

THE SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM (VI) USING N, N-DIETHYL-P-PHENYLENEDIAMINE IN SYNTHETICALLY PREPARED WASTEWATER, AND TAP WATER

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ABSTRACT

The DPD (N, N-diethyl-p-phenylenediamine) is introduced in the present study as an analytical reagent for the direct, rapid, easy, and sensitive spectrophotometric detection of hexavalent chromium Cr (VI) species which is health hazard. The oxidization of the colorless DPD (N, N-diethyl-p-phenylenediamine) reagent with Cr (VI) results in a red color DPD radical (DPD⁺) at pH 4.39. The color intensity is directly proportional to the Cr (VI) concentration. By utilizing a UV-Vis spectrophotometer, the measurement of the produced DPD⁺ can be identified in term of quantity at 551 nm. The linear calibration graphs for 0.2 – 2 mg. L⁻¹ of Cr (VI) are obtained with a correlation coefficient value of 0.9997. The molar absorption coefficient and Sandell's sensitivity are 2.5449×10⁴ L.mol⁻¹cm⁻¹ and 0.028 mg. Cr (VI), cm⁻², respectively. The present work develops, optimizes, and validates a new spectrophotometric method for determining Cr (VI) in the samples of the synthetically prepared wastewater and tap water. The method is effectively applied and the findings are statistically evaluated with those of the reference method.

KEYWORDS: Chromium, Cr (VI), N, N-diethyl-p-phenylenediamine, Synthetically prepared Wastewater.

1 INTRODUCTION

Chromium, as a hazardous organic and inorganic water pollutant, is listed in the U.S. Environmental Protection Agency (EPA) Priority Pollutant List (Jamroz et al., 2019). In human biochemistry, Chromium has a dual paradoxical function. While it forms an essential element in trace amounts, the large quantities of it are both toxic and cancerous (Meneses, Júnior and Costa, 2018), albeit the carcinogenic process mechanism remains unclear (Dima, Sequeiros and Zaritzky, 2015; Vaz et al., 2017).

Permissible Cr (VI) concentrations as 0.05 mg. L⁻¹ or less have been established and the tracking of their concentration has been made compulsory by both WHO and Japanese environmental guidelines (Yokota et al., 2019). On this basis, Cr (VI) is regarded as a contaminant in water supplies, at a time when the essentiality and toxicity of chromium are based on its oxidation states. Several oxidation stages, namely 0 to VI, for Chromium are known to exist. Yet, both Cr (III) and Cr (VI) are commonly found in their thermodynamically stable forms. Hence, Cr (VI) is viewed as a

contaminant in water supplies (Tóth and Baze 2019).

Accordingly, the development of the analytical procedures to effectively identify chromium is required. Examples of the procedures for determining total chromium and Cr(VI) in water samples, are FIA with spectrophotometric detection (Meneses, Júnior and Costa, 2018; Zhu et al., 2018; Shekho and Mahmoud 2016) derivative spectrophotometry (Wrobel et al., 1997), ion chromatography coupled with UV-Vis detection (Onchoke, and Salomey, 2016), spectrophotometric method (Nagaraj et al., 2009; Tayone, 2015; Soomro et al., 2011; Stoyanova, 2005) colorimetric (Parmar, Pillai and Gupta, 2010), and atomic absorption spectrometry (AAS) detection, (Divrikli, Soylak and Elci, 2008; Oreste et al., 2020).

In the expanding analytical areas, viz. environmental, biological, and material monitoring of the trace levels of heavy metal ions, the development of easy and fast analytical techniques, not costly in nature, is heavily demanded. Similarly the correct detection of Cr (VI) traces forms a significant task and challenge.

The spectrophotometric methods, as an analytical method, are quite advantageous in terms of being an easy and low-cost operation (Zou *et al.*, 2019).

The commercial reagent *N, N*-diethyl-*p*-phenylenediamine (DPD) is vastly used as an indicator to determine the various oxidants on treating water (Gokulakrishnan, Mohammed, and Prakash, 2016). By means of just one-electron transfer, the red DPD can be obtained by the oxidation of the colorless DPD (Liu *et al.*, 2019). In other words, DPD may be oxidized by Cr (VI) so as to generate DPD⁺; a process that results in a red color with an intensity that is directly proportional to the concentration of Cr (VI).

A spectrophotometric method that is based on the reaction between Cr (VI) and DPD to identify the trace Cr (VI) concentration in water is not known yet. As such, the current study aims at developing the DPD spectrophotometric method to determine the trace concentration of Cr (VI) in the synthetically prepared samples of wastewater and tap water.

2 MATERIALS AND METHODS

2.1 Apparatus

In the current study, an apparatus that consists of a UV-visible spectrophotometer (Jenway, 7315, spectrophotometer) with 1 cm quartz cell is used to measure the absorbance. Also, a pH meter for measuring the pH values (pH-2005, JP Selecta, Spain) is used.

2.2 Reagents

For preparing all the solutions, analytical grade reagent chemicals were used. Also, a fresh preparation of buffer solution and double distilled water were used in all the experiments.

Acetate buffer solutions (HAC/AC⁻ buffer) pH 3.6-5.6 were being prepared as the required amounts of equimolar 0.1 M acetic acid and 0.1 M sodium acetate (trihydrate) were combined.

Phosphate buffer solutions (PBS) pH 5.8-8.0 were prepared by mixing sufficient amounts of equimolar (1 M) potassium di-hydrogen phosphate and potassium monohydrate phosphate in DDW and the pH was adjusted by 0.2 M HCl and 0.2 M NaOH.

A stock standard solution of (1000 mg. L⁻¹) Cr (VI) was prepared by dissolving 2.8290 g potassium dichromate (K₂Cr₂O₇) in double distilled water, then being diluted to a final

amount of 1000 ml. By the serial dilution, working standard solutions were prepared from an intermediate stock solution (100 mg. L⁻¹).

(1000 mg. L⁻¹) of N, N-Diethyl-P-phenylenediamine oxalate salt (DPD) was prepared by dissolving 0.1 g in double distilled water, then being diluted to a final volume of 100 ml.

The synthetically prepared Wastewater;

X₁: A solution containing 10 mg. L⁻¹ of each ion [Al³⁺, Ca²⁺, Fe²⁺, Pb²⁺, Mg²⁺].

X₂: A solution containing 10 mg. L⁻¹ of each ion [Cd²⁺, Ba²⁺, Cr⁺³, Na⁺, Pb²⁺].

X₃: a mixture of [X₁+ X₂]

2.3 The General Procedure

To identify the Cr (VI) concentration in the proposed DPD method, the following general procedure was carried out: Firstly, 1.4 mL buffer reagent (HAC/AC⁻ buffer, PH 4.39), and 1.8 mL DPD reagent (1000 mg. L⁻¹), were put in 10 mL calibrated flasks. Secondly, to complete the reaction, the resultant solution was mixed with a 1.0 mL standard solution containing 2-20 mg. L⁻¹ of Cr (VI) and held at room temperature for 15 min. The solutions, with distilled water, were then quantitatively diluted to the mark, and the absorbance were evaluated against the blank reagent at 551 nm. The sample was also prepared under similar conditions.

To determine the Cr (VI) concentration in the synthetically prepared wastewater and tap water, the researchers have adopted general procedures in terms of the proposed DPD method under similar conditions. This method was carried out as follows: Firstly, 1.4 mL buffer reagent (HAC/AC⁻ buffer, PH 4.39), and 1.8 mL DPD reagent (1000 mg. L⁻¹), were put in 10 mL calibrated flasks. Secondly, to complete the reaction, the resultant solution was mixed with a 5.0 mL standard solution containing 2-20 mg. L⁻¹ of Cr (VI) and held at room temperature for 15 min. The solutions, with distilled water, were then quantitatively diluted to the mark, and the absorbances were evaluated against the blank reagent at 551 nm.

The Cr (VI) concentration in water samples was calculated from the measured absorbance at 551 nm by the Eq.:

$$[\text{Cr (VI)}]_{\text{sample}} = \Delta A V_{\text{final}} / \gamma \epsilon l V_{\text{sample}}$$

where ΔA is the absorbance at 551 nm after subtracting the blank absorbance; γ represents the stoichiometric factor of DPD⁺ generation identified in $\gamma = k_s/\epsilon$ equation; k_s is the calibration curve slope of pure water gained at

551 nm; and ϵ stands for the coefficient of the molar absorption of DPD^{++} at 551 nm which was measured at pH 4.39 based on the reaction between chlorine and DPD in order to produce DPD^{++} (Palin, 1957). The value of ϵ was found out to be $\epsilon = 2.13 \times 10^4 \text{ L.mol}^{-1}\text{cm}^{-1}$. Such a value corresponded to the value $2.10 \times 10^4 \text{ L.mol}^{-1}\text{cm}^{-1}$ reported by Bader, Sturzenegger, and Hoigné, (1988), and the value $2.17 \times 10^4 \text{ L.mol}^{-1}\text{cm}^{-1}$ reported by Zou *et al.* (2019); l represents the path length of the cuvette; V_{sample} refers to the volume of the tested Cr (VI) samples; and V_{final} is the final volume after adding all solutions.

3 RESULTS AND DISCUSSION

3.1 Absorption Spectra

Fig. 1 shows the absorption spectrum (400-600 nm) of the DPD solution after reacting with Cr (VI) under the optimal conditions. It demonstrates that the produced DPD^{++} has a broad and intense absorption spectrum in the visible region with two peaks of absorption at 510 nm and 551 nm. This is in agreement with the absorption spectral features listed by other researchers in this field, namely Liu *et al.*, 2018 and Zou *et al.*, 2019.

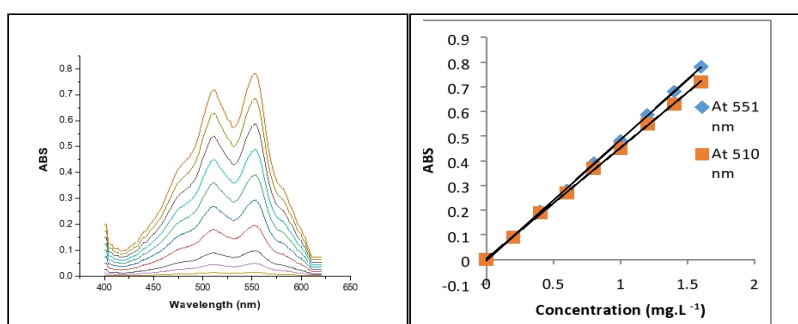


Fig. 1 The absorption spectrum of reaction product of different Cr (VI) concentrations and DPD

It is worthy to outline that no change in the absorption curves and peaks with the Cr (VI) dose was reported. Additionally, there was an increase in the values of absorbance of the produced DPD^{++} at 510 and 551 nm which was concomitant with the increasing concentration of Cr (VI). The standard curves got a remarkable linear relationship for Cr (VI) concentration in the range of 0.2-2 mg.L^{-1} and R^2 values were up to 0.9997, and the sensitivities were computed as $2.33 \times 10^4 \text{ L.mol}^{-1}\text{cm}^{-1}$ and $2.54 \times 10^4 \text{ L.mol}^{-1}\text{cm}^{-1}$ corresponding to 510 nm and 551 nm. Accordingly, a spectrophotometric method based on DPD as a reagent for measuring traces of Cr (VI) concentration at 551 nm and relying

on the reaction of oxidation between DPD and Cr (VI) has been suggested in this paper. Since the value of absorbance at 551 nm was higher than the absorbance value at 510 nm, 551 nm was chosen as the wavelength of detection in this study.

3.2 The Effect of pH and buffer Volume

To determine Cr (VI) in the pH range of 3.9–8.8, there had been an intensive investigation of the effects of different buffer solutions. Fig. 2 indicates that the highest analytical signal of the buffer system was recorded at pH 4.39. As such, it was accounted for as the optimum pH value for forthcoming investigations or studies.

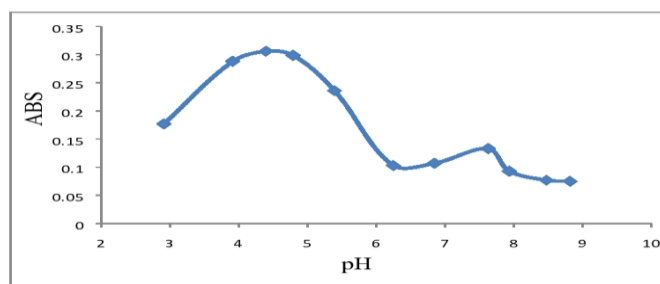


Fig. 2 Effect of pH on the absorbance of the reaction product of Cr (VI) and DPD

Additionally, the volume of the buffer solution that gave the highest analytical signal was also investigated within the range of 0.2–2.0 mL (Fig. 3). On the basis of the arrived at results,

1.4 mL of buffer solution at pH 4.39 was applied to the aqueous solutions to maintain the pH already referred to in further studies.

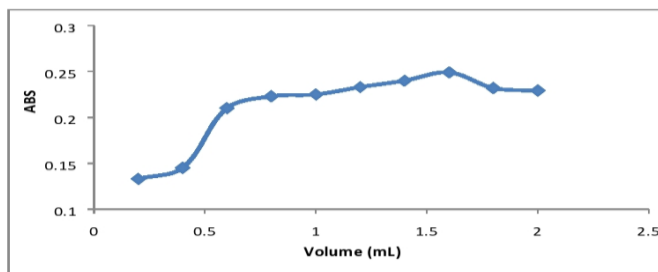


Fig. 3 Effect of buffer volume on the absorbance of the reaction product of Cr (VI)

and DPD

3.3 The effect of reagent concentrations.

A different excess of the DPD reagent was added to the concentration range Cr(VI), followed by measuring the absorbance. Fig. 4

shows that the addition of 1.8 ml (1000 mg.L⁻¹) of DPD resulted in the achievement of maximum absorbance.

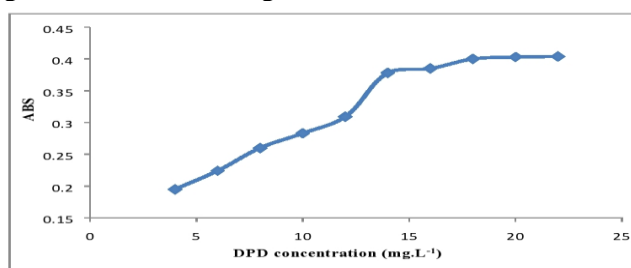


Fig. 4 Effect of DPD concentration on the absorbance of the reaction product of Cr

(VI) and DPD

3.4 The Effect of surfactant.

Various surfactants, namely [nonionic polyoxyethylene sorbitan mono-palmitate (Tween40), TritonX100]; cationic, cetyltrimethylammonium bromide (CTAB); and anionic, sodium dodecyl sulfate (SDS) had been tested.

Table 1 shows that maximum absorbance was observed in the 10% cetyltrimethylammonium bromide (CTAB) medium and aqueous solution without surfactants. Hence, the aqueous solution was used in the determination process.

Table (1): Effect of surfactants on the absorbance of the reaction product of Cr (VI) and DPD

Surfactant	ABS
Tween-40	0.370
Triton X-100	0.368
CTAB	0.479
SDS	0.336
Without Surfactant	0.438

3.5 The effect of time and temperature

The generated DPD⁺ stability in the suggested DPD method was evaluated by investigating, at various temperatures (25–45°C) and at different times, the changes in DPD⁺ absorbance at 551 nm, following the reaction between DPD and Cr (VI) pure water. Fig. 5 shows that the reaction speed increases with the

increase in temperature; and that a maximum, yet unstable, absorption occurs at a temperature of 45° C after 5 minutes. At room temperature, and after the elapse of 15 minutes, the maximum absorption remained constant for more than two hours. This absorption stability shared consistency with the stability revealed by Bader *et al.* (1988), where DPD⁺ was produced by the oxidation of DPD with H₂O₂ in the existence of

peroxidase at pH 6.0. Accordingly, room temperature of the remaining experiments. temperature could be selected for the completion

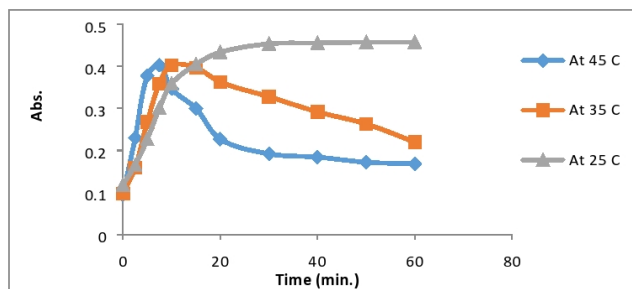


Fig. 5 Effect of time and temperature on the absorbance of the reaction product of Cr (VI) and DPD

Table (2) demonstrates the statistical treatments, viz. linear ranges, limits of detection, limits of quantification, calibration equation, and correlation coefficient for Cr (VI), of the calibration results.

The calculated stoichiometric coefficient (γ) of DPD•+ produced in the suggested DPD method was 1.192.

In an attempt to determine the precision and accuracy of the proposed method, the

researchers have duplicated four test trials to get calculations on the three different concentrations of the standard Cr (VI) solutions. The accuracy level of the method was tested with a relative error of (E %), whereas precision was checked with a relative standard deviation (RSD) of the same solutions. The results illustrated in Table 3 indicate that the method has exhibited good accuracy and precision.

Table (2) : Analytical data for the determination of Cr(VI)

Parameters	
λ_{max}	550 nm
Stability	1 h
Linear regression equation	$y = 0.4895x - 0.0047$
Correlation coefficient (R^2)	0.9997
Linear range (mg. L ⁻¹)	0.2-2
Limit of detection(mg. L ⁻¹)	0.0421
Limit of Quantification (mg. L ⁻¹)	0.127
Molar absorptivity(L.mol ⁻¹ cm ⁻¹)	2.5449×10^4
Sandell's sensitivity(mg.cm ⁻²)	0.028
stoichiometric factor γ	1.192

Table (3): Accuracy and precision of the present method

Compound	Conc. of Cr(VI) (mg. L ⁻¹)	Mean (abs)	E (%)	SD	RSD%
chromium(VI)	0.4	0.221	+3.70%	0.015	0.068
	1.0	0.362	+1.69	0.002	0.007
	1.6	0.542	-1.45%	0.003	0.006

4 INTERFERENCES

To assess the analytical applicability of the method used for determining Cr(VI), the effect of some interfering substances, that could be

found in the water, was tested by analyzing a standard solution of Cr(VI) (0.8 mg. L⁻¹) with the addition of increasing amounts of interfering

ions. The tolerable concentration ratios pertinent to (0.8 mg. L⁻¹) of Cr(VI) for interference at (± 5) % level are listed in Table (4).

Table (4) : Tolerance of non-target species on determining 10 ppm of Cr(VI)

Ion	Tolerance level (mg. L ⁻¹)	Ion	Tolerance level (mg. L ⁻¹)	Ion	Tolerance level (mg. L ⁻¹)
Al ³⁺	100	Cd ²⁺	100	Oxalate	100
Ca ²⁺	80	Ba ²⁺	100	Sulfate	100
Cr(III)	100	Mn ²⁺	100	Chloride	40
Fe ²⁺	80	IO ₃ ⁻	100	Nitrate	100
Na ⁺	100	HCO ₃ ⁻	100	PO ₄ ³⁻	100
Pb ²⁺	100	F ⁻	100	Acetate	100
Ni ²⁺	60	CO ₃ ²⁻	100	EDTA	100
Cu ²⁺	20	Tartarate	100		
Mg ²⁺	100	Sulphite	100		

5 APPLICATION

The accuracy of the proposed method was evaluated on the basis of the analysis of the water samples. The procedure was successfully applied to determine Cr(VI) in both Synthetically prepared Wastewater, and tap water samples by means of the standard method

as (2, 4, 6, 8, and 12 mg .L⁻¹ of Cr(VI) were added to water samples (Fig. 6). Table 5 shows that the slope of the aqueous standard and the standard addition graphs is identical. This means that there was no interference by the water sample matrix.

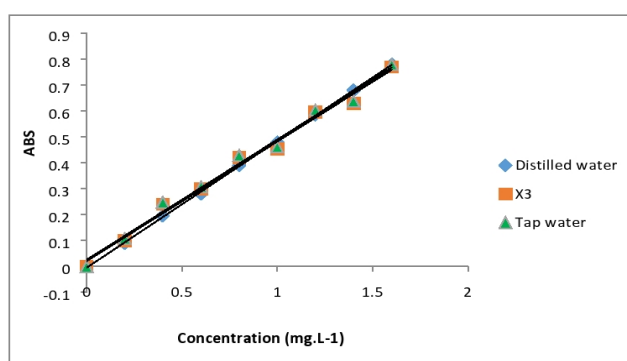


Fig. 6 Standard addition calibration graph

Table (5) : Analytical data of the standard addition calibration graph.

Sample	Linear regression equation	Correlation coefficient	Molar absorptivity liter. mol ⁻¹ cm ⁻¹
Standard Cr(VI) solution+ distilled water	Y= 0.4895X – 0.0047	0.9997	2.5449x 10 ⁴
Standard Cr(VI) solution+ distilled water + X ₃	Y= 0.4615X – 0.0208	0.9893	2.3991x10 ⁴
Standard Cr(VI) solution + tap water	Y= 0.4641X – 0.0258	0.9888	2.4129x10 ⁴

Table (6): Analytical results of Cr (VI) determination in synthetic and tap water samples.

Sample	Proposed method				Reference method			
	Added (mg. L ⁻¹)	Found (mg. L ⁻¹)	Recovery (%)	S.D. (%)	Added (mg. L ⁻¹)	Found (mg. L ⁻¹)	Recovery (%)	S.D. (%)
Synthetic sample X ₁	8	8.13	101.6±0.21	0.10	8	7.86	98.25±0.4	0.22

Synthetic sample X ₂	8	8.99	99.9±0.55	0.26	8	8.87	99.18±0.3	0.16
							4	
Tap water sample	8	8.50	99.5±0.21	0.1	8	8.31	98.2±0.21	0.1
	-----	0.44	-----		-----	0.45		

For the purpose of comparison, the reference method was used for analyzing the samples (Suvardhan, et al, 2005) and came out with the results presented in Table (6). The results demonstrate a strong agreement between the results arrived at by the proposed method and those of the reference method.

The results of the suggested method and the reference method have been put into comparison by means of the F-test and t-test. The comparison outlines no significant dissimilarities between the two methods in terms of accuracy and precision (t-calculated = 0.72 < t-table = 2.31 and F-test calculated = 3.52 < F-table = 5.05 with a limit of confidence of 95 %).

6 CONCLUSION

The proposed method is based on an oxidation-reduction coloring reaction where Cr (VI) can oxidize the DPD reagent to form a red-colored water-soluble product (DPD^{•+}) at pH 4.39. The product can remain stable for more than two hours and have the maximum absorption at 551 nm. The DPD method adopted to determine the trace Cr (VI) concentration in the water samples has proved to be beneficial as Cr (VI) reacts very rapidly with DPD. The suggested process is also very easy for measuring the concentration of Cr (VI) in water and requires a cheap UV spectrometer and low-cost reagents. It is further quite economical for measuring Cr (VI). Also, the DPD method is highly sensitive ($2.5449 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) and more suitable for low Cr (VI) concentrations in water (0.2 – 2 mg.L⁻¹). Finally, the DPD method is accurate and suitable for measuring the Cr (VI) concentrations in the synthetic and natural water samples that contain a number of colored substances.

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