Detection of Methylene Blue from textile by Differential Pulse Voltammetry Using Cobalt Hexacyanoferrate Modified Carbon Paste Electrode

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Abstract

Aim: Detection of Methylene Blue from textile waste water by Differential Pulse Voltammetry Using Cobalt Hexacyanoferrate Modified Carbon Paste Electrode

Study Design: Modified carbon paste electrode (CPE) by cobalt hexacyanoferrate (CoHCF) was prepared and sensitivity of prepared electrode was analyzed

Place and Duration: Wollega University, Nekemte, Ethiopia and ten months for experimental session

Methodology: Carbon paste electrode was prepared and modified by cobalt hexacyanoferrate (CoHCF) and the detection limit of the method were analyzed through differential pulse Voltammetry.

Result: The proposed method was successfully applied for the assay of methylene blue in textile waste water samples. On prepared electrode 1.222×10^{-4} M, 1.214×10^{-4} M and 1.217×10^{-4} M Methylene blue was detected in textile effluent at three sample sites and 100.5-104.5 % of recovered was calculated.

Conclusion: The prepared modified electrode was efficiently detects 1.053×10^{-6} limit of detection.

1. Introduction

Waste water contain a wider variety of materials of both organic and inorganic nature including toxic substances which are usually discharged without treatment into the surface water such as rivers, streams,lakes or into oceans or on land from textile influents. From these influents coloured substance is the most common water pollutant. They find their way into the water by the discharge of dyes from different industries such as: paper and pulp industries, textile industries, tanning industries and many other industries [1, 2, 3].

The textile dyeing industry consumes large quantities of water and produces large volumes of wastewater from different steps in the dyeing and finishing processes. Wastewater from printing and dyeing units is often rich in color, containing residues of reactive dyes and chemicals, and requires proper treatment before being released into the environment. Unfortunately, dyes are unfavorable from an ecological point of view, because the effluents generated are heavily colored, contain high concentrations of salts, and exhibit high biological oxygen demand/chemical oxygen demand (BOD/COD) values [4].

In the recent years, growing concern and awareness about issues on environment have brought together both analytical and material science researchers to investigate appropriate process or method in removing and monitoring various pollutants worldwide [5]. But many of treatment methods for removal of dyes from industrial effluents do not operated at low concentration of coloured compounds. Special measures are necessary to be taken to remove them from the effluents [6]. Modified electrode has got attention to measure the minimum possible detection limits and for this study, cobalt hexacyanoferrate modified carbon paste electrode was used to determine the possible detection limits of methylene blue from textile waste water.

2. Materials and Methods

2.1. Materials and Chemicals

The electrochemical experiments were carried out by using materials, three-electrode system containing Ag/AgCl as a reference electrode, platinum wire as a counter electrode and unmodified carbon paste electrode (UMCPE) or CoHCF, Voltammetric (BAS 50W)analyzer, Dell Pentium personal computer. Digital pH meter (353 ATC) and reagents and chemicals used were Methylene Blue (ORG, United Kingdom), Alizarin (1, 2- dihydroxyanthraquinone) (Kiran Light, India), Graphite powder (ORG, India), paraffin oil (Nice, India), di-sodium hydrogen orthophosphate anhydrous (LABMERK CHEM., India), sodium dihydrogen orthophosphate (BLULUX), Sodium Hydroxide (BAHADURGARH, India), Phosphoric Acid (Nice, India) Potassium Chloride (BAHADURGARH, India), Cobalt(II) Chloride (Kiran Light, India), Potassium Hexacyanoferrate (III) (Kiran Light, India), Potassium Nitrate (Nice, India) and methanol (nice, India) were used in the experiment.

2.2. Synthesis of Cobalt (II) Hexacyanoferrate (III)

Precipitation of Cobalt (II) Hexacyanoferrate (III) was prepared by dissolving 4.12 g (0.125M) potassium hexacyanoferrate (III) and 5.95 g (0.25M) cobalt (II) chloride in 100 mL 0.5M potassium Chloride solution. The precipitate obtained was filtered by 541 Whatmanfilter paper and washed with distilled water five times. The precipitate was dried in an oven at $60\,^0C$ overnight.

2.3. Preparation of Working Electrode

2.3.1. Preparation of Bare Carbon Paste Electrode (BCPE)

The bare carbon paste electrode (BCPE) was prepared by thoroughly mixing 2.4 g of graphite powder with 1 ml of paraffin oil with mortar and pestle for 30 minutes. The optimized composition of the paste was 75% (w/w) graphite powder and 25% (w/w) paraffin oil. The homogenized mixture was allowed to rest at room temperature for 24 hours. Then the carbon paste was packed into the cavity of a syringe and smoothed on a clean paper until it had a shiny appearance. The electrode body was constructed by pressing a small rod inside a tip and a thin copper wire was inserted through the opposite end of the syringe to establish electrical contact.

3.3.2 Preparation of Modified Carbon Paste Electrode (MCPE)

Modification of carbon paste electrode was achieved by carefully mixing 1.92 g (60% w/w) graphite powder with 0.48 g (15% w/w) Cobalt hexacyanoferrate (CoHCF) and 1ml (25% w/w)of paraffin oil in a mortar with pestle for 30 minutes, until a uniformly wetted paste was obtained. The homogenized mixture was allowed to rest at room temperature for 24 hours. The modified carbon pastewas packed into an electrode body, consisting of plastic syringe equipped with copper wire serving as an electric contact. The electrode surface was smoothed by simple extrusion of small amount of paste from the tip of electrode surface.

2.4. Method Selectivity Test

Selectivity was tested in the mixture of 20 % of methanol and 80 % of phosphate buffer solution. 0.0024 g (0.1mM) of Alizarin was dissolved in the 100 ml of volumetric flask. With the same concentration of Alizarin solution different concentration of Methylene blue was prepared in 25 ml of volumetric flask.

2.5. Sample Preparation of Methylene Blue ($C_{16}H_{18}ClN_3S.2H_2O$)

Textile waste water was taken from three sites of textile factory. Then the sample was transported to laboratory and adjusted to the optimized pH (7.5). From each of the solution 15 ml was taken into three different cells for the measurement and the average of the three measurements were used. Differential pulse voltammograms responses were recorded in the potential range between -600 and +200 mV Vs Ag/AgCl. The concentration of Methylene Blue in the samples was determined from the calibration curve of the analyte.

3. Results and Discussions

3.1 Effect of Electrode Composition

The working electrode composition strongly influences the voltammetric response of the electrode in determination of the analyte [7]. The effect of the amount of CoHCF in the carbon paste electrode on the voltammetric response has been studied. In order to modify carbon paste electrode, amount of CoHCF was verified as depicted in the Figure1. The peak current of the analyte was increased with increasing amount of CoHCF in composition up to 15% (w/w). For CoHCF amount higher than 15% (w/w), the peak current decreased significantly. This occurs due to a decrease in the graphite content in the paste. The best carbon paste electrode composition was found at 15% (w/w) CoHCF, 60% (w/w) graphite and 25% (w/w) paraffin oil.
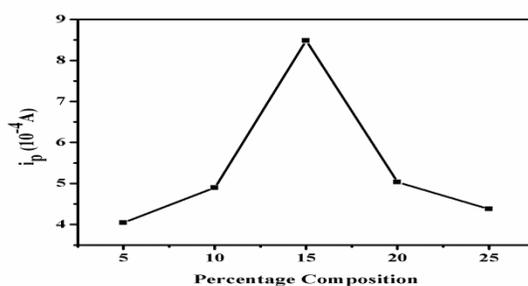

Figure 1: Effect of electrode composition on anodic peak current of 1mM Methylene Blue in 0.05M phosphate buffer solution, ranging from 5 to 25% CoHCF modifier at a scan rate 50 mVs^{-1}.

3.2 Effect of pH

The effect of pH on the anodic peak current was investigated on differential pulse voltammetry in the solution containing 1 mM Methylene blue over a pH range of 5 to 10. The electrochemical

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107 behavior of the carbon paste electrode modified with CoHCF was studied in this pH towards the

108 oxidation and reduction of Methylene blue in the 0.05M phosphate buffer solution. The graph of

109 the anodic peak current as a function of different pH values at CoHCF in 0.05M phosphate buffer

110 solution is depicted in Figure 2.

111 The anodic peak current was increased with increasing pH from 5 to 7.5 and decreased at higher

112 pH values. The electrode was not stable and the results were not reproducible at higher pH values

113 as similarly reported [8, 9, 10]. The best sensitive and sharp shape peak of the voltammogram was

114 observed at pH 7.5 and suggested as optimum pH value and used for further studies.
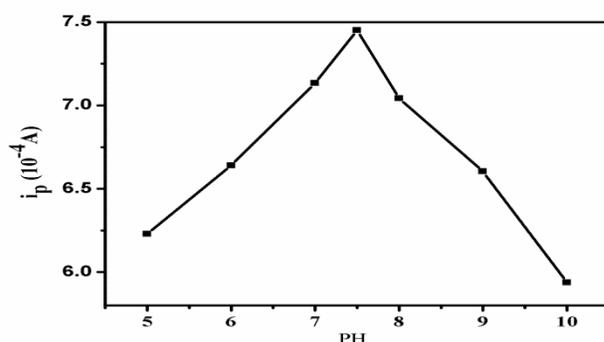
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116 **Figure 2**: Effect of variation of pH on the anodic peak current of 1mM Methylene blue in 0.05M

117 Phosphate buffer at CoHCF modified carbon paste electrode at a scan rate 50 mVs^{-1}.

118 ## 3.3. Electrochemical Behaviors of Methylene Blue on CoHCF/MCPE

119 Cobalt hexacyanoferrate modified carbon paste electrode was investigated with differential pulse

120 voltammetric techniques. The oxidation peak potential shifts towards negative value indicating that

121 the CoHCF modified CPE accelerate the electron transfer reaction at the electrode surface. The

122 electrode was further studied by differential pulse voltammetry for the detection of Methylene blue

123 in the potential range -600 mV to 200mV.

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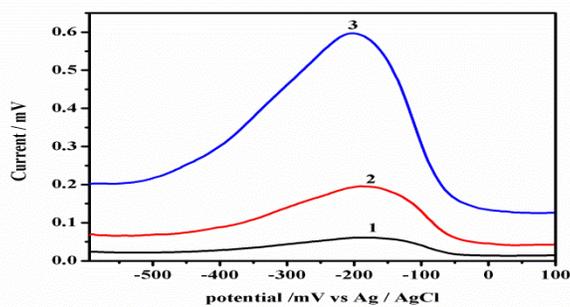
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125 **Figure 3**: Differential pulse voltammograms of (1) in the absence of Methylene blue (2)
126 unmodified carbon paste Electrode in the presence of 1mM Methylene blue and (3)
127 CoHCF modified Carbon paste electrode in the presence of 1mM Methylene blue in
128 0.05M PBS of pH 7.5 at a scan rate of 50mVs^{-1}.

129 **3.3.1   Differential Pulse Voltammetric Parameters**
130 **i. Differential Pulse Amplitude**

131 The influence of the pulse amplitude on the peak current was investigated between 20 to 130 mV
132 by 10 intervals at 50 mVs^{-1}. From 20 to 100mV separation gap between the consecutive peaks is
133 linearly increases while at higher pulse amplitude (above 100 mV) linear increment was changed
134 as indicated in the figure 4. 100 mV pulse amplitude was chosen for its sharpness and invariability
135 situation for further studies as optimum value.
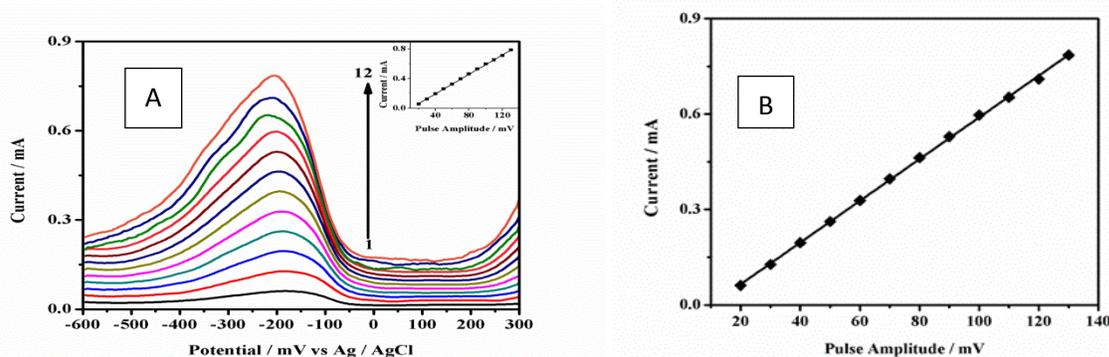
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137 **Figure 4 (A):** Differential pulse voltammogram of 1mM Methylene blue in 0.05 M PBS of pH 7.5
138 at CoHCF modified Carbon paste electrode at a scan rate 50 mVs^{-1} and different pulse
139 amplitudes of (1)20; (2) 30; (3) 40; (4) 50; (5) 60; (6) 70; (7) 80; (8) 90; (9) 100; (10)
140 110; (11) 120 and (12) 130 mV.
141 **(B)**. Effect of pulse amplitude on anodic peak currents of 1 mM Methylene blue in 0.05 M PBS
142 of pH 7.5.

6

143 **ii. Differential Pulse Period**

144 The influence of the pulse period on the peak current was investigated between 100 to 240 mV by

145 20 intervals. The peak heights fluctuates relatively with decrement as pulse period increases. On

146 the basis of peak sharpness and shift of potential peaks to negative value 200 mV was chosen as

147 optimum parameter for further studies. Lower pulse periods have highest peak current and broader

148 (noisy) peak. In order to minimize this problem the selection was concerned with the highest pulse

149 period as shown in the figure 5.

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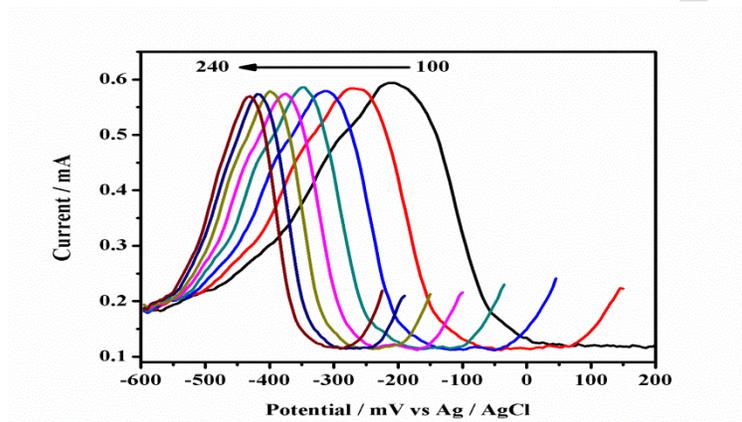
151 **Figure 5**: Differential pulse voltammogram of 1mM Methylene blue in 0.05 M PBS of pH 7.5 at

152 CoHCF modified Carbon paste electrode at a scan rate of 50 mVs^{-1} and different pulse

153 period (100, 120, 140, 160, 180, 200, 220, 240 ms) from right to left.

154 **iii. Differential Pulse Width**

155 Differential pulse width of peak current was investigated at pulse amplitude 100 mV, pulse period

156 200 mV and scan rate 50 mVs^{-1}. As pulse width increases from 20 to 40 mV, peak height

157 decreases in this interval. 25 mV was selected due to sharp peak as shown in figure 6.

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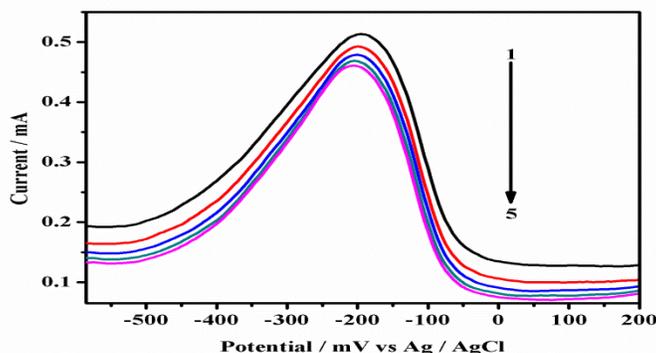
Figure 6: Differential pulse voltammograms of 1mM Methylene blue in 0.05 M PBS of pH 7.5 at CoHCF modified Carbon paste electrode at a scan rate 50 mVs^{-1} and different pulse width of (1) 20, (2) 25, (3) 30, (4) 35 and (5) 40 mV.

3.3.2   Effect of Concentration of methylene blue by differential pulse Voltammetry

As shown in the Figure7, the concentration of MB is lower than 10^{-5} M the peak currents were very small and shows closer peaks. However, in the range of 1×10^{-5} M to 1×10^{-3} M concentration MB the oxidation peak currents increase linearly. When the concentration of methylene blue was larger than 1×10^{-3} M the peak currents of oxidation peak are not linearly increasing, rather implies closer peaks and above 2.5×10^{-3} M became to decrease. This phenomenon indicates the formation of dimer or higher aggregate in higher concentration [11].
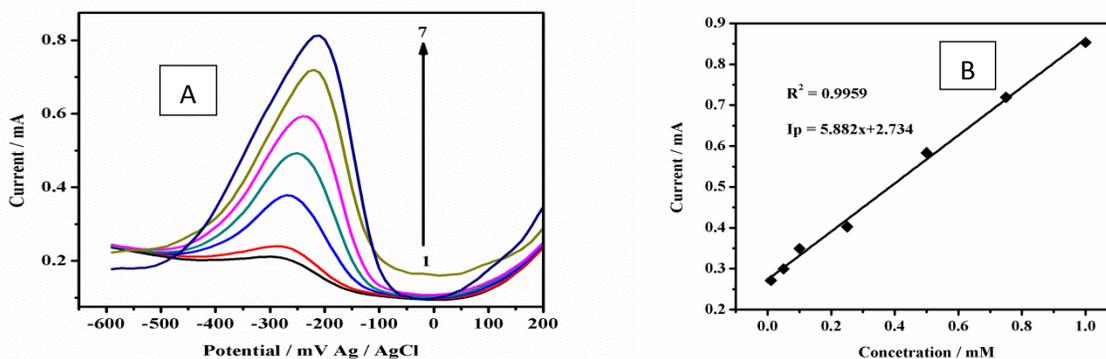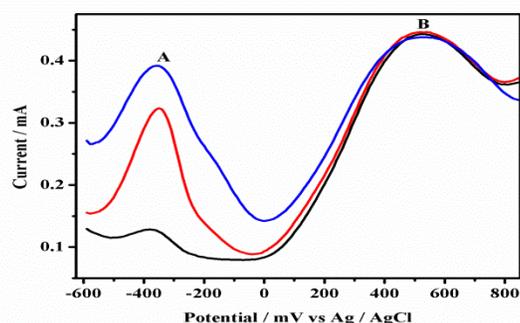

Figure 7 (A): Differential pulse voltammograms of different methylene blue concentrations: (1) 0.01 (2) 0.05; (3) 0.1; (4) 0.25; (5) 0.5, (6) 0.75 mM and (7) 1 mM in 0.05 M PBS of pH 7.5 at a scan rate of 50 mVs^{-1}and at CoHCFModified carbon paste electrode.

(B). Plot of differential pulse peak currents versus concentration of methylene blue from 0.01 to 1.0 mM.

175   As shown from Figure 7(B) the plot of differential pulse voltammetric peak current versus the

176   concentrations of Methylene blue was found to be linear in the range of 1×10^{-5} M to1×10^{-3}M with

177   a correlation coefficient of $R^2 = 0.9959$. The linear regression equation was found to be I_p (10^{-4}A)

178    $= 5.8824x+2.734$ with the detection limit of 1.053×10^{-6} and limit of quantification 3.511×10^{-6}

179   respectively. The enhancement of the differential pulse voltammograms peak current on increasing

180   methylene blue concentration was due to the presence of more ions in the solution adsorbed at the

181   surface of electrode [12, 13].

182   ### 3.3.3 Simultaneous Detection

183   Selectivity of the method towards the analyte was studied by Simultaneous detection of mixtures

184   of methylene blue and alizarin. Mixtures of MB in a concentration of 0.1 mM, 0.25 mM, 0.5 mM

185   and AZ 0.1 mM were prepared separately. As shown in the Figure 8 the change was observed on

186   its corresponding voltammogram. As concentration of MB increases from 0.1 mM to 0.5 mM the

187   peak height on current response also increases and Constant peak height was observed that

188   indicates that the same concentration of AZ was present in the solution.

189

190   **Figure 8:** Differential pulse voltammograms of different concentration 0.1 mM, .0.25 mM, 0.5

191   mM of MB (A) and 0.1 mM AZ

192   ### 3.3.4 Validation of the method

193   A calibration graph from the standard solution of MB according to the procedures described above

194   was constructed using DPV. In order to establish the DPV procedures, the dependence between the

195   MB concentration and peak current was conducted. The detection limits (LOD) and quantification

196   limits (LOQ) were calculated on the peak current using the following equations: LOD = 3s/m;

197   LOQ = 10s/m and selectivity is tested [14, 15].

198 **Table** 1: Regression data of the calibration lines for quantitative determination of Methylene Blue
199   in pH 7.5 phosphate buffer by means of Differential Pulse Voltammetry.

Parameters	DPV
Linearity range (M)	1×10^{-5} to 1×10^{-3}
Slope of calibration graph (A M^{-1})	5.8824×10^{-4}
Intercept (A)	2.734×10^{-4}
Correlation coefficient	0.9959
LOD	1.053×10^{-6}
LOQ	3.511×10^{-6}

200 **3.3.5 Method Validation and its application for the Determination of Methylene Blue**
201   **in textile Waste Water Samples**

202 In order to demonstrate the capability of the CoHCF modified carbon paste electrode for catalytic
203 oxidation of MB was examined in the real sample. The sensor used through differential pulse
204 voltammetry for the detection of methylene blue in textile waste water samples collected from
205 three sample site. From each 15 ml was taken into a cell and the current response was measured
206 and recorded. 500 µL of 7.5 mM standard solution was added. Amount of the analyte in the sample
207 was tested in the linear range of the standard solution concentration. From this linear range the
208 amount of analyte in the sample was calculated and summarized in Table 2.

209 Table 2: Assay results of MB in spiked textile waste water samples adopting the DPV technique.

Technique	Sample sites	Amount of MB detected	Methylene Blue Added		n	Level Determined	Average Recovery
		(10^{-4} M)	(10^{-3} M)	(µL)		(10^{-4} M)	(%)
	1	1.222	7.5	500	7	1.31	104.4
DPV	2	1.214	7.5	500	7	1.26	100.5
	3	1.217	7.5	500	7	1.28	103

210 Level: 1-before entering into the lagoon, 2- in the lagoon before neutralization, 3-in the lagoon
211 after neutralization

4. Conclusion

The electrochemical behavior of methylene blue on cobalt hexacyanoferrate modified carbon paste electrode (CoHCF / MCPE) has been investigated by differential pulse voltammetric technique. The effect of modifier, pH, and other parameters of the methods were optimized on their voltammetric responses. The oxidation peak potential of MB shifted towards negative value at the CoHCF modified carbon paste compared to the bare carbon paste electrode. Selectivity of the electrode towards the analyte was studied on a mixture of methylene blue and alizarin solution simultaneously. The limit of detection and the limit of quantification (LOQ) obtained were 1.053 µM and 3.511 µM, respectively. The developed method has proved its accuracy in MB detection in textile waste water, having the value of recovery of known quantities of MB ranging between 100.5 % and 104.5 %.

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