acid Orange7 (Figure 3.1.a) showed that the height of the reduction peak increased gradually in the pH range 2.6-3.0, then decreased markedly at pH greater than 3.0 to reach a minimum at pH 7.0. Any further increase in the pH affected gradual increase in the peak height until it reached a maximum value in the pH range 10.0-11.0.

Acid Orange10 (Figure 3.1.b) showed that the height of the reduction peak increased gradually in the pH range 2.6-3.0, then decreased markedly at pH greater than 3.0 to reach a minimum at pH 5. Any further increase in the pH affected gradual increase in the peak height until it reached a maximum value at pH 8.0, another gradual decrease in the peak height occurred at pH greater than 8.0 until it reached a minimum at pH 11.0.

Acid Orange12 (Figure 3.1.c) showed that the height of the reduction peak increased gradually in the pH range 2.6-3.0, then decreased gradually at pH greater than 3.0 to reach a minimum at pH 7. Any further increase in the pH affected gradual increase in the peak height until it reached a maximum value at pH 10.0, another gradual decrease in the peak height occurred at pH greater than 10.0 until it reached a minimum at pH 11.0.

From the above mentioned results the obtained peak corresponds to the reduction of azo group in each dye and formation of the products of aromatic amines. The mechanism of reduction of azo group had been reported by many authors (5,17and 18).

The position of the peak was shifted to more negative potential by increasing pH from 2.6 to 11.0 that indicates greater consuming of hydrogen ions in reduction process. The first peak at pH 3.0 is relatively high, sharp, and reproducible. Therefore pH 3.0 was selected as optimum pH for determination of the three dyes.

3.2 Cyclic voltammetric measurement

Formation of aromatic amines during the reduction of the three dyes (Acid Orange7, Acid Orange 10, and Acid Orange 12) was confirmed by studying the cyclic voltammetric behavior of $3.0 \times 10^{-6}M$ of the three dyes in Britton-Robinson buffer (pH 3.0), for 5 repetitive cyclic voltammograms. A clearly single cathodic peak without anodic response is observed, that indicates irreversible reduction process.

The peak current decreases sharply in the second cycle with little shift in the peak potential to more negative side. Results are shown in Figures 3.2.a, 3.2.b and 3.2.c, for Acid Orange7, Acid Orange 10, and Acid Orange 12 respectively.

3.3 Effect of scan rate

The effect of scan rate on the peak current of 5.0×10^{-7} M of the three studied dyes had been investigated on DC-AdCSV. A gradual increase in the peak current was associated with the increase of scan rate with little shift in the peak potential to more negative values indicating that the reduction is of adsorbed species. Results are shown in Figures 3.3.a*1* and 3.3.a*2* for Acid Orange 7, Figures 3.3.b*1* and 3.3.b*2* for Acid Orange 10, and Figures 3.3.c*1* and 3.3.c*2* for Acid Orange 12.

3.4 Effect of accumulation potential

The effect of changing the accumulation potential on the peak current of $1.0x10^{-6}$M of the three dyes was evaluated over potential range 0.0 to -1.0V. Slight decrease in the peak current was observed upon changing potential from 0.0 to - 0.1V, and then rapid drop in the peak current occurred upon going down to more negative values. Results are shown in Figures 3.4.a, 3.4.b and 3.4.c for Acid Orange7, Acid Orange10, and Acid Orange12 respectively. The accumulation potential of 0.0V offered the best sensitive and reproducible peak current and was used in all subsequent work.

3.5 Effect of accumulation time

Differential pulse adsorptive cathodic stripping voltammograms (DP-AdCSV) for (5.0×10^{-7}M and 1.0×10^{-6}M) of the three dyes (Acid Orange7, Acid Orange 10, and Acid Orange 12) were studied after different accumulation times. Plots of the resulting peak currents versus accumulation times had been done. At first current increases linearly with time and then starts to level off causing a steady current value. This is due to increase in the amount adsorbed at the electrode surface as accumulation time increases, until adsorption phenomenon occurs at longer accumulation time. The optimum accumulation times for maximum peak currents were found to be 120s for 5.0×10^{-7}M, and 60s for 1.0×10^{-6}M of each dye. Results for 5.0×10^{-7}M of the three dyes are shown in Figures 3.5.a*1* and 3.5.a*2* for Acid Orange 7, Figures 3.5.b*1* and 3.5.b*2* for Acid Orange 10 and Figures 3.5.c*1* and 3.5.c*2* for Acid Orange 12.

3.6 Effect of metal ions on dye determination

The effect of metal ions on the determination of 5.0×10^{-7}M of the three studied azo dyes using the proposed voltammetric method was studied. The obtained Results are listed in Tables 3.6.a, 3.6.b and 3.6.c for Acid Orange7, Acid Orange 10, and Acid Orange 12 respectively. All metal ions showed negative interferences in the determination of any of the studied dyes. The peak height was found to decrease gradually by increasing concentration of metal ions added .This might be due to hydrolysis of dye in present of metal ion.

Table (3.6.a)

Effect of metal ions on the DP-AdCSV voltammograms for 5.0×10^{-7}M Acid Orange 7 (peak current = 3.5µA). Conditions: accumulation potential 0.0V, accumulation time 60s, pulse amplitude 50mV, current range 5µA, scan rate 20mVs^{-1}, scanned from 0.0 to -1.0V. Note: (-) decreasing the peak height.

Metal Ions added	Peak Current (µA) at different concentration of metal ions added (M)			Error (%) at different concentrations of metal ions added		
	1×10^{-6}M	1×10^{-5}M	1×10^{-4}M	1×10^{-6}M	1×10^{-5}M	1×10^{-4}M
Fe^{+2}	3.40	3.31	3.12	-2.7	-5.4	-10.8
Fe^{+3}	3.40	3.35	3.25	-2.8	-4.2	-7.0
Cu^{+2}	3.40	3.35	3.26	-2.7	-4.1	-6.8
Cr^{+3}	3.39	3.34	3.29	-3.0	-4.5	-6.0
Mn^{+2}	3.40	3.36	3.22	-2.7	-4.0	-8.0
Ni^{+2}	3.40	3.30	3.20	-2.8	-5.7	-8.4
Co^{+2}	3.39	3.34	3.23	-3.0	-4.6	-7.6
Cl^{-1}	3.40	3.38	3.25	-2.8	-3.3	-7.0
NO_3^{-1}	3.39	3.29	3.01	-3.0	-6.0	-14.0
SO_4^{-2}	3.39	3.24	3.13	-3.0	-7.5	-10.4
$C_6H_5O_7^{-}$	3.27	3.22	3.18	-3.0	-4.6	-7.6

Table (3.6.b)
Effect of metal ions on the DP-AdCSV voltammograms for 5.0×10^{-7}M
Acid Orange 10 (peak current = 2.5µA). Other conditions: as listed in
Table (3.6.a)

Metal Ions added	Peak Currents (µA) at different concentrations of metal ions added (M)			Error (%) at different concentrations of metal ions added		
	1×10^{-6}M	1×10^{-5}M	1×10^{-4}M	1×10^{-6}M	1×10^{-5}M	1×10^{-4}M
Fe^{+2}	2.35	2.25	2.15	-6.0	-10.0	-14.0
Fe^{+3}	2.40	2.25	2.00	-4.0	-10.0	-20.0
Cu^{+2}	2.41	2.33	2.20	-3.4	-6.8	-12.0
Cr^{+3}	2.36	2.27	2.05	-5.4	-9.0	-18.0
Mn^{+2}	2.38	2.32	2.14	-4.7	-7.1	-14.2
Ni^{+2}	2.23	2.11	1.78	-11.0	-15.0	-28.8
Co^{+2}	2.30	2.15	2.00	-5.0	-10.0	-12.5
Cl^{-1}	2.31	2.27	2.08	-7.4	-9.2	-16.6
NO_3^{-1}	2.35	2.28	2.00	-5.7	-8.5	-20.0
SO_4^{-2}	2.25	2.21	1.75	-7.7	-11.5	-30.0
$C_6H_5O_7^{-}$	2.43	2.36	2.08	-2.7	-5.5	-16.6

Table (3.6.c)
Effect of metal ions on the DP-AdCSV voltammograms for 5.0×10^{-7}M
Acid Orange 12 (peak current $= 2.1\mu$A). Other conditions: as listed in
Table (3.6.b)

Metal Ions added	Peak Currents (μA) at different concentrations of metal ions added (M)			Error (%) at different concentrations of metal ions added		
	1×10^{-6}M	1×10^{-5}M	1×10^{-4}M	1×10^{-6}M	1×10^{-5}M	1×10^{-4}M
Fe^{+2}	2.00	1.91	1.66	-4.3	-8.7	-21.0
Fe^{+3}	1.99	1.94	1.78	-5.0	-7.5	-15.0
Cu^{+2}	2.05	2.00	1.97	-2.2	-4.5	-6.3
Cr^{+3}	1.98	1.91	1.80	-5.7	-8.6	-14.0
Mn^{+2}	2.01	1.98	1.85	-3.8	-5.7	-11.5
Ni^{+2}	1.89	1.83	1.68	-10.0	-12.50	-20.00
Co^{+2}	1.99	1.89	1.83	-5.00	-10.00	-12.50
Cl^{-1}	1.99	1.95	1.74	-4.80	-7.30	-17.0
NO_3^{-1}	2.03	1.97	1.62	-3.0	-6.0	-23.0
SO_4^{-2}	1.98	1.92	1.75	-5.5	-8.5	-16.6
$C_6H_5O_7^{-}$	1.98	1.94	1.75	-5.5	-7.4	-16.6

3.7 Effect of Purging Time

The effect of purging time was studied for 1.0×10^{-6}M of the three dyes (Acid Orange 7, Acid Orange 10, and Acid Orange 12) for 0 -8 min. 4 minutes were selected as purging time in our work because it gave suitable and reproducible peak current.

3.8 Effect of drop size

The effect of drop size on the peak current was studied for 1.0×10^{-6}M of the three dyes (Acid Orange7, Acid Orange 10, and Acid Orange 12). In our work medium drop size was selected since it gave suitable and reproducible peak current.

3.9 Effect of pulse amplitude

The effect of pulse amplitude on the peak current was studied for 5.0×10^{-7}M of the three dyes (Acid Orange7, Acid Orange 10, and Acid Orange 12). Peak current was found to increase as pulse amplitude increased. In our work 25 mV and 50 mV were mostly used because of giving suitable and reproducible peak current.

3.10 Calibration curve

The applicability of voltammetric method as an analytical technique for determination of the studied dyes (Acid Orange 7, Acid Orange 10, and Acid Orange 12) had been tested under the optimum conditions. The recommended conditions for DP-AdCSV determination of the studied dyes were selected and presented in Table 3.10.

Under the recommended conditions, the height of the DP-AdCSV peak was found to increase gradually with increasing concentration of dye. For each dye a calibration curve was constructed by plotting the peak current vs. concentration. The reproducibility of the method was checked on solutions containing 5.0×10^{-8}M and 1.0×10^{-7}M of each dye (5 measurements each).

Typical voltammograms showing successive enhancements of peak current with increasing Acid Orange 7 concentration are shown in Figure 3.10.a1, calibration curve was linear over the range 1.0×10^{-8}M-3.0×10^{-7}M as shown in Figure 3.10.a2, with detection limit of 5.0×10^{-9}M and average relative standard deviation (RSD) of 1.96%.

Typical voltammograms showing successive enhancements of peak current with increasing acid orange 10 concentration are shown in

Figure 3.10.b*1*, calibration curve was linear over the range 2.0×10^{-8}M-4.0×10^{-7}M as shown in Figure 3.10.b*2* with detection limit of 1.0×10^{-8}M and average relative standard deviation (RSD) of 2.10%.

Typical voltammograms showing successive enhancements of peak current with increasing acid orange 12 concentration are shown in Figure 3.10.c*1*, calibration curve was linear over the range 2.0×10^{-8}M-4.0×10^{-7}M as shown in Figure 3.10.c*2*, with detection limit of 1.0×10^{-8}M and average relative standard deviation (RSD) of 2.15%.

 The optimum conditions for voltammetric determination of the three dyes as well as the characteristics of calibration curves are summarized in Table 3.10.

Table (3.10)
Characteristics of calibration curves and optimum conditions for voltammetric determination of Acid Orange 7, Acid Orange 10, and Acid Orange 12

Parameters	Acid Orange 7	Acid Orange 10	Acid Orange 12
Optimum pH	3.0	3.0	3.0
Accumulation potential (V)	0.0	0.0	0.0
Accumulation time (s)	120.0	120.0	120.0
Pulse Amplitude (mV)	50.0	50.0	50.0
Scan Rate (mVs^{-1})	20.0	20.0	20.0
Drop size	Medium	Medium	Medium
Current range(μA)	5.0	5.0	5.0
Linear conc. Range (ppm)	0.004- 0.105	0.009- 0.180	0.007- 0.140
Detection limit (ppm)	0.002	0.005	0.004
Average RSD %	1.96	2.10	2.15

3.11 Simultaneous determination of three dyes

According to the obtained optimum conditions for DP-AdCSV method for determination of the three studied dyes. It can be seen that the peak potentials are 0.24V, 0.25V, and 0.26V for Acid Orange7, Acid Orange 10, and Acid Orange 12 respectively. The resolution of the peak potential is not good enough to determine any of the three dyes in presence of the other two dyes. The similarity of the three dyes in their voltammetric behaviour is due to the close similarity in their chemical properties and structural formula.

CHAPTER FOUR

RESULTS and DISCUSSION USING

HPLC Analysis

Chapter Four
Results and discussions using
HPLC Method

HPLC Analysis

4.1 Absorption Spectra

The absorption spectra of 10 ppm of the three dyes (Acid Orange7, Acid Orange 10 and Acid Orange 12) were studied in the wavelength range (400-800) nm at pH 7.4.

For each dye the maximum absorbance was selected for the HPLC analysis, these were, 477nm for Acid Orange 10, and 485nm for Acid Orange7 and Acid Orange 12. The obtained results are presented in Figures 4.1.a, 4.1.b and 4.1.c for Acid Orange 7, Acid Orange 10 and Acid Orange 12 respectively. Comparison between the spectra of the three dyes is presented in Figure 4.1.d.

4.2 Retention time

HPLC Analysis was applied for determination of the retention times of the three dyes. Standard solution of 10 ppm of each dye at pH 7.4 was chromatographed individually and detected at its maximum wavelength, and retention times were monitored. The obtained results presented in Figures 4.2.a, 4.2.b and 4.2.c, showed retention times of 2.8 min, 4.8 min, and 3.1 min for Acid Orange 7, Acid Orange 10 and Acid Orange 12, respectively. The closed readings in retention times for Acid Orange 7 and Acid Orange 12 are due to the closed structure and polarity in the two dyes, while Acid Orange 10 possessing two sulphonic acid groups has the longest retention time.

4.3 Calibration curves

The applicability of HPLC method as an analytical technique for determination of the studied dyes (Acid Orange7, Acid Orange 10 and Acid Orange 12) had been tested under the optimum conditions.

The recommended conditions for HPLC determination of the three dyes were selected and presented in Table 4.3.

Under the recommended conditions, the calibration curves were constructed by plotting the absorbance vs. concentration of each dye. The reproducibility of the method was checked on solutions containing 1ppm of each dye (5 measurements each).

Calibration curve for Acid Orange7 was linear over the range 0.05-4.0 ppm as shown in Figure 4.3.a, with detection limit of 0.03 ppm and relative standard deviations of 3.8%.

Calibration curve for Acid Orange10 was linear over the range 0.1-4.0 ppm as shown in Figure 4.3.b with detection limit of 0.05 ppm and relative standard deviations of 4.1%.

Calibration curve for Acid Orange12 was linear over the range 0.1-4.0 ppm as shown in Figure 4.3.c with detection limit of 0.05 ppm and relative standard deviations of 4.2%.

The optimum conditions for HPLC determination of the three dyes as

well as the characteristics of calibration curves are summarized in

Table 4.3

Table (4.3)
Characteristics of calibration curves and optimum conditions for
HPLC determination of Acid Orange 7, Acid Orange 10, and Acid
Orange 12

Parameter	Acid Orange 7	Acid Orange 10	Acid Orange 12
Mobile phase composition acetonitrile: water (v/v) containing 0.45M CTAB	60 :40	60 :40	60 :40
Separation coloum	RP C18 coloum 125mm,5μm i.d	RP C18 coloum 125mm,5μm i.d	RP C18 coloum 125mm,5μm i.d
Flow rate (ml min^{-1})	0.5	0.5	0.5
Detection wavelength (nm)	485	477	485
Injection volume (μL)	20	20	20
pH	7.4	7.4	7.4
Retention time (min)	2.8	4.8	3.1
Range of linearity (ppm)	0.05-4.0	0.1 -4.0	0.1 -4.0
Detection limit (ppm)	0.03	0.05	0.05
RSD (%)	3.8	4.1	4.2

4.4 Samples Analysis

In order to study the behaviour of the three dyes (Acid Orange 7, Acid Orange 10, and Acid Orange 12) in sewage water, two standards of exactly the same concentrations of each dye were prepared; the first was dissolved in deionised water and the second in sewage water. Both standards were injected to the HPLC and the absorbance was measured at the corresponding retention time.

Comparison between the absorbance of dye in sewage water with that in deionised water showed that the absorbance was less in sewage water than that of deionised water. Results are listed in Tables 4.4.a, 4.4.b and 4.4.c for Acid Orange 7, Acid Orange 10 and Acid Orange 12 respectively. The reduction in the absorbance might be due to the hydrolysis of dyes by sewage water components of metals and detergents.

Table (4.4.a)
Comparison of HPLC analysis for determination of Acid Orange 7 in sewage water and deionised water Note: (-) decreasing the peak height.

Concentrations of dyes	Absorbance in standard solution (mAU)	Absorbance in sewage water (mAU)	% Deviation
0.4	1.64	1.10	-32.92
0.8	3.21	1.85	-42.36
2.0	8.15	4.41	-45.88

Table (4.4.b)
Comparison of HPLC analysis for determination of Acid Orange 10 sewage water and deionised water Note: (-) decreasing the peak height.

Concentrations of dyes	Absorbance in standard solution (mAU)	Absorbance in sewage water (mAU)	% Deviation
0.4	0.99	0.75	-24.24
0.8	1.85	1.2	-35.13
2.0	4.86	2.8	-42.38

Table (4.4.c)
Comparison of HPLC analysis for determination of Acid Orange 12 sewage water and deionised water Note: (-) decreasing the peak height.

Concentrations of dyes	Absorbance in standard solution (mAU)	Absorbance in sewage water (mAU)	% Deviation
0.4	0.73	0.51	-30.14
0.8	1.35	0.91	-32.59
2.0	3.65	1.86	-49.04

4.5 Simultaneous determination of three dyes

Quantitave determination of the three studied using HPLC method is based on differences in retention times 2.8 min, 4.8 min, and 3.1 min for Acid Orange 7, Acid Orange 10, and Acid Orange 12 respectively.

From the above mentioned results, quantitave determination of the two dyes (Acid Orange 7 and Acid Orange 12) in presence of each other is not possible due to the closed readings in retention times. But determination of the two dyes (Acid Orange 7 and Acid Orange 10) or (Acid Orange 10 and Acid Orange 12) in presence of each other is possible due to significant difference in retention times. Separation of 6ppm mixture of Acid Orange 7 and Acid Orange 10 is presented in Fig. 4.5.

However the resolution could be improved by using longer separation coloum (i.e. 250 mm) that will allow determination of Acid Orange 7 and Acid Orange 12, in presence of each other.

CHAPTER FIVE

REDUCING DEGRADATION OF AZO DYES

BY ZERO VALANET IRON

IN AQUEOUS SOLUTION

CHAPTER Five

Reducing degradation of azo dyes by zero –valent iron in aqueous solution

The degradation kinetics of the mono azo dyes (Acid Orange 7, Acid Orange 10, and Acid Orange 12) by zero–valent iron in aqueous - solutions were studied at pH 7.4, 2g Iron powder was added to 100 ml of 30 ppm standard solution of each dye, with shaking. At intervals, 3ml was removed and subjected to UV-VIS spectrum scanning using the maximum visible absorption wavelengths of the tested dye, (477nm for Acid Orange 10, 485nm for Acid Orange 7 and Acid Orange 12). The visible absorbance of each degradation solution decreased during the degradation process as shown in Figures 5.a, 5.b, and 5.c, for Acid Orange7, Acid Orange 10 and Acid Orange 12, respectively.

This might be explained by considering the breaking down of azo bond and formation of the products of aromatic amines as shown in Figures 5, where the azo group (-N=N-) of the dye is the basic reason for its visible color (22).

The degradation rates were calculated by the disappearing rates of the dyes. The disappearing of each dye fits well with zero order reaction with rate constants of 0.0042, 0.0015 and 0.0025 mmol/L.min and half-lives of 10, 22 and 17min for Acid Orange7, Acid Orange 10, and Acid Orange 12 respectively, which indicates effective degradation of the studied azo dyes by zero–valent iron in aqueous solution.

78

CHAPTER SIX

COMPARATIVE STUDY

Chapter Six
Comparative study

Comparison of the voltammetric and HPLC methods with other published methods for quantitave determination of textile dyes

Table (6) summarizes the results obtained for the determination of the three studied azo dyes (Acid Orange7, Acid Orange 10, and Acid Orange 12) using the proposed voltammetric and HPLC methods as well as other reported methods.

It was found that the suggested methods compete well with most of other methods in sensitivity and precision and are suitable for routine analysis of textile dyes. The voltammetric method was found to be the most sensitive method with the lowest detection limits and relative standard deviations. These advantages make the proposed voltammetric method based on adsorptive cathodic stripping analysis at (HMDE), more suitable for trace determination of the three dyes (Acid Orange7, Acid Orange 10, and Acid Orange 12)

Table (6)

Comparison of the voltammetric and HPLC methods in present work as well as with other published methods for determination of the three dyes (Acid Orange 7, Acid Orange 10, and Acid Orange 12).

Methods	Dyes	Detection limit ppm	Linear range ppm	RSD %	Ref.
Voltammetric	Acid orange7	0.002	0.0035 - 0.105	1.96	Present work
	Acid orange 10	0.005	0.009 - 0.180	2.10	Present work
	Acid orange 12	0.004	0.007- 0.140	2.15	Present work
HPLC	Acid orange 7	0.03	0.05 - 4.0	3.8	Present work
	Acid orange 7	0.01	0.02 - 0.36	-	40
	Acid orange 10	0.05	0.10 - 4.0	4.1	Present work
	Acid orange 12	0.05	0.10 - 4.0	4.2	Present work
	Acid orange 12	0.02	0.04 - 0.46	-	40
Capillary electrophoresis	Acid orange 7	0.90	-	-	39
	Acid orange 12	1.82	-		39

References

1) A. Rahim H.M.Yusoff., et al. Tlanta, 47, 1998, (797-801).

2) Abollino o, Aceto M., Sarzanini C, Mentasti E, Electroanalysis (NY). Aug 1999, 11(12), (870-878).

3) AnlikerR., Clarke E.A.,Moser P.,Chemosphere. 10,1981, (263-274).

4) Ballantyne B., Hum. Exp. Toxicol. 13, 1994, (694-699).

5) Barek Jiri, Fogg Arnold G., Moreira Josino C, Zanoni M.V.B., Analytical Chimica Acta. 320, 1996 (31-42).

6) Barros AA, Rodrigues JAM, Electroanalysis (NY). Apr 1991, 3(3) (243-245).

7) Baughman G.L., Perenich T.A., Environ. Toxicol.Chem.7, 1988, (183-199).

8) Bhongade SL, Kasture AV, Talanta. Oct 1993, 40(10), (1525-1528).

9) Blatny Pavel, Fischer Christian-Herbert, Rizzi Andreas, Kenndler Ernst , Journal of Chromatography A, 717, 1995, (157-166).

10) Buckley C.A., Wat.Sci.Tech.Vol.25, No.10, 1992, (203-209).

11) Clarke E.A., Anliker R., 1980. Organic dyes and Pigments. In the Hand book of Environmental Chemistry.Vol.3, partA. Anthropogenic Compounds, ed.O, Hutzinger, Springer, Heidelberg (181-215).

12) Coughlin Michael F., Kinkle Brain K., Bishop Paul L. Chemosphere. 46 ,2002, (11-19).

13) Dipple A., Bigger C.A.H, Mutat.Res.259, 1991, (263-267).

14) Eastin W.C.,Elwell M.R.,Grumbien S.,yuan j.H.,Toxicol. Environ. Health. 48, 1996, (197-213).

15) Elsine L. Appleton, A Nickel-Iron wall against contaminated Groundwater, Environ. Sci Technol. 30, 1996, (536-539).

16) Fan J, shen XJ, Wang JJ, Anal-Chim-Acta. 25 May 1998; 364 (1-3), (275-280).

17) Fogg Arnold G., Rahim A.; Yusoff H.M., Ahmad, Rahmalan Talanta 44,1997 (125-129).

18) Fogg Arnold G., Zanoni M.V.B., Rahim A., Yusoff H.M., Ahmad Rahmalan, Analytical Chimica Acta. 362, 1998 (235-240).

19) Gorensek Marija. Dyes and Pigments. 40, 1999 (225- 233).

20) Hansa,-A;Pillay,-V.L.;Buckkley,-C.A, Wat. Sci Tech. Vol. 39, No 10-11, 1999, PP. (169-172).

21) Jaskot R.H., Costa ,D.L., Fundam. Appl. Toxicol. 22, 1994, (103- 112)

22) Jiasheng Cao, Liping Wei, Qingguo Huang Liansheng Wang Shuokui Han, Chemosphere, Vol.38, No.3, 1999, (565-571).

23) Jiménez M.M. Dávila, González M.P. Elizalde, González A. Gutiérrez, Cid A.A. Peláez, Journal of Chromatography A, 889 2000, (253-259).

24) Ince, N.H. , Water Res. 33(1999) 1080.

25) Nassar M.M., Magdy Y.H., Chem. Eng.J.66 (1997) 223.

26) Ng H.L., Araki S., Tanigawa T, Sakura S., Arch. Environ. Health
. 50, 1995(109-196).

27) Nikulina G.L., Deveikes D.N, Pyshnov G., Meb. Tr. Prom. Ekol.
6, 1995 (25-28).

28) Przybojewska B., Mutat. Res. 367, 1996 (93-97).

29) Rindle E., Troll W.J., Natl. Cancer Inst. 55 (1975) 181.

30) Riu J., Schönsee I., Barcelò D., Trends in analytical chemistry,vol.
16 , No.7, 1997, (405-418).

31) Riu J., Schönsee I., Barcelò D., Journal of Mass Spectrometry 33,
1998 (653 –663).

32) Sankar DG,Sastry CSP; Reddy MN, Aruna M, Indian- Drugs. Apr
1989; 26 (7): 348-351.

33) Sastry,-csp; Aruna,-M, Reddy, MN; Sanker,-DG, Indian-J-Pharm-
Sci.Mar-Apr 1988; 50(2):140-142

34) Sook- Hee Bae., et al. Dyes and Pigments. Vol. 34, No. 1, 1997
pp. (25-35).

35) Spadaro J.T., Isabelle L., Renganathan V., Environ.Sci.Technol,
Vol. 28, 1994, (1389-1393).

36) Straub R, Voyksner D, Keever JT, J-Chromatogr.25Dec 1992,
627(1-2), (173-186).

37) Su J.C., Horton J.J, Australas, J.Dermatol. 39 (1), 1998, (48-49).

38) Urquiza M. Pèrez, Bertrand J.L, Journal of Chromatography A, 917
2001, (331-336).

39)Urquiza M. Pèrez., Ferrer R, Beltran J.L.,Journal of Chromatography
A, 883 , 2000, (277-283).

40) Urquiza M. pérez, Prat M.D., Beltrán J.L., journal of Chromatography A, 871 , 2000, (227-234).

41) Walter Z. Tang and Huren An, UV/TiO$_2$ Photo catalytic Oxidation of Commercial Dyes in Aqueous Solutions, Chemosphere-31: 4157-4170, (1995).

42) Weatherall IL, J-Liq-Chromatogr. Jun 1991, 14(10), (1903-1912).

43) Weber E.J., Adams R.L., Environ. Sci.Technol. Vol. 29, 1995, (1163-1170).

44) Weber E.J., Stickney V.C., Water Research WATRAG, 1993, Vol. 27, No.1, (63-67).

45) Zamor,-Patricio Peralta; Kunz, -Airton;Natgatas,- Noemi; Poppi,- Ronei J. ,Talanta 47, 1998 (77-84).

الملخص :

تم في هذا البحث إيجاد طرق جديدة بسيطة وحساسة في تحديد تراكيز ضئيلة جدا من ثلاثة أنواع من الأصباغ البرتقالية (Acid Orange7, Acid Orange10, Acid Orange12) عن طريق استخدام طريقتين للتحليل، طريقة الانتزاع ألمهبطي الفولتمتري ذات النبض التفاضلي -DP) (AdCSV، وطريقة الكروموتوغرافيا السائلة عالية الأداء (HPLC) . خلال هذا البحث تم دراسة تأثير مختلف العوامل المخبرية على حساسية كل من الطريقتين للتوصل إلى أفضل الظروف لاعتمادها في عملية التحليل .

فطريقة الانتزاع ألمهبطي الفولتمتري اعتمدت على اختزال الأصباغ على مهبط الزئبق المعلق ومن ثم قياس فرق الجهد. لقد تمت دراسة الظروف النموذجية من حيث درجة الحموضة، الجهد التجميعي، الوقت التجميعي اللازم و غيرها من المتغيرات التي تم استخدامها للتوصل إلى منحنى قياسي ذو علاقة خطية محصورة بين:

[(0.004-0.105) mgL^{-1}, (0.009-0.180) mgL^{-1}, (0.007-0.140) mgL^{-1}] ، وبدرجة انحراف معياري نسبي:

(% 2.15 2.10%, 1.96%) للأصباغ البرتقالية:

(Acid Orange7, Acid Orange10, Acid Orange12) على التوالي.

أما طريقة الكرو موتوغرافيا السائلة عالية الأداء (HPLC) فلقد تم تطبيقها باستخدام الظروف النموذجية.

وقـــد تبـــين أن أعلـــى امتصـــاص لهـــذه الأصـــباغ البرتقاليـــة عنــد طــول موجـــة (485nm,477nm,485nm) و كـان الـزمن الـذي تسـتغرقه هـذه الأصـباغ للانتقـال عبـر عمـود الفصل (2.8 min, 4.8 min, 3.1 min) للاصباغ البرتقالية :

(acid orange7, acid orange10, acid orange12) على التوالي .

باستخدام الظروف النموذجية تم التوصل إلى منحنى قياسي ذو علاقة خطية محصورة مـا بيـن:
(0.05- 4.00) mgL^{-1}, (0.10- 4.00) mgL^{-1}, (0.10- 4.00) mgL^{-1}

وبدرجة انحراف معياري يساوي:

(3.8%, 4.1% , %, 4.2%) للاصباغ البرتقالية:

(Acid Orange7, Acid Orange10, Acid Orange12)على التوالي .

ايضا لقد تم دراسة تفكك الأصباغ المذكورة باستخدام مسحوق معدن الحديد في محلول سائل و لقد وجد ان معدل تفكك الاصباغ فعالأ ، حيث حصل انخفاض في معدل الامتصاص الضوئي للأصباغ المفككة بسبب كسر الرابطة و إنتاج المركبات الأمينية التي يسهل تفككها بواسطة الكائنات الحية الدقيقة في الطبيعة.