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

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Abstract

Modified carbon paste electrode (CPE) by cobalt hexacyanoferrate (CoHCF) was prepared and sensitivity of prepared electrode was analyzed by differential pulse voltammetry.The electrochemical behavior of methylene blue on cobalt hexacyanoferrate modified carbon paste electrode (CoHCF / MCPE) has been investigated by differential pulse voltammetric technique. Also the detection limit of modified electrode was investigated on methylene blue dyes from textile industrial waste water. By 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.The prepared modified electrode was efficiently detects 1.053 $\text{x}10^{-6}$ limit of detection.

Key words: Cobalt hexacynoferrate; Differential pulse voltammetry; Methylene blue; Modified Carbon paste electrode;

1. Introduction

Carbon electrodes have got advantages such as a wide potential window, low background current, chemical inertness and low cost that has resulted in their wide use in electrochemical detections. Among the carbon electrodes, the carbon paste electrode (CPE) has a particular importance. Thehigh speed of preparation, new reproducible surface, low residual current, porous surface and low cost are some advantages of CPEs over all other carbon electrodes. The development of carbon paste electrodes in electrochemistry and electro-analysis has been recently reviewed [1]. Because of the simplepreparation and easy renewal of the surface, carbon paste has been used extensively as a working electrode for a variety of electrochemical applications. Therefore, the CPE can provide a suitable electrode substrate for preparation of modified electrodes. Chemically modified electrodes are extensively applied in the electrochemical determination of a wide variety of electroactive species as a sensitive and selective analytical method. One of the most important properties of modified electrodes, in comparison to unmodified electrodes, has been their ability to catalyze the electrode process by a significant decrease in the necessary over potential [1,2]. Several researchers have reported the use of chemically modified electrodes (CMEs) in electro-analysis, using differential pulse techniques. Thus, electroanalytical technique less sensitive to the effects of matrix interferences, a property which characterizes its success in electro-analysis. CMEs have several advantages such as low background current, wide range of usable potential, rapid renewability and easy fabrication [3].Modification of electrode surfaces with electroactive materials is an important and interesting area of research in electrochemistry. Various organic and inorganic modifiers have been immobilized on electrode surfaces to prepare chemically modified electrodes. Among the inorganic materials, transition metal hexacyanoferrates (MeHCF) have been studied extensively because of their outstanding properties [4]. Among the carbon-based electrodes that can be modified not only on the surface but also in bulk during their preparation, carbon paste electrodes (CPE) are belong to the most frequent choice. For modifications, various organic and inorganic compounds can be employed, as modifiers and mediators [5].The formation and properties of cobalt hexacyanoferrate films are dependent on the cation selected. Cobalt hexacyanoferrate modified film electrodes have been synthesized from various cation aqueous solutions. These results have been concerned with analytical applications of Electrocatalytic measurements, and with the electrochemical oxidation or reduction of electroactive compounds [6].

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. From these influents colored substance is the most common water pollutant. 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 [7-10].

One of the high consuming materials in the dye industry is methylene blue (MB) which is used for cotton and silk painting.Methylene blue ($C_{16}H_{18}ClN_3S{\cdot}3H_2O$)is chemical group ofthiazine dye of the quinonoimine, and chemical name phenothiazin-5-ium, 3,7- bis(dimethylamino)-, chloride, trihydrate.It is a dark blue, crystalline powder with a copper-colored sheen, or green crystals with a bronze-colored sheen soluble in water, slightly soluble in alcohol.Also it has high affinity for zeolitic surfaces and is readily adsorbed when added to zeolite suspensions due to its redox properties [11].

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 ormethodin removing and monitoring various pollutants worldwide [12,13]. But many of treatment methods for removal of dyes from industrial effluents do not operated at low concentration of colored compounds. Special measures are necessary to be taken to remove them from the effluents and modified electrode has got attention to measure the minimum possible detection limits and for this study, CoHCF 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 Whatman filter paper and washed with distilled water five times. The precipitate was dried in an oven at 60 ^{0}C 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 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 syringeand smoothed on a clean paper until shiny appearance appear. 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.

2.3.2 Preparation of Modified Carbon Paste Electrode (MCPE)

Modification of carbon paste electrode was achieved by carefully mixing 1.92 g (60% w/w) graphitepowder with 0.48 g (15% w/w) CoHCF and 1ml (25% w/w) of paraffin oil in a mortar and 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 servingas 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 of synthesized electrode was tested in the mixture of 20 % of methanol and 80 % of phosphate buffer solution. 0.0024 g 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 Sampling methods for Preparation of methylene blue dye detection limit

Textile waste water was taken from three sites after dyeing process (before inter into waste water store, in the store but not neutralized and after neutralized) of textile factory.Then the sample was transported to laboratory and adjusted to the optimized pH (7.5). From each of the solution 15ml 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. From the differential pulse voltammetry response there is no voltammograms of other dyes present in the given potential range.

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 [14]. 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.

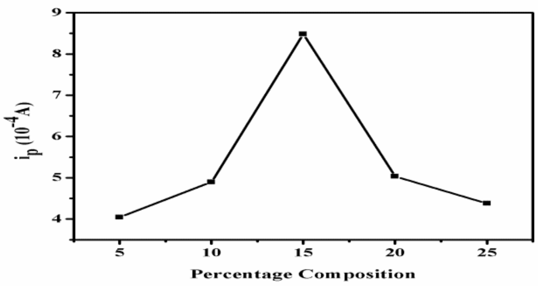

Figure1: Effect of electrode composition on anodic peak current of 1mM methylene blue in 0.05M phosphate buffer solution, ranging from 5 to 25% CoHCF modifier at a scan rate $50mVs^{-1}$.

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 behavior of the carbon paste electrode modified with CoHCF was studied in this pH towards the oxidation and reduction of methylene blue in the 0.05M phosphate buffer solution. The graph of the anodic peak current as a function of different pH values at CoHCF in 0.05M phosphate buffer solution is depicted in Figure 2.The anodic peak current was increased with increasing pH from 5-

7.5 and decreased at higher pH values.The electrode was not stable and the results were not reproducible at higher pH values as similarly reported [15-17]. The best sensitive and sharp speak shape of the voltammogram was observed at pH 7.5 and suggested as optimum pH value and used for further studies.

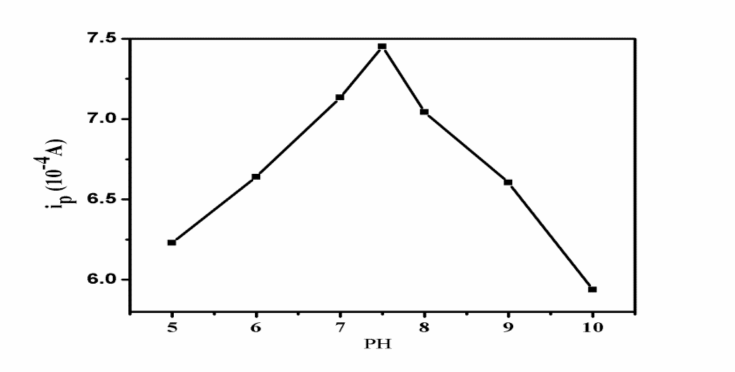

Figure2: Effect of variation of pH on the anodic peak current of 1mM methylene blue in 0.05M Phosphate buffer at CoHCF modified carbon paste electrode at a scan rate 50 mVs^{-1}.

3.3 Electrochemical Behaviors of Methylene Blue on CoHCF/MCPE

Cobalt hexacyanoferrate modified carbon paste electrode was investigated with differential pulse voltammetric techniques. The oxidationpeak potentialshifts towards negative value indicating that the CoHCF modified CPE accelerate the electron transfer reaction at the electrode surface.The electrode was further studied by differential pulse voltammetry for the detection of methylene blue in the potential range -600 mV to 200mV.

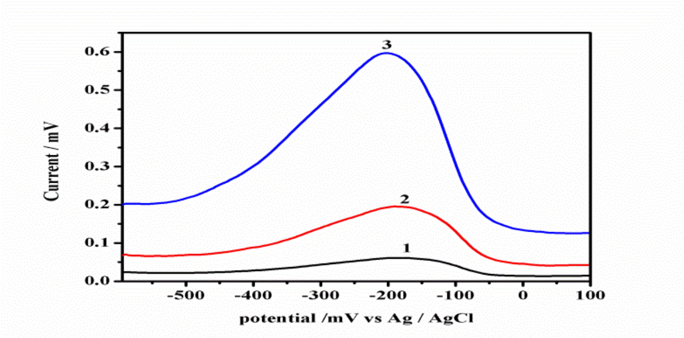

Figure3: Differential pulse voltammograms of (1) in the absence of methylene blue (2) unmodified carbon paste Electrode in the presence of 1mM methylene blue and (3) CoHCF modified Carbon paste electrode in the presence of 1mM methylene blue in 0.05M PBS of pH 7.5 at a scan rate of 50mVs^{-1}.

3.3.1 Differential Pulse Voltammetric Parameters

i. Differential Pulse Amplitude

The influence of the pulse amplitude on the peak current was investigated between 20 to 130mV by 10 intervals at 50 mVs^{-1}. From 20 to 100mV separation gap between the consecutive peaks is linearly increases while at higher pulse amplitude (above 100mV) linear increment was changedas indicated in the figure 4.100 mV, pulse amplitude was chosen for its sharpness and invariability situation for further studies as optimum value.

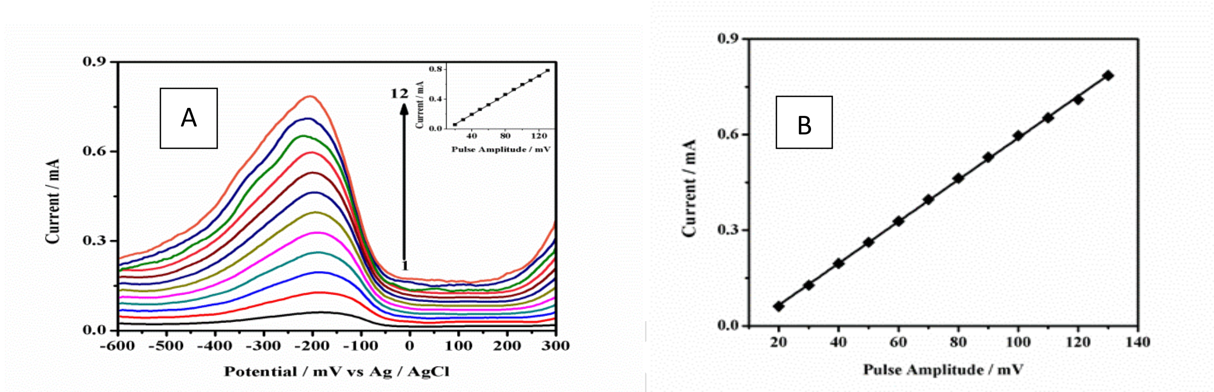

Figure 4(A): Differential pulse voltammogram of 1mM methylene blue in 0.05 M PBS of pH 7.5 at CoHCF modified carbon paste electrode at a scan rate 50 mVs^{-1} and different pulse amplitudes of (1)20; (2) 30; (3) 40; (4) 50; (5) 60; (6) 70; (7) 80; (8) 90; (9) 100; (10) 110; (11) 120 and (12) 130 mV.

(B): Effect of pulse amplitude on anodic peak currents of 1 mM methylene blue in 0.05 M PBS of pH 7.5.

ii. Differential Pulse Period

The influence of the pulse period on the peak current was investigated between 100 to 240 mV by 20 intervals.The peak heights fluctuates relatively with pulse period. On the basis of peak sharpness and shift of potential peaks to negative value 200mV was chosen as optimum parameter for further studies. Lower pulse periods have highest peak current and broader (noisy) peak. In order to minimize this problem the selection was concerned with the highest pulse period as shown in the figure 5.

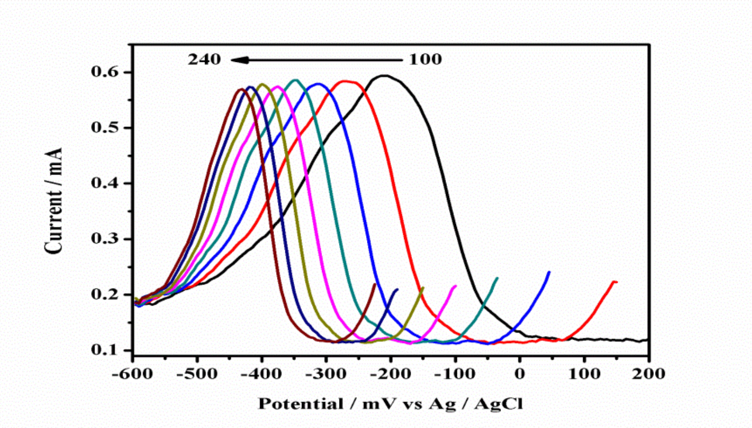

Figure5: Differential pulse voltammogram of 1mM methylene blue in 0.05 M PBS of pH 7.5 at CoHCF modified Carbon paste electrode; at a scan rate of 50 mVs^{-1} and different pulse period (100, 120, 140, 160, 180, 200, 220, 240 ms) from right to left.

iii. Differential Pulse Width

Differential pulse width of peak current was investigated at pulse amplitude 100 mV, pulse period 200 mV and scan rate 50 mVs^{-1}. As pulse width increases from 20 to 40 mV, peak height decreases in this interval. 25 mV was selected due to sharp peak as shown in figure 6.

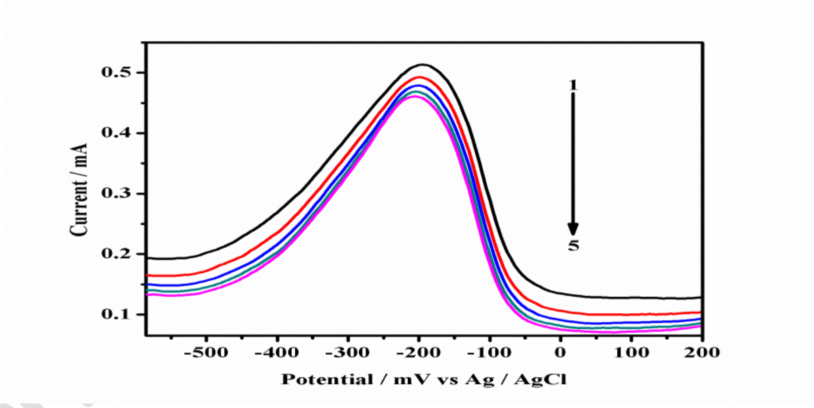

Figure6: Differential pulse voltammograms of 1mM methylene blue in 0.05 M PBS of pH 7.5 at CoHCFmodified Carbon paste electrode at a scan rate 50 mVs^{-1} and different pulse width of (1) 20, (2) 25, (3) 30, (4) 35 and (5) 40mV.

3.3.2 Effect of Concentration of methylene blue by differential pulse Voltammetry

As shown in the Figure7, the concentration of methylene blue was 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 methylene blue, the oxidation peak currents increase linearly with increasing concentration. When the concentration of methylene blue was larger than 1×10^{-3} M the peak currents of oxidation peak are not linearly increasing concentration, 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 [18].

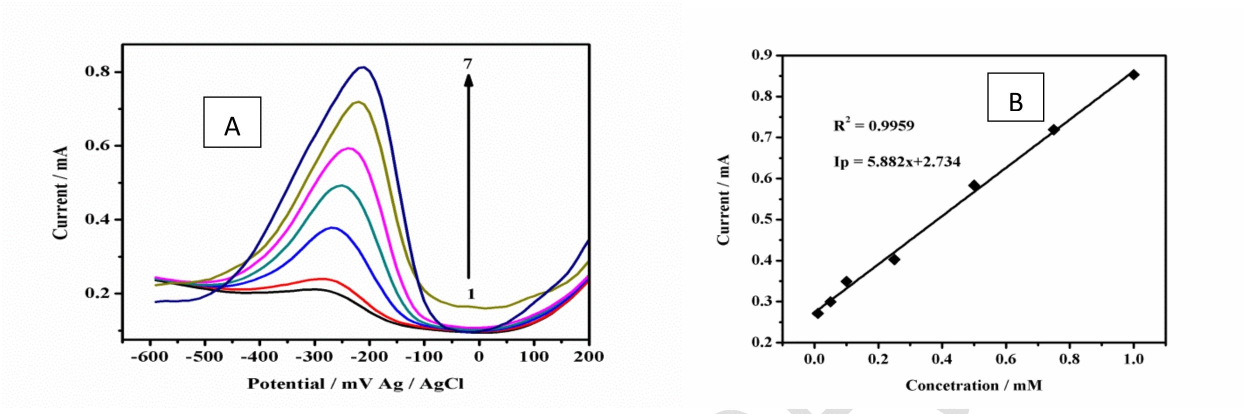

Figure7(A): Differential pulse voltammograms of different methylene blue concentrations: (1) 0.01 (2) 0.05; (3) 0.1; (4) 0.25; (5) 0.5, (6) 0.75 mM and (7) 1 mM in 0.05 M PBS of pH 7.5 at a scan rate of 50 $mVs^{-1}$and at CoHCF modified carbon paste electrode.

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

As shown from Figure 7(B) the plot of differential pulse voltammetric peak current versus the concentrations of methylene blue was found to be linear in the range of 1×10^{-5} M to1×10^{-3}M with a correlation coefficient of R^2 = 0.9959. The linear regression equation was found to be I_p (10^{-4}A) = 5.8824x+2.734 with the detection limit of 1.053×10^{-6}andlimit of quantification 3.511×10^{-6} respectively. The enhancement of the differential pulse voltammograms peak current on increasing methylene blue concentration was due to the presence of more ions in the solution adsorbed at the surface of electrode [19, 20].

3.3.3 Real sample Analysis

CoHCF modified carbon paste electrode for catalytic oxidation of methylene blue was examined in the real sample. The sensor used through differential pulse voltammetry for the detection of methylene blue in textile waste water samples as shown in figure 8.

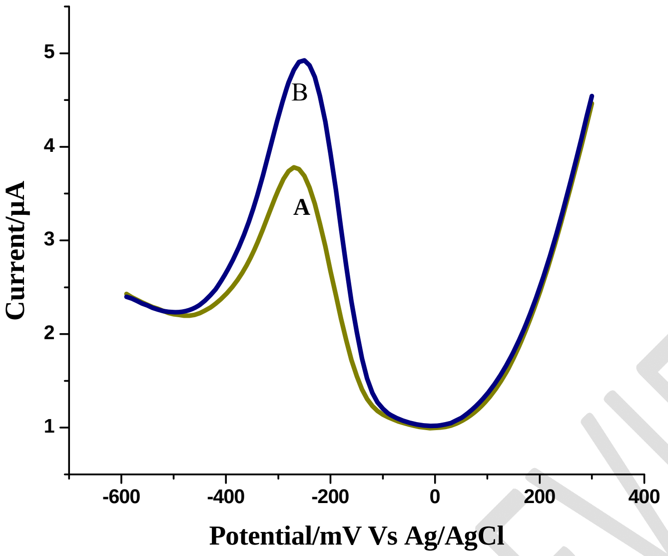

Figure8: Differential pulse voltammograms of methylene blue concentrations in real sample (A) before spiking and (B) after spiking in 0.05 M PBS of pH 7.5 at a scan rate of 50 mVs^{-1}and at CoHCF modified carbon paste electrode.

3.3.4 Simultaneous Detection

Selectivity of the methodtowards the analytewas studied by Simultaneous detection of mixtures of methylene blue and alizarin. Mixtures of methylene blue in a concentration of 0.1 mM, 0.25 mM, 0.5 mM and alizarin 0.1 mM were prepared separately. As shown in the Figure 8 the change was observed on its corresponding voltammogram. As concentration of methylene blue increases from 0.1 mM to 0.5 mM thepeakheight on current response also increases and constant peak heightwas observed that indicates that the same concentration of alizarinwas present in the solution.

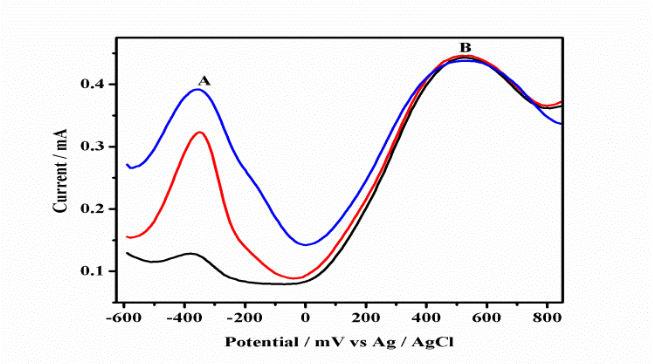

Figure9: Differential pulse voltammograms of different concentration 0.1 mM, .0.25 mM, 0.5 mMof methylene blue (A) and 0.1 mM alizarin

3.3.5 Validation of the method

A calibration graph from the standard solution of methylene blue according to the procedures described above was constructed using differential pulse voltammetry. In order to establish the Differential Pulse Voltammetry procedures, the dependence between the methylene blue concentration and peak current was conducted. The detection limits (LOD) and quantification limits (LOQ) were calculated on the peak current using the followingequations: LOD = 3s/m; LOQ = 10s/m and selectivity is tested [21, 22].

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

Parameters	DPV
Linearity range (M)	$1x10^{-5}$ to $1x10^{-3}$
Slope of calibration graph (A M^{-1})	$5.8824x10^{-4}$
Intercept (A)	$2.734\ x10^{-4}$
Correlation coefficient	0.9959
LOD	$1.053\ x10^{-6}$
LOQ	$3.511\ x10^{-6}$

3.3.6 Method Validation and its application for the Determination of Methylene blue in textile Waste Water Samples

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

Table 2: Assay results of methylene blue in spiked textile waste water samples adopting the differential pulse voltammetry technique.

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

Level: 1-before entering into the lagoon, 2- in the lagoon before neutralization, 3-in the lagoon after neutralization, n-number of trials for sample. DPV- differential pulse voltammetry

4. Conclusion

The synthesized CoHCF/MCPE) was investigated for its sensitivity and detection limits. Also, it showed better sensitive and detection limit as compared to bare carbon paste electrodes. The operational parameters like; effect of pH, and other parameters of the methods were optimized on their voltammetric responses. The oxidation peak potential of methylene blue 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) was obtained at 1.053 µM and 3.511 µM, respectively. The developed method showed better detection limit of methylene blue from textile waste water and percent of recovery from 100.5 % and 104.5%.

5. References

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