

Accepted Manuscript

A comparison between digital camera and spectrophotometer for sensitive and selective kinetic determination of brilliant green in wastewaters

Saeed Damirchi, Maliheh Ahmadi-Kalateh Khooni, Tahereh Heidari, Zarrin Es'haghi, Mahmoud Chamsaz



PII: S1386-1425(18)30782-0
DOI: doi:[10.1016/j.saa.2018.08.011](https://doi.org/10.1016/j.saa.2018.08.011)
Reference: SAA 16386

To appear in: *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*

Received date: 10 May 2018
Revised date: 29 July 2018
Accepted date: 4 August 2018

Please cite this article as: Saeed Damirchi, Maliheh Ahmadi-Kalateh Khooni, Tahereh Heidari, Zarrin Es'haghi, Mahmoud Chamsaz , A comparison between digital camera and spectrophotometer for sensitive and selective kinetic determination of brilliant green in wastewaters. Saa (2018), doi:[10.1016/j.saa.2018.08.011](https://doi.org/10.1016/j.saa.2018.08.011)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

**A comparison between Digital camera and Spectrophotometer for
Sensitive and selective kinetic determination of Brilliant Green in
Wastewaters**

Saeed Damirchi^a, Maliheh Ahmadi-Kalateh Khooni^b, Tahereh Heidari^{a,*}, Zarrin

Es'haghi^b, Mahmoud Chamsaz^a

^a *Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad,
Mashhad, Iran*

^b *Department of Chemistry, Faculty of Sciences, Payame Noor University, PO Box
19395-3697, Tehran, Iran*

**E-mail: taherehheidari@um.ac.ir*

Abstract

In this study, a simple and novel kinetic spectrophotometric method has been proposed for the sensitive and highly selective determination of Brilliant Green. The method is based on the interaction of Brilliant Green with Triton X-100 in micellar media at room temperature. As a result of this interaction, the peak wavelength (625nm) is gradually shifted toward longer wavelength region (634 nm) and more intensive hyper chromic effect has been seen. As well as, variations in the red, blue and green (RGB) component of the images as a function of time were observed. The kinetic interaction of Brilliant Green with Triton X-100 was recorded, using UV-Vis Spectrophotometer-diode array detector and a digital camera. The fixed-time method was used for the construction of a calibration curves. Brilliant Green can be measured in the range of 1.0 to 12.0 mg L⁻¹

and 1.0 to 10.0 mg L⁻¹ with the detection limit of 0.047 mg L⁻¹ and 0.037 mg L⁻¹ using spectrophotometer and digital camera, respectively. The proposed method has been successfully used to determine Brilliant Green in some wastewaters such as textile dye effluent and goldfish farming water in the presence of some triphenylmethane dyes as the interferences.

Key words: Kinetic colorimetric; spectrophotometry; Digital camera; Brilliant Green; Triton X-100.

1. Introduction

Triphenylmethane (TPM) dyes, as an important class of commercial dyes, have various applications in industries. In textile industry, they are used as sensitizers for photoconductivity and in medicine they act as antibacterial and sterilization agents during blood transfusions [1-5]. The TPM dyes are characterized by intense colors, which include vivid red, blue, green and violet. Due to the wide range of applications, TPM dyes are often found in wastewaters [3, 4]. It has been shown that dyes of this family can act as a tumor promoter [6, 7]. Among the TPM dyes, Brilliant Green (BG) is widely used (usually with other TPM dyes, such as Malachite Green (MG) and Crystal Violet (CV)) around the world in the textile industry to color silk, wool, leather, cotton and paper. It is also widely used in fish farming industry because of its broad anti-microbial, anti-parasitic and anti-fungal spectrum, high efficiency in the prevention and treatment of certain fish diseases and low cost [8]. BG is toxic with mutagenic and carcinogenic effects that can influence both aquatic biota and humans [9-12]. Because of its carcinogenic properties, BG is not authorized by the European Union and the US Food and Drug Administration (FDA) [13]. Thus, developing a sensitive, simple,

inexpensive and reliable method is necessary for determining BG in environmental samples such as wastewaters.

Several methods have been proposed for this purpose, including liquid chromatography–mass spectrometry [14], micelle-mediated phase separation method for pre-concentration of Brilliant Green using spectrophotometric determination [8] conductometric method [15], indirect competitive enzyme-linked immunosorbent assay [16], derivative spectrophotometry [17] and in 2011, we developed a new design of hollow fiber solid/liquid phase micro extraction (HF-SLPME) for determining the trace amount of BG residues in water fish ponds [18]. Some of these methods are often non-selective and require complicated pretreatment procedures, which prompted us to develop an alternative method with simple pretreatments for the determination of BG in case of its coexistence with some chromophores interference in complex mixture.

Kinetic methods have certain advantages such as sensitivity, selectivity and interference elimination, which can affect direct spectrophotometric methods [19-24]. There is still a paucity of literature on the analytical methods based on kinetic analysis of BG.

In recent years, popular communications and IT equipment (mobile phones, digital cameras, scanners, webcams, etc.) have been developed as detection devices for chemical analysis [25-33]. A digital image consists of many pixels which each pixel have being formed by three basic colors (Red, Green and Blue), that are abbreviated as “RGB”. The colorimetric analysis could be done by determining RGB values of the digital photo image as the analytical signal, instead of absorbance in the traditional UV-vis spectrophotometry, which provide more precise and accurate results [32]. Image processing software, such as Image J and Matlab integrated with image processing tool box can easily extract the intensity of basic color (RGB) for desired pixels.

In this paper, a novel, simple, selective, sensitive, cost-effective and rapid kinetic method based on the spectrophotometric and colorimetric analysis of BG has been developed. The proposed method is based on the interaction of BG with Triton X-100 . A fixed-time method was used for constructing calibration curves and determining BG in some wastewaters with complex matrices which contains other TPM dyes as the unknown interferences.

2. Experimental

2.1. Apparatus

All measurements were carried out at room temperature (about 25⁰C) and quartz cell with 1 cm in diameter was used. Absorbance measurements were carried out on a Cecile 7200 UV–Vis double beam spectrophotometer. All reflectance colorimetric measurements were performed with a Canon A2400 IS digital camera in a homemade light box. The light box (Fig. 1) [34] has been made from a polystyrene foam box. Dimensions of the box (width × length × height) are as follow: outside: 18 × 28 × 23cm and inside: 17 × 27.5 × 22.5cm. The box interior has been covered with two layers of white paper to enhance image quality and reduce noise. Three red LEDs, as the light sources, have been mounted on the box wall on the top of camera. The digital camera was put in front of the center of the light box. Image J- software was used for image processing.

A digital pH meter (Model 744, Metrohm, Switzerland) was used for all pH measurements.

2.2. Reagents

All chemicals used in the experiments were of analytical grade and applied without further purification. All solutions were prepared with deionized water. Stock solutions of 100 mgL^{-1} of BG (Darmstath, Germany) was prepared by dissolving 0.0100 gr of BG in 20 mL of acetic-acetate buffer solution with pH 4 (1.0 molL^{-1}) and diluting it to 100 mL in a volumetric flask and was stored in a plastic amber bottle at a temperature of 4°C protected from light [9]. Working solutions were prepared by appropriate dilution of stock solution using 0.1 molL^{-1} of acetic-acetate buffer solution (pH 4). Buffer 1 molL^{-1} was prepared by adding 1 molL^{-1} of sodium hydroxide (Merck) to acetic acid (1 molL^{-1}), and a pH meter was used to adjust pH to 4. A solution of 170 mmolL^{-1} of Triton X-100 was prepared by dissolving 10 mL of Triton X-100 (Aldrich) in water using hot water bath and diluting it to 100 mL in a volumetric flask.

Potassium chloride solution (2.5 molL^{-1}) was made by dissolving 46.5938 g KCl (Merck) in water and diluting it to 250mL in a volumetric flask.

2.3. Procedure

An appropriate volume of BG stock was added to a 10 mL volumetric flask. The solution was diluted using 0.1 molL^{-1} of acetic-acetate buffer solution (pH 4). For each measurement, 2mL of the above solution was transferred to a quartz cell and placed in the cell holder in the spectrophotometer. Room Temperature (about 25°C) was selected as the working temperature. The ambient temperature could help the prompt and convenient implementation of the study. The variations of the absorbance versus time were measured immediately after adding and mixing of 1.0 mL of Triton X-100 (17

mmolL⁻¹) at 634 nm with time intervals equal 0.5 second. The absorbance measurement was stopped automatically after 20 min.

For reflectance colorimetric measurements using the digital camera the procedure was same as the spectrophotometric measurements. Because of fixed time method was proposed in this kinetic study, the images were recorded in the initial time and after 20 min. Quantitative changes of red color intensity between the sample and the blank was calculated using Image J- software.

2.4. Preparation of real sample

The fish aquarium wastewater was obtained from a fish store in Mashhad, Iran. We diluted 15 mL of this sample and 2 mL of potassium chloride (2.5 molL⁻¹) to 50 mL using 0.1 molL⁻¹ of acetic-acetate buffer solution (pH 4).

Textile wastewater was obtained from the textile factories, around the city of Mashhad. We then diluted 2.5 mL of this sample and 2 mL of potassium chloride (2.5 molL⁻¹) to 50 mL using 0.1 molL⁻¹ of acetic-acetate buffer solution (pH 4). In the first step, the impurities of all waste waters were removed by a Whatman ® filter paper, grade 40, and the filter paper was washed repeatedly with deionized water. The samples were then immediately used for experiments.

3. Results and discussion

It was observed that the color intensity of BG increased gradually in the presence of Triton X-100. It seemed that nonionic surfactant Triton X-100 interacted with BG - the cationic dye that carries a positive charge [18]- when its concentration in aqueous media was well above critical micellar concentration (0.22 to 0.24 mmolL⁻¹).

The rate of this interaction was amplified by increasing BG concentration. This interaction suggested that the absorption spectra and RGB of BG after adding of Triton X-100 were a variable of time.

As shown in Fig. 2a red shift in the absorption maxima has been happened and the absorbance (at $\lambda_{\max(\text{in micellar media})} = 634 \text{ nm}$) was increasing along with time (Fig. 3).

When the concentration of nonionic surfactant such as TX-100 is reached to the CMC of the respective surfactants, micellar aggregates are formed. The red shift of the λ_{\max} indicates incorporation of the TPM cationic dyes(in this case BG) in the nonionic micelles, the main driving force being hydrophobic interaction between the two moieties. To give an outline of, changes in the λ_{\max} for all of TMP dyes, which were studied in this paper, and intensity of the 634 nm for BG + reflect alteration of the microscopic environment available to the dye after incorporation within the nonionic micellar aggregates[35].

The following optimizations were undertaken to achieve maximum sensitivity and the greatest linear dynamic range.

3.1 Effect of Triton X-100 concentration

Triton X-100 concentration is an important analytical parameter because the rate of interaction between BG (Equation 1) and Triton X-100 is dependent on Triton X-100 concentration.

$$\text{Rate} = k[\text{BG}]^n[\text{TX} - 100]^m \quad (\text{Eq. 1})$$

Where k is the constant rate, [BG] is the concentration of Brilliant Green (molL^{-1}), [TX-100] is the concentration of Triton X-100 micelles, and n and m are the partial order of reaction with respect to BG and Triton X-100 respectively.

As shown in Fig. 4a, the rate of the interaction rises with an increase in Triton X-100 micelles concentration. Unfortunately, at greater concentration, fast measuring of initial absorbance is needed, which is highly difficult and unrepeatable.

To select the optimum Triton X-100 concentration, ΔA ($\Delta A = A_{20\text{min}} - A_{0\text{min}}$; at $\lambda_{\text{max}} = 634$ nm, where A is absorbance) was calculated in the range of 1.7 to 51 mmolL^{-1} of Triton X-100 (Fig. 4b). It remained almost constant at concentrations greater than 8.5 mmolL^{-1} . Therefore, 17.0 mmol L^{-1} was selected as the optimum concentration of Triton X-100 for further studies.

3.2 Effect of pH

The effect of pH was studied in the range of 3.5-6.0, by an acetic-acetate buffer [30] to achieve the desired pH. According to the results presented in Fig. 5, the maximum ΔA is observed at pH 4.0. At higher or lower pH BG renders colorless [8, 18, 37]. Therefore pH 4.0 was selected as the optimum pH for future works. The effect of buffer concentration was also studied in the range of 0.05-0.4 molL^{-1} with the results suggesting the insignificance of this parameter on the interaction rate. Therefore, the concentration of 0.1 molL^{-1} was chosen for further studies.

3.3 Effect of ionic strength

The effect of ionic strength on the rate of interaction was also investigated. The ionic strength varied from 0.05 to 0.25 molL^{-1} in KCl solution. The results showed that this parameter did not have any effect on the interaction.

3.4 Assessment of the basic colors (Red or Green or Blue) as the analytical signal

In colorimetric measurements by digital camera, to achieve the most sensitive analytical signal, we investigated changes of red, green and blue values of 8 mgL^{-1} of BG(after 20 min)under 3 white LEDs that were used as the sources of light. Since the white light is a mixture of three basic colors (Red, Green and Blue) we can check that which color of light can provide a stronger and sensitive signal for analysis. As shown in Fig. 6, red signal reveals the highest response. Also, as depicted in Fig. 7, red signal is the most sensitive signal. Therefore red signal selected as the optimum analytical signal and for amplifying the response, we used 3 red LEDs as the sources of light for subsequent investigations.

3.5 Discovering of analytical signal for reflectance colorimetric analysis by the digital camera

To obtain the suitable analytical response, some analytical signals were calculated. The best analytical signal (highest and most sensitive) was difference between Red (R) value derived from sample (containing 2mL BG solution and 1.0 mL of Triton X-100 (17 mmolL^{-1})) and R value derived from blank after 20min.

$$\text{Response (A.U)} = \Delta R = \text{Blank Red intensity} - \text{Sample Red intensity} \quad \text{Eq.2}$$

This simple analytical signal give us the best linear rang and good repeatability, without the need for complex calculations.

4. Kinetics study of the interaction between BG and Triton X-100

The rate of interaction was found to be BG concentration dependent. The rates were followed at room temperature with various concentrations of BG in the range of 1- 12 mg ml⁻¹, keeping Triton-X100 constant at high concentration (17mmolL⁻¹).

From the graphs which are shown in Fig. 3, it is clear that the rate increases as the

BG concentration increases, indicating that the reactions rates obeys the following equation:

$$\text{Rate} = K' [\text{BG}]^n \quad \text{Eq.3}$$

Where K' is the pseudo-order constant of the reaction and n is the order of the reaction. The rate of the reaction may be estimated by the variable-time [38] method measured as $\Delta A/\Delta t$, where A is the absorbance and t is the time in seconds. Taking logarithms of rates and concentration (Eq. 3) is transformed into:

$$\log(\text{rate}) = \log \Delta A/\Delta t = \log K' + n \log [\text{BG}] \quad \text{Eq.4}$$

Regression of $\log(\text{rate})$ versus $\log [\text{BG}]$ (molL⁻¹) gives the regression equation:

$$\log(\text{rate}) = -2.908 + 0.7906 \log [\text{BG}] \quad (r=0.9982) \quad \text{Eq.5}$$

Hence, the kinetic interaction is first order with respect to BG concentration.

5. Analytical performance

According to the measurements performed under the optimum conditions (Table 1) the calibration samples were analyzed to obtain the linear range of BG concentration. The

calibration curve in spectrophotometric method was obtained by plotting ΔA (difference between absorbance at 0 and 900 s at 634 nm) versus BG concentration (Fig. 8). For reflectance colorimetric method by the digital camera, the calibration curve was obtained by plotting ΔR versus BG concentration (Fig. 9).

It was found to be linear in the range of 1.0 to 12.0 mg L⁻¹ of BG concentration in spectrophotometric method and 1.0 to 10.0 mg L⁻¹ of BG concentration in reflectance colorimetric method. The line equation was $\Delta A = 0.0916C - 0.0309$ and $\Delta R = 10.971C - 1.9205$ where C is the concentration of BG in mgL⁻¹. The correlation coefficient of 0.996 and 0.999 indicates a good linear correlation between ΔA and ΔR versus BG concentration, respectively. The limit of detection was 0.047 and 0.037 mgL⁻¹ for spectrophotometric and reflectance colorimetric method, respectively. The relative standard deviation for five replicate analysis of 2.0, 6.0 and 10.0 mgL⁻¹ of BG solutions were 1.75%, 8.12%, 3.04% and 7.0%, 2.29%, 0.73% respectively for spectrophotometric method and reflectance colorimetric method.

6. Interference study

To assessment the possible analytical applications of the proposed method, the selectivity and the influence of several triphenylmethane (TPM) dyes such as Malachite green, Crystal Violet, New Fuchsine and Methyl green, which usually co-exist with BG in wastewaters were studied by analyzing synthetic sample solutions containing 4.0 mg L⁻¹ of BG and 2.0 mg L⁻¹ of each dye. The results are presented in Table 2a and 2b.

It can be concluded from Table 2a and Fig. 10 that the absorption spectra of these dyes overlap with BG, even in the micellar media, and it is not possible to measure BG by a spectrophotometer combined with univariate calibration.

The interaction between the aforementioned dyes and Triton X-100 led to a shift of peak wavelength towards the long wavelength area though no hyper chromic effect was observed over time. According to the results, it is obvious that the presence of these dyes does not affect the kinetic determination of BG.

Also as can be seen in Table 2b, in the analysis of BG using reflectance colorimetric method by the digital camera, the good recoveries were obtained in the presence of common co-existing dyes.

It indicates that the method is highly selective and free from interferences of common co-existing dyes and can be applied, using both spectrophotometer and digital camera as detector, in every laboratory and field test.

As can be seen in Fig.10. the absorption spectra of Malachite green, Crystal Violet, New Fuchsine and Methyl green overlap with BG and with each other, So, in direct spectrophotometrically analysis(no kinetic) for simultaneous determination of these TPM dyes, the multivariate or multiway calibration chemometrics methods could be applied. Which, these techniques need additional data accusation and computing.

7. Real sample analysis

To evaluate the analytical applicability of the proposed method, the recommended procedure was utilized to determine BG in two different samples of wastewaters: fish aquarium water and textile wastewater.

The results are shown in Table 3. As can be seen, the good correlation between the results and known values indicate the successful performance of the proposed method in determining BG in complex environmental samples with the presence of many unknown interferences and without of any sample preparation.

8. Conclusion

In this study, a simple method based on the kinetic interaction of BG and micellar media of Triton X-100 was developed for the spectrophotometric and reflectance colorimetric determination of BG for the first time. To the best of the authors' knowledge, this is a novel kinetic method for the determination of BG. The ability of determining BG in complex wastewaters in presence of unknown interferences, eliminates the need for pre-preparation, that is commonly exists in many other methods [39] or the use of expensive instruments like liquid chromatography–mass spectrometry [19] are the main advantages of proposed method. The other excellent advantage of this method is the employment of a cheap and available detector (digital compact camera) beside the spectrophotometer and compares their performance. The proposed method is highly simple and rapid as it avoids the time-consuming steps of preparing samples and experimental conditions. Also with using a digital camera as detector, the presented method can be used as a field test. The proposed method, have more sensitivity than common colorimetric methods and excellent selectivity for determining BG over the

other triphenylmethane dyes. The proposed method was compared with the some previous works (see Table 4). In comparison with the other conventional analysis methods, the cost-effective developed method has the most selectivity and simplicity efficiency.

References:

- [1] D.F. Duxbury, The photochemistry and photophysics of triphenylmethane dyes in solid and liquid media, *Chemical Reviews* 93 (1993) 381-433.
- [2] D.F. Duxbury, The sensitized fading of triphenylmethane dyes in polymer films. Part 2, *Dyes and Pigments* 25 (1994) 179-204.
- [3] S. De, A. Girigoswami, S. Mandal, Enhanced fluorescence of triphenylmethane dyes in aqueous surfactant solutions at supramicellar concentrations—effect of added electrolyte, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 58 (2002) 2547-2555.
- [4] V. Fessard, T. Godard, S. Huet, A. Mourot, J.M. Poul, Mutagenicity of malachite green and leucomalachite green in in vitro tests, *Journal of Applied Toxicology* 19 (1999) 421-430.
- [5] M. Sarkar, S. Poddar, Studies on the Interaction of Surfactants with Cationic Dye by Absorption Spectroscopy, *Journal of Colloid and Interface Science* 221 (2000) 181-185.
- [6] J.J. Jones, I.J. Falkinham, Decolorization of Malachite Green and Crystal Violet by Waterborne Pathogenic Mycobacteria, *Antimicrobial Agents and Chemotherapy* 47 (2003) 2323-2326.
- [7] S. Srivastava, R. Sinha, D. Roy, Toxicological effects of malachite green, *Aquatic Toxicology* 66 (2004) 319-329.

- [8] H. Tavallali, M. Ostovar, Trace spectrophotometric determination of brilliant green in fish farming water samples, *International Journal of ChemTech Research* 1 (2009) 199-203.
- [9] S. Seshadri, P.L. Bishop, A.M. Agha, Anaerobic/aerobic treatment of selected azo dyes in wastewater, *Waste Management* 14 (1994) 127-137.
- [10] G. McKay, M. Otterburn, J. Aga, Fuller's earth and fired clay as adsorbents for dyestuffs, *Water, Air, and Soil Pollution* 24 (1985) 307-322.
- [11] A.R. Gregory, J. Elliott, P. Kluge, Ames testing of direct black 38 parallels carcinogenicity testing *Journal of Applied Toxicology* 1 (1981) 308-313.
- [12] K.G. Bhattacharyya, A. Sarma, Adsorption characteristics of the dye, Brilliant Green, on Neem leaf powder *Dyes and Pigments* 57 (2003) 211-222.
- [13] S.M. Plakas, K.R. el Said, G.R. Stehly, J.E. Roybal, Optimization of a liquid chromatographic method for determination of malachite green and its metabolites in fish tissues, *Journal of AOAC International* 78 (1995) 1388-1394.
- [14] W.C. Andersen, S.B. Turnipseed, C.M. Karbiwnyk, R.H. Lee, S.B. Clark, W.D. Rowe, M.R. Madson, K.E. Miller, Multiresidue method for the triphenylmethane dyes in fish: Malachite green, crystal (gentian) violet, and brilliant green, *Analytica Chimica Acta* 637 (2009) 279-289.
- [15] R.M.Z. Kakhki, S. Heydari, A simple conductometric method for trace level determination of brilliant green in water based on β -cyclodextrin and silver nitrate and determination of their thermodynamic parameters, *Arabian Journal of Chemistry*, 7 (2014) 1086-1090.
- [16] Y.-D. Shen, X.-F. Deng, Z.-L. Xu, Y. Wang, H.-T. Lei, H. Wang, J.-Y. Yang, Z.-L. Xiao, Y.-M. Sun, Simultaneous determination of malachite green, brilliant green and

crystal violet in grass carp tissues by a broad-specificity indirect competitive enzyme-linked immunosorbent assay, *Analytica Chimica Acta* 707 (2011) 148-154.

[17] N. Zeinali, M. Ghaedi, G. Shafie, Competitive adsorption of methylene blue and brilliant green onto graphite oxide nano particle following: Derivative spectrophotometric and principal component-artificial neural network model methods for their simultaneous determination, *Journal of Industrial and Engineering Chemistry* 20 (2014) 3550-3558.

[18] Z. Es'haghi, M.A.-K. Khooni, T. Heidari, Determination of brilliant green from fish pond water using carbon nanotube assisted pseudo-stir bar solid/liquid microextraction combined with UV-vis spectroscopy-diode array detection, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 79 (2011) 603-607.

[19] S. Ashour, R. Bayram, Development and validation of sensitive kinetic spectrophotometric method for the determination of moxifloxacin antibiotic in pure and commercial tablets, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 140 (2015) 216-222.

[20] D. Pérez-Bendito, A. Gómez-Hens, M. Silva, Advances in drug analysis by kinetic methods, *Journal of Pharmaceutical and Biomedical Analysis* 14 (1996) 917-930.

[21] M. E. Mahmoud, A. E. H. Abdou, A. K. Shehata, H. M. A. Header, E. A. Hamed, Sustainable super fast adsorptive removal of Congo red dye from water by a novel technique based on microwave-enforced sorption process, *Journal of Industrial and Engineering Chemistry* 57 (2018) 28-36.

[22] M.E. Mahmoud, G.M. Nabil, N. M. El-Mallah, H. I. Bassiouny, S. Kumar, T. M. Abdel-Fattah, Kinetics, isotherm, and thermodynamic studies of the adsorption

of reactive red 195 A dye from water by modified Switchgrass Biochar adsorbent, *Journal of Industrial and Engineering Chemistry* 37(2016) 156-167.

[23] M. E. Mahmoud, G.M. Nabil, N. M. El-Mallah, S. B. Karar, Assessment of the adsorptive color removal of methylene blue dye from water by activated carbon sorbent-immobilized-sodium decyl sulfate surfactant, *Desalination and Water Treatment* 57 (2016) 8389-8405.

[24] M. E. Mahmoud, G.M. Nabil, N. M. El-Mallah, S. B. Karar, Improved removal and decolorization of C.I. anionic reactive yellow 145 A dye from water in a wide pH range via active carbon adsorbent-loaded-cationic surfactant, *Desalination and Water Treatment* 55 (2015) 227-240.

[25] E.P. Moraes, N.S.A. da Silva, C.d.L.M. de Moraes, L.S.d. Neves, K.M.G.d. Lima, Low-Cost Method for Quantifying Sodium in Coconut Water and Seawater for the Undergraduate Analytical Chemistry Laboratory: Flame Test, a Mobile Phone Camera, and Image Processing, *Journal of Chemical Education*, 91 (2014) 1958-1960.

[26] W. da Silva Lyra, F.A. Castriani Sanches, F. Antonio da Silva Cunha, P.H. Goncalves Dias Diniz, S.G. Lemos, E. Cirino da Silva, M.C. Ugulino de Araujo, Indirect determination of sodium diclofenac, sodium dipyron and calcium gluconate in injection drugs using digital image-based (webcam) flame emission spectrometric method, *Analytical Methods*, 3 (2011) 1975-1980.

[27] R. Gupta, R.G. Reifenberger, G.U. Kulkarni, Cellphone Camera Imaging of a Periodically Patterned Chip as a Potential Method for Point-of-Care Diagnostics, *ACS Applied Materials & Interfaces*, 6 (2014) 3923-3929.

- [28] K. Grudpan, S.D. Kolev, S. Lapanantnopakhun, I.D. McKelvie, W. Wongwilai, Applications of everyday IT and communications devices in modern analytical chemistry: A review, *Talanta*, 136 (2015) 84-94.
- [29] S. Ayas, A. Cupallari, O.O. Ekiz, Y. Kaya, A. Dana, Counting Molecules with a Mobile Phone Camera Using Plasmonic Enhancement, *ACS Photonics*, 1 (2014) 17-26.
- [30] Q. Wei, R. Nagi, K. Sadeghi, S. Feng, E. Yan, S.J. Ki, R. Caire, D. Tseng, A. Ozcan, Detection and Spatial Mapping of Mercury Contamination in Water Samples Using a Smart-Phone, *ACS Nano*, 8 (2014) 1121-1129.
- [31] E.H. Doeven, G.J. Barbante, E. Kerr, C.F. Hogan, J.A. Endler, P.S. Francis, Red–Green–Blue Electrogenated Chemiluminescence Utilizing a Digital Camera as Detector, *Analytical Chemistry*, 86 (2014) 2727-2732.
- [32] N. Moonrungrsee, S. Pencharee, J. Jakmunee, Colorimetric analyzer based on mobile phone camera for determination of available phosphorus in soil, *Talanta*, 136 (2015) 204-209.
- [33] J. Sankaran, N. Bag, R.S. Kraut, T. Wohland, Accuracy and Precision in Camera-Based Fluorescence Correlation Spectroscopy Measurements, *Analytical Chemistry*, 85 (2013) 3948-3954.
- [34] S. Damirchi, T. Heidari, Evaluation of digital camera as a portable colorimetric sensor for low-cost determination of inorganic arsenic (III) in industrial wastewaters by chemical hydride generation assisted-Fe(III) – 1, 10-phenanthroline as a green color agent, *Journal of the Iranian Chemical Society* (2018). <https://doi.org/10.1007/s13738-018-1443-7>.

- [35] S. De, A. Girigoswami, S. Mandal, Enhanced fluorescence of triphenylmethane dyes in aqueous surfactant solutions at supramicellar concentrations —effect of added electrolyte, *Spectrochimica Acta Part A* 58 (2002) 2547– 2555.
- [36] J. Ghasemi, D.M. Ebrahimi, L. Hejazi, R. Leardi, A. Niazi, Simultaneous kinetic-spectrophotometric determination of sulfide and sulfite by partial least squares and genetic algorithm variable selection, *Journal of Analytical Chemistry*, 62 (2007) 348-354.
- [37] O. Olanrewaju, J. Ige, O. Soriyan, O. Grace, O.S. Esan, O. Olanrewaju, Kinetics and Mechanism of the Alkaline Fading of Brilliant Green in Aqueous Solutions of a Double-tailed and Some Single-tailed Cationic Surfactants, *Acta Chimica Slovenica*, 54 (2007) 370-374.
- [38] H. E. Abdellatef, Kinetic spectrophotometric determination of tramadol hydrochloride in pharmaceutical formulation, *Journal of Pharmaceutical and Biomedical Analysis*, 29 (2002) 835– 842.
- [40] P.K. Dutta, an overview of textile pollution and its remedy, *Indian Journal of Environmental Protection*, 14 (1994) 443-446.

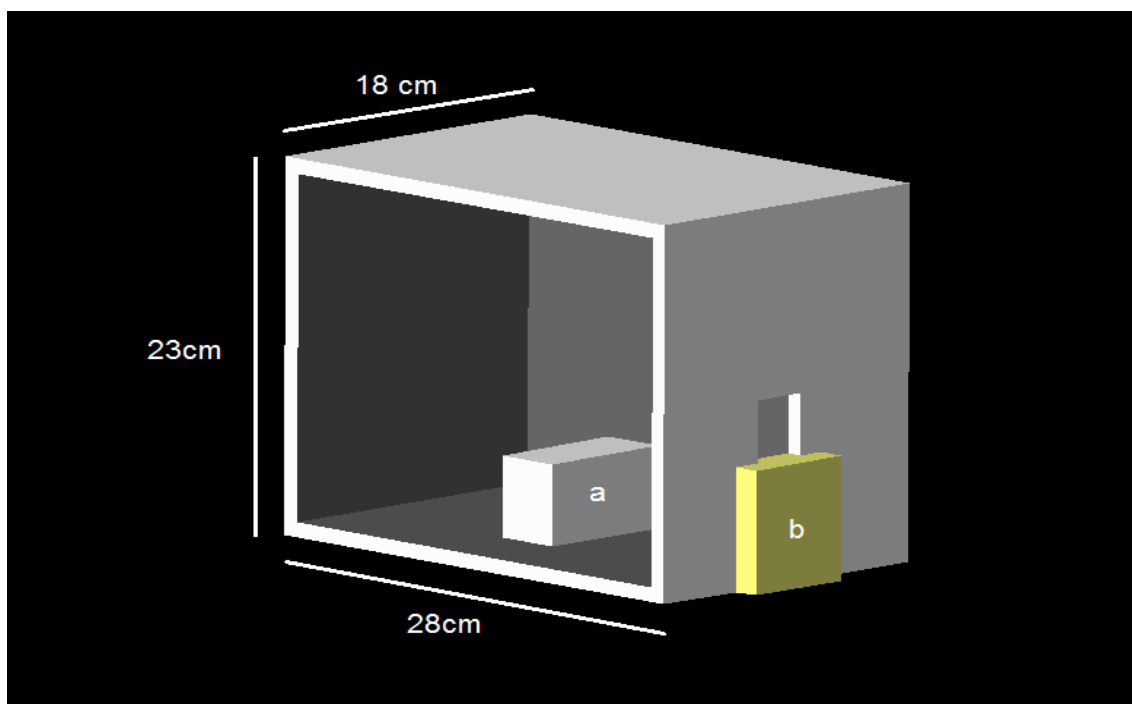


Fig.1. The schematic diagram of the light box: (a) sample location; (b) camera location [34].

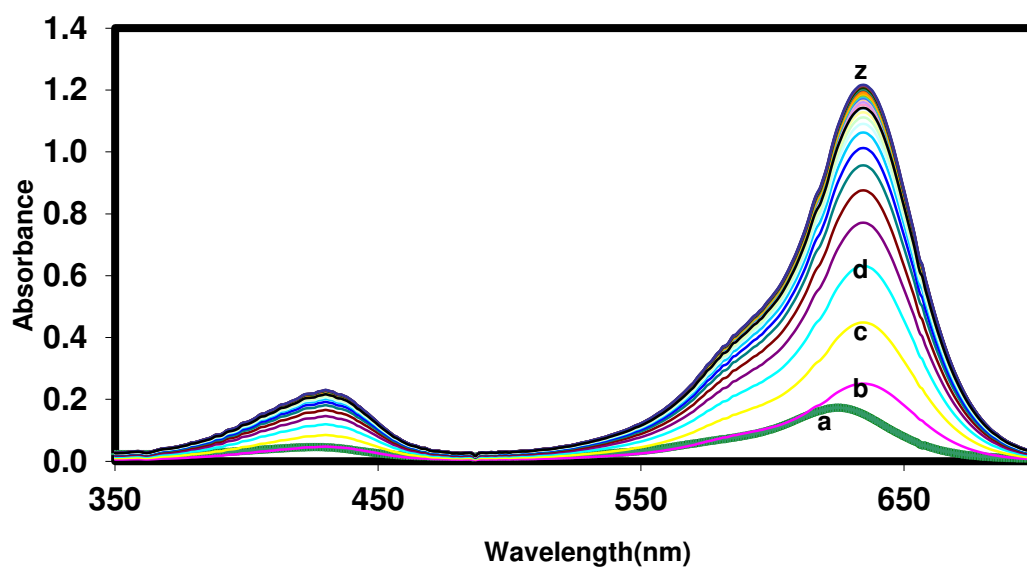


Fig.2. Absorption spectra of (a) BG in the absence of Triton X-100 (λ_{\max} =625nm) and (b-z) BG in the presence of Triton X-100 (λ_{\max} =634 nm) as a function of time (0 to 900 s). Conditions: 10 mgL⁻¹ of BG; 17 mmolL⁻¹ of Triton X-100; pH= 4; time interval= 30 s and temperature=25±0.1 °C.

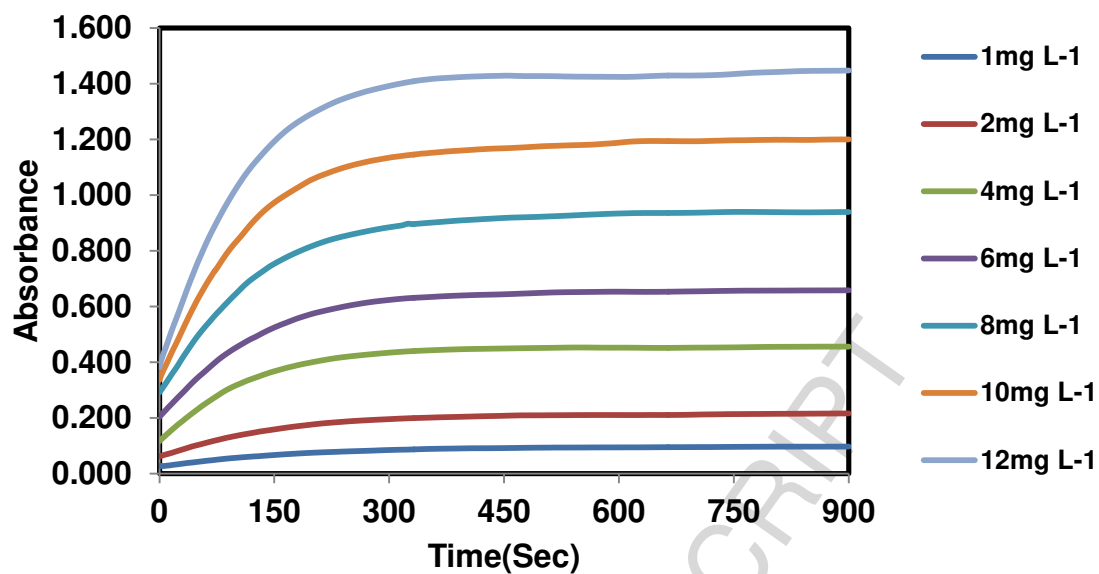


Fig.3. Kinetic curves for the interaction of BG (1-12 mg L⁻¹) with Triton X-100 (17mmolL⁻¹) at pH =4; time interval= 0.5 s, temperature= 25±0.1 °C and λ_{\max} =634 nm.

Fig.4a

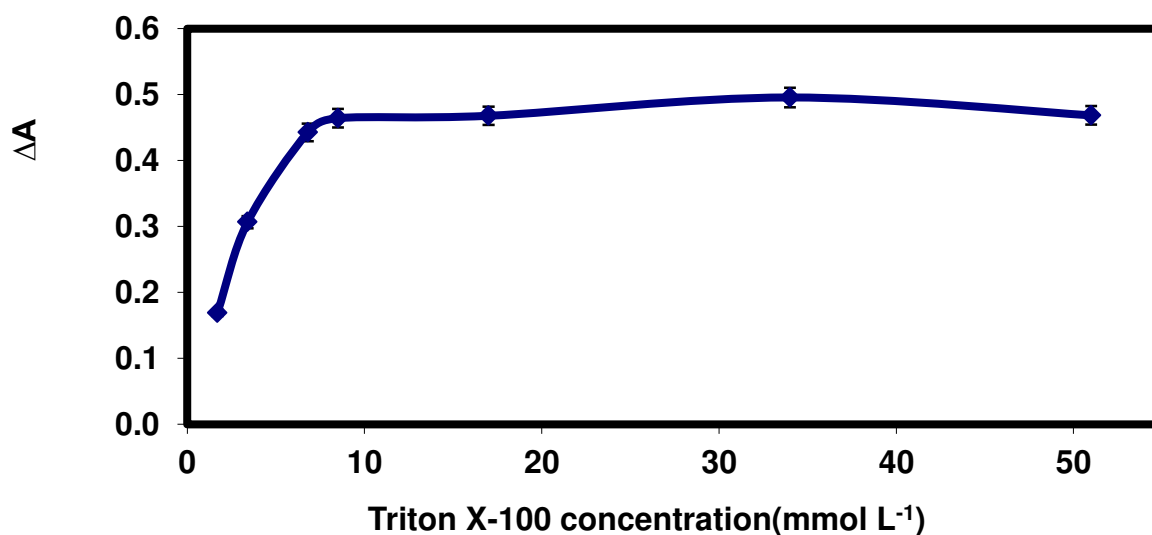
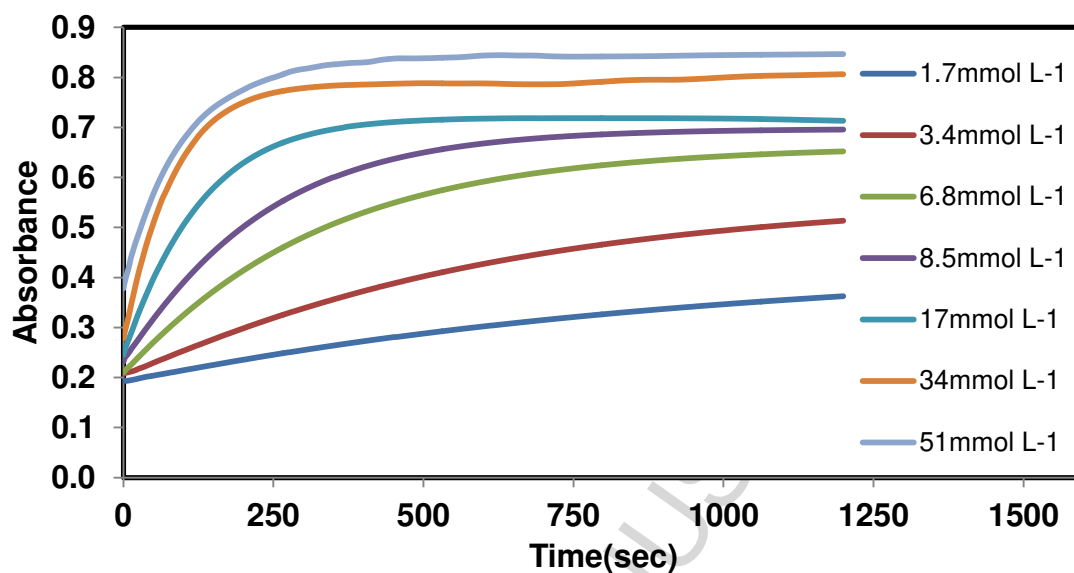


Fig.4b.

Fig.4. Effect of Triton X-100 concentration on the interaction between BG and Triton-X-100 (Fig. 5a) and ΔA of BG (Fig. 5b). Conditions: 4 mgL⁻¹ of BG; pH,=4; 0.1 molL⁻¹ of acetic acid/sodium acetate buffer; $\Delta A=A_{20\text{min}}-A_0$; $\lambda_{\text{max}}=634\text{ nm}$ and temperature = 25±0.1 °C.

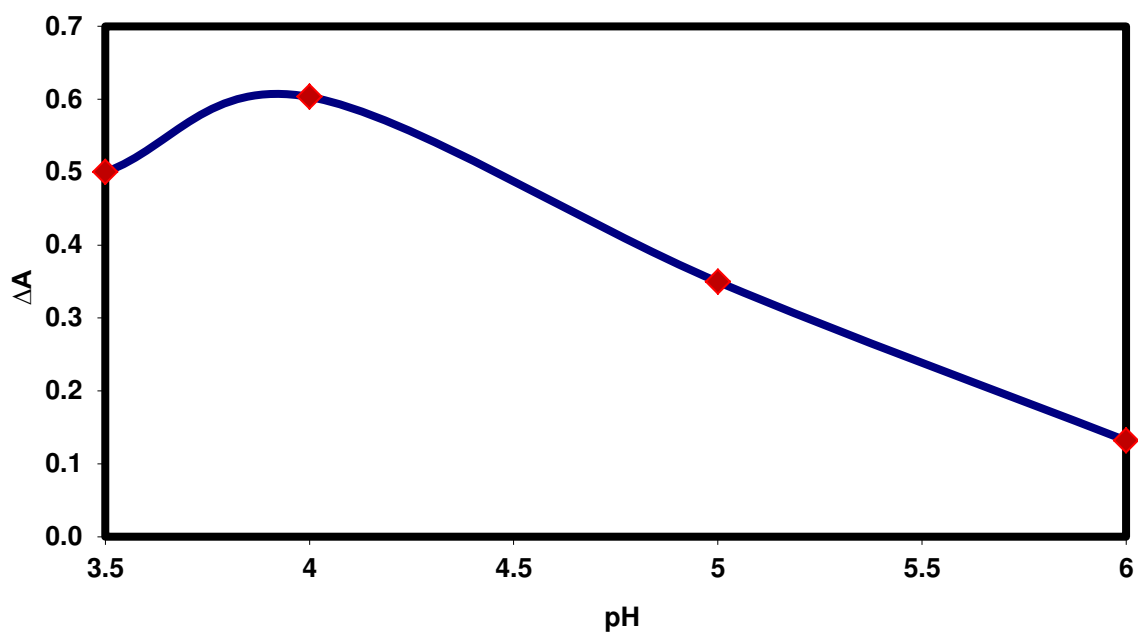


Fig.5. Effect of pH on ΔA of BG. Conditions: 4 mg L^{-1} M of BG; 17.0 mmolL^{-1} of triton X-100; 0.1 molL^{-1} of acetic acid/sodium acetate buffer; $\Delta A = A_{20\text{min}} - A_0$; $\lambda_{\text{max}} = 634 \text{ nm}$ and temperature = $25 \pm 0.1 \text{ }^\circ\text{C}$.

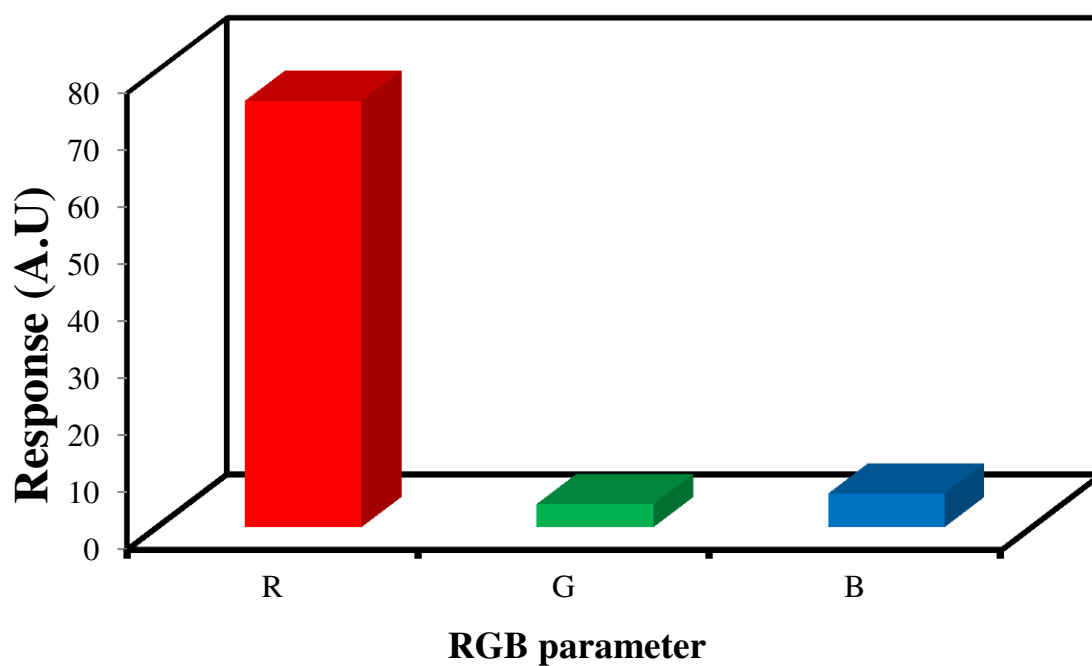


Fig.6. Monitoring of basic colors (Red, Green and Blue) conversion. Red signal indicates highest response. Conditions: BG: 8 mg l^{-1} ; all other conditions are as in Table.1.

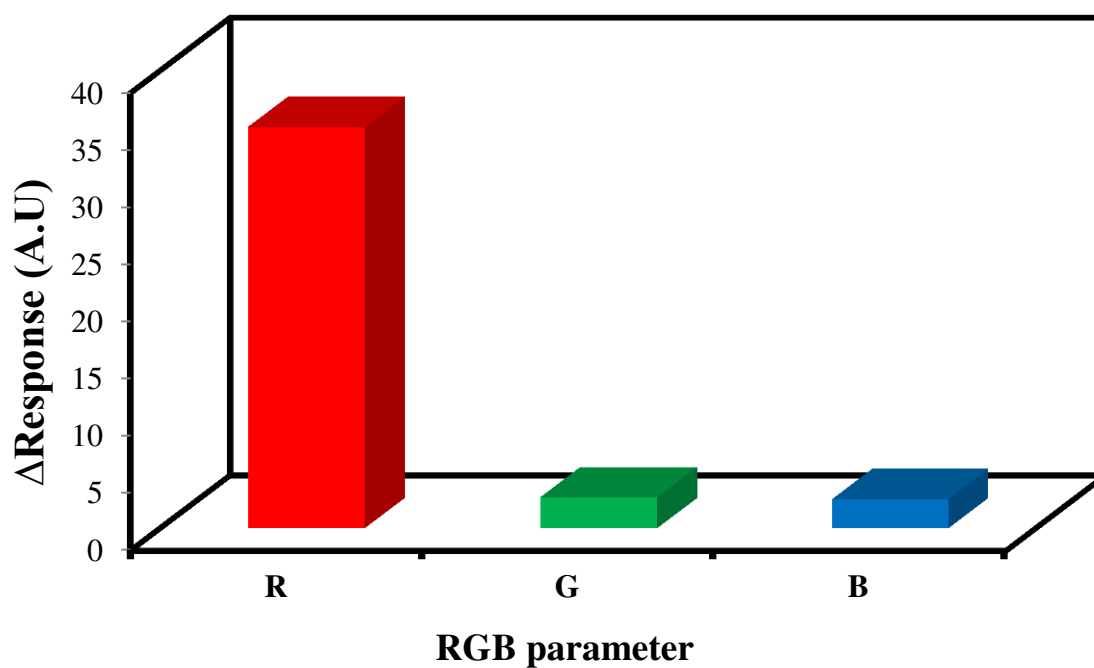


Fig.7. Δ Response between low concentration of BG, 4 & 8 mg l^{-1} , as seen in the figure, red signal was the best sensitive signal. Conditions: all conditions are as in Table.1

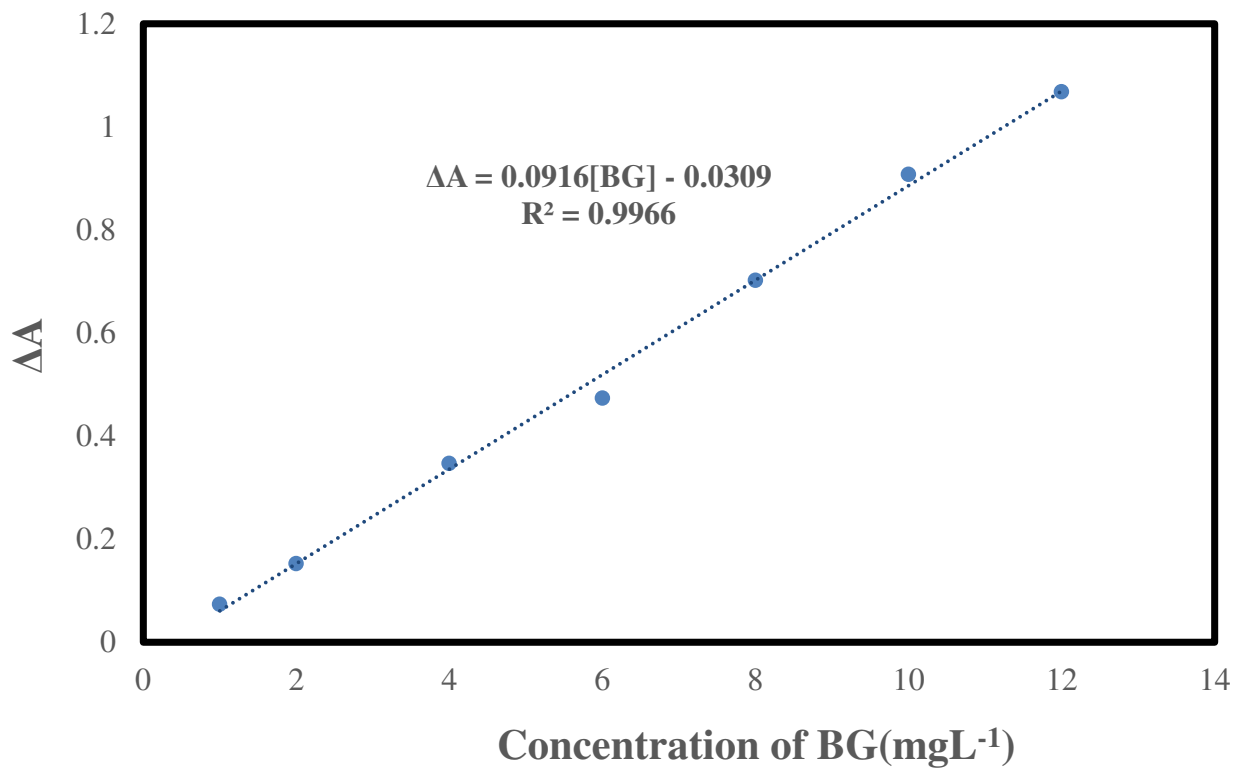


Fig.8. Calibration graph of BG for spectrophotometric method .

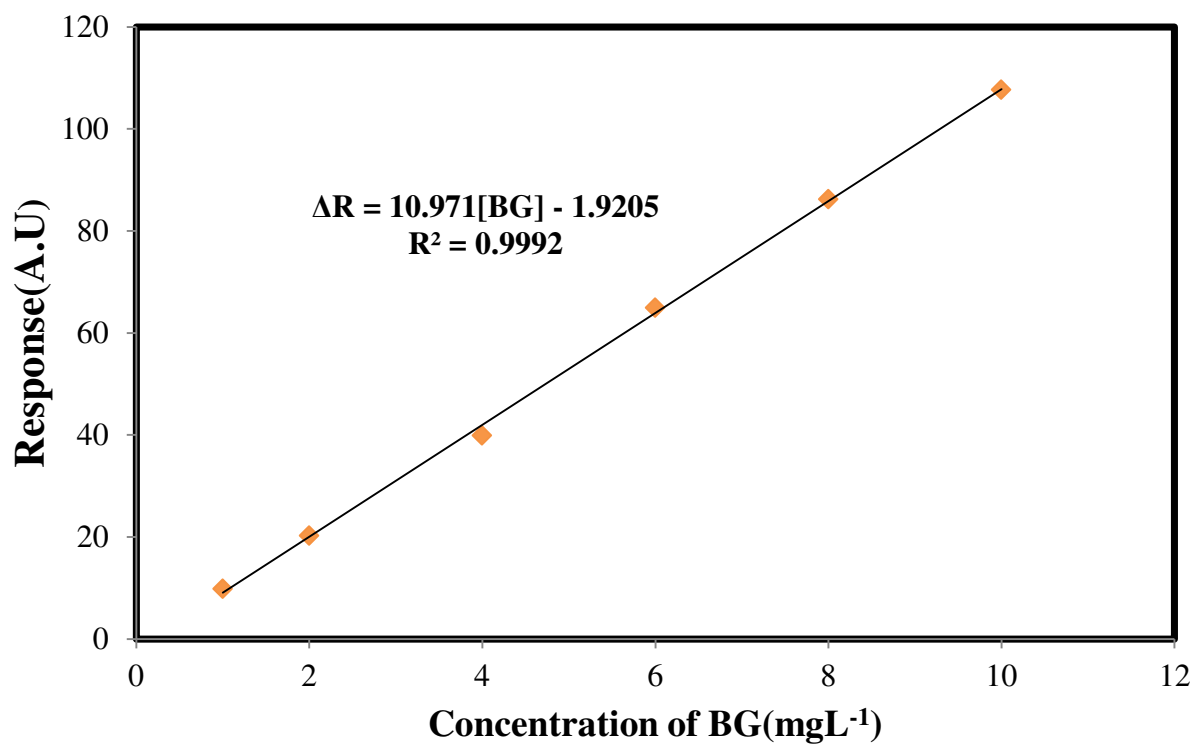


Fig.9. Calibration graph of BG for reflectance colorimetric method by the digital camera.

Fig.10.a

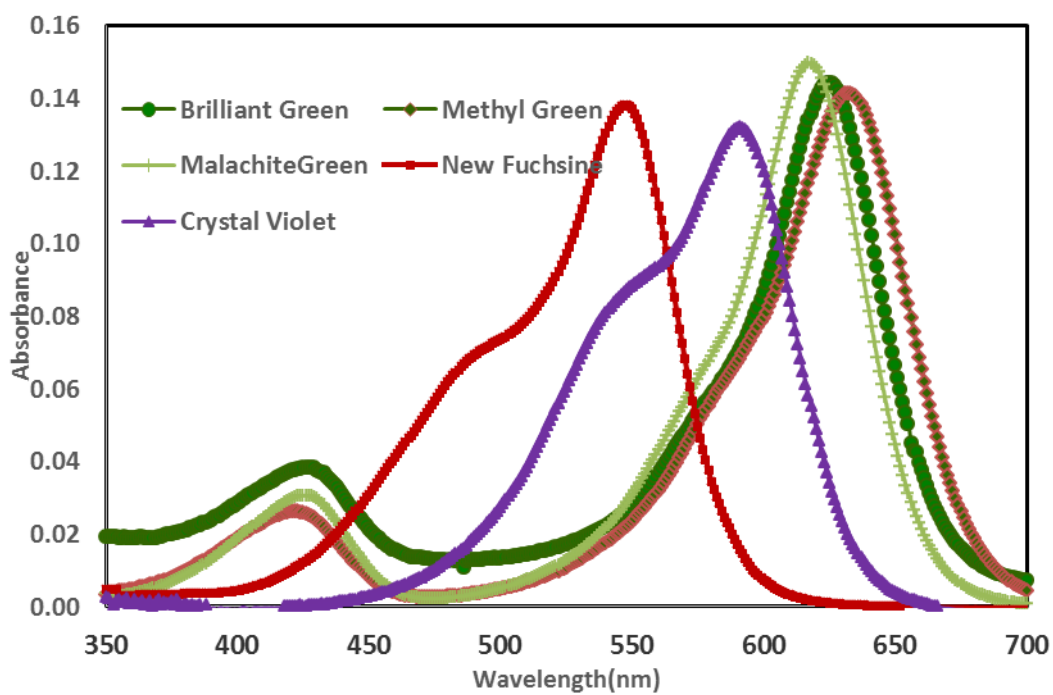


Fig.10.b

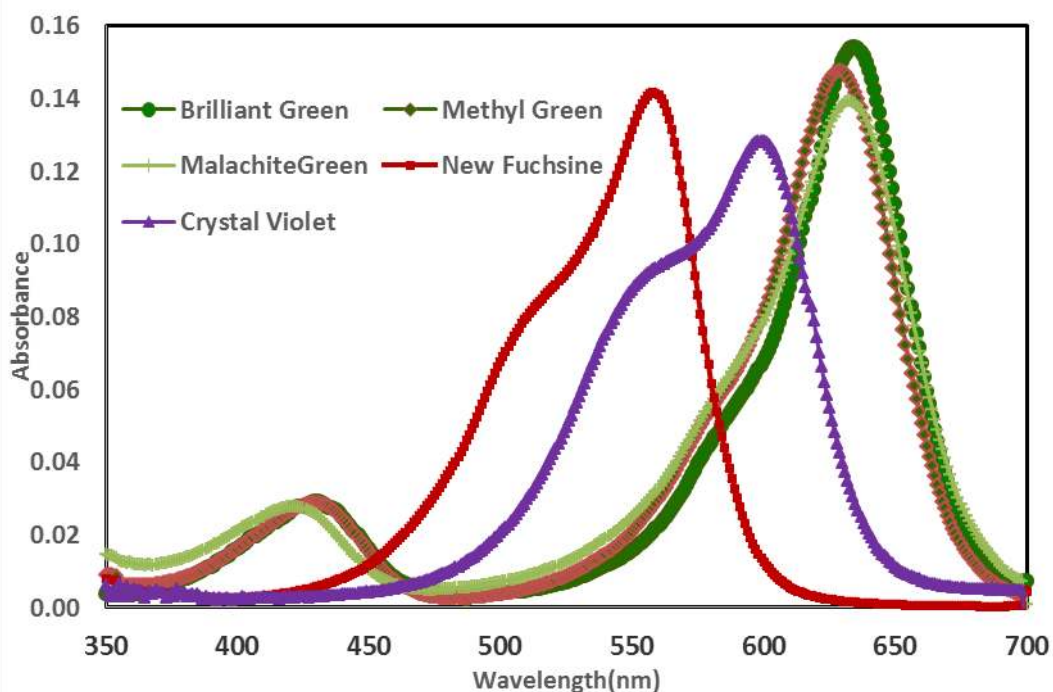


Fig.10. Normalized spectra of BG, New fuchsin, Crystal violet, Methyl Green and Malachite Green in water (Fig.10.a) and in Triton X-100 micellar media (Fig.10.b). Conditions: 17mmolL⁻¹ of Triton X-100; pH=4; and temperature= 25±0.1 °C.

Table 1

The optimized conditions.

Parameters	Studied range	Selected condition
Best signal of light	Red, Green, Blue	Red
Source of light	White, red, green and blue LED	3 red LED
Response (A.U) = ΔR (for reflectance colorimetric method)	–	Blank Red intensity _ Sample Red intensity
Triton X-100 concentration (mmolL^{-1})	1.7- 51	17
pH	3.5 - 6	4
acetic acid/sodium acetate buffer concentration	0.05-0.4 molL^{-1}	0.1 molL^{-1}
temperature	–	$25 \pm 0.1 \text{ }^\circ\text{C}$.
ΔA (for spectrophotometric	–	$A_{20\text{min}} - A_0$

method)		
KCl	0.05 _ 0.25molL ⁻¹	0.1mol L ⁻¹

ACCEPTED MANUSCRIPT

Table 2.a Effect of interferences on the determination of 4.0 mgL^{-1} BG in the presence of 2.0 mg L^{-1} co-existing dyes applied spectrophotometric method.

Dye	λ_{max} in water	λ_{max} in tritonX-100	$\Delta A_{\lambda_{\text{max}}}$ = $A_{20\text{min}} - A_0$	$\Delta A_{634.4\text{nm}}$ = $A_{20\text{min}} - A_{0\text{min}}$	Recovery(%)***
Brilliant green	625	634.4	0.371	0.371	-
Methyl green	632	633	0.017	0.393	9.105
Malachite green	617	629	0.037	387.0	3.104
New Fuchsine	548	558	0.041	399.0	5.107
Crystal violet	590	599	0.025	378.0	0.102

* λ_{max} of the desired dye in Triton X-100.

** ΔA of Brilliant green in the presence of foreign species.

***Recovery= (ΔA of Brilliant green in the presence of foreign species / ΔA of Brilliant green).

Table 2.b

Effect of interferences on the determination of 4.0 mgL^{-1} BG in the presence of 2.0 mg L^{-1} co-existing dyes applied reflectance colorimetric method by the digital camera.

Dye	Response (A.U) = ΔR^*	Response (A.U) = ΔR^{**}	Recovery (%)***
Brilliant green	39.866	39.866	100.0
Methyl green	0.491	40.642	101.9
Malachite green	3.186	43.714	109.6
New Fuchsine	0.582	41.553	104.2
Crystal violet	4.433	46.140	115.7

* ΔR of the desired dye in Triton X-100.

** ΔR of Brilliant green in the presence of foreign species.

*** Recovery = (ΔR of Brilliant green in the presence of foreign species / ΔR of Brilliant green).

Table 3

Determination of BG in fish aquarium wastewater and textile wastewater by the proposed method.

No. of sample	Sample matrix	BG Spike (mg L ⁻¹)	BG Found ^a (mg L ⁻¹)		Recovery ^b (%)	
			Spectrophotometric method	Reflectance colorimetric method	Spectrophotometric method	Reflectance colorimetric method
1	Fish aquarium wastewater ^{r*}	-	1.22	1.20	-	-
2		1.5	2.81	2.76	106.0	104.0
3		2.0	3.43	3.11	110.5	95.5
4		3.0	4.51	4.04	109.6	94.6
5		4	5.34	5.0	109.8	95.0
1	Textile wastewater ^{r**}	-	3.22	2.95	-	-
2		1.5	4.74	4.46	101.3	100.6
3		2.0	5.45	4.97	111.5	101.0
4		3.0	6.33	6.12	103.6	105.6
5		4	7.24	6.98	100.5	100.7

^a Mean of triplicate determination.

^b Recovery (%) = $100 \times \left(\frac{\hat{c}_t - \hat{c}_i}{c_s} \right)$, where \hat{c}_t is the total concentration achieved after standard addition, \hat{c}_i is the initial concentration found before standard addition and c_s is

the standard added concentration.

*It was obtained from the city of Mashhad, Iran containing BG, MG and CV.

**It was obtained from textile factories around the city of Mashhad, Iran containing BG, MG, CV and methyl green.

ACCEPTED MANUSCRIPT

Table 4

Comparison of some methods which were used for determination of Brilliantgreen.

N O.	Sample matrix	Method	Detection device	LOD ($\mu\text{g L}^{-1}$)	RSD (%)	Linear range ($\mu\text{g L}^{-1}$)	Ref .
1	Fish farming and water samples	CPE ^a	Spectrophotometer	15	2.7 at 100 ($\mu\text{g L}^{-1}$) and 1.8 at 1000 ($\mu\text{g L}^{-1}$)	50-2000	[8]
2	Fish and water samples	^b IL-DLLME-ZCDSP	Spectrophotometer	2.7	4.7 at 50 ($\mu\text{g L}^{-1}$)	10-500	[40]
3	Fish (catfish)	^c LC-VIS	Visible detection	0.07 (ng g^{-1})	5.5 at 0.5 (ng g^{-1}) and 13.6 at 2 (ng g^{-1})		[14]
4	Water	Gravimetric and complexometric titration method based on conductometric technique	Conductometer	4.7 (mg l^{-1}) in gravimetric titration method and 0.00475 (mg l^{-1}) in complexometric titration method		4.7- 475 (mg l^{-1}) in gravimetric titration method and 0.00475-475 (mg l^{-1}) in complexometric titration method	[15]
5	Fish	^d HF-SLPME	Spectrophotometer	0.55 ($\mu\text{g L}^{-1}$)	8.32 at 5 ($\mu\text{g L}^{-1}$) and 5.89 at 100 ($\mu\text{g L}^{-1}$)	1-10000 ($\mu\text{g L}^{-1}$)	[18]

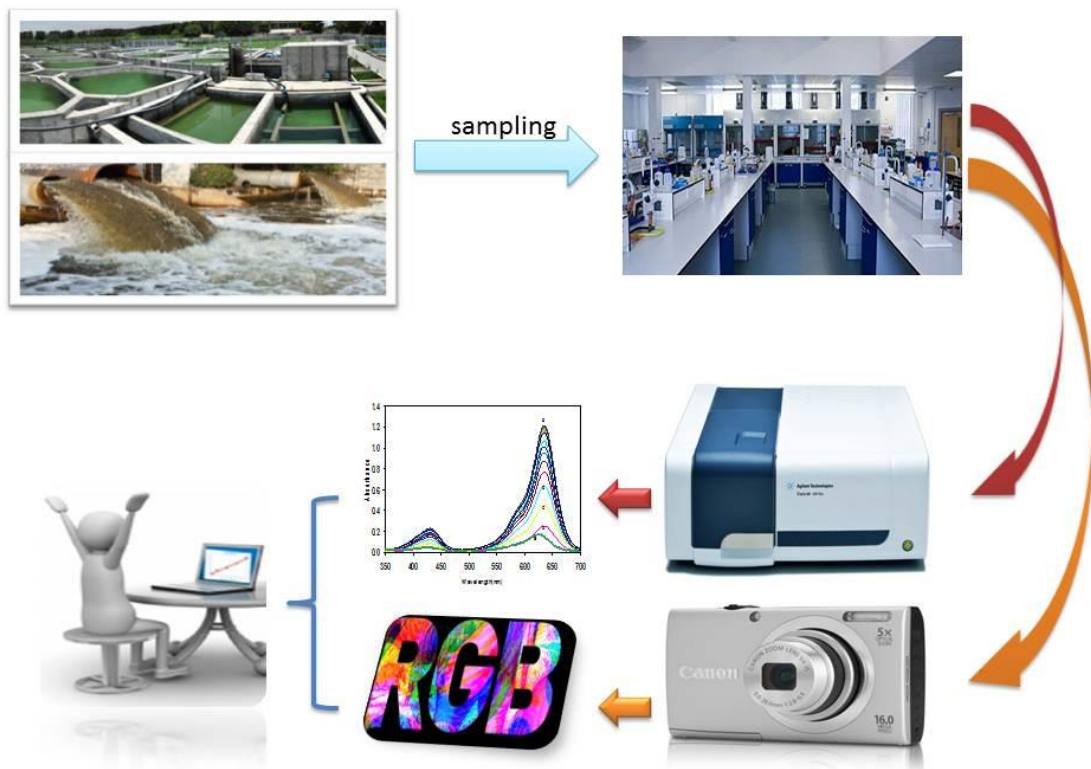
	pond water		meter		and 4.8 at 5000($\mu\text{g L}^{-1}$)]
6	Fish aquarium wastewater and textile wastewater	Kinetic spectrophotometric method	Digital camera and spectrophotometer	0.037 (mg L^{-1}) with digital camera detector and 0.047 (mg L^{-1}) with Spectrophotometer detector	7.0 at 2(mg L^{-1}) and 2.29 at 6(mg L^{-1}) and 0.73 at 10(mg L^{-1}) with digital camera detector and 1.75 at 2(mg L^{-1}) and 8.12 at 6(mg L^{-1}) and 3.04 at 10(mg L^{-1}) with Spectrophotometer detector	1.0 - 10.0(mg L^{-1}) with digital camera detector and 1.0 - 12.0(mg L^{-1}) with Spectrophotometer detector	Thesis work

a : Cloud point extraction.

b : Ionic liquid based dispersive liquid-liquid microextraction followed by Zero-crossing first derivative spectrophotometric method.

c : Liquid chromatography with visible detection.

d : Hollow fiber solid/liquid phase microextraction.



Graphical abstract

Highlights

- It was observed that the color intensity of BG increased gradually in the presence of Triton X-100.
- The absorption spectra of other triphenylmethan dyes such as malachite green, methyl green overlap highly with BG, even in the micellar media.
- The interaction between other triphenylmethan dyes and Triton X-100 didn't led hyper chromic effect over the time. So, the presence of these dyes does not affect the kinetic determination of BG.
- A cost-effective digital camera could use as the detector device and, in comparison with spectrophotometry, satisfactory results were obtained .