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# Voltammetric Analysis of Reactive Blue 49 Dye using Graphene Modified Glassy Carbon Electrode as Working Electrode

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ABSTRACT

The stock solution of reactive blue 49 (RB 49) made up 1000 ppm in mile pure water. The voltammetric behaviour of RB 49 has been studied in aqueous solution on glassy carbon and modified glassy carbon electrode. The influence of pH on the cyclic voltammetric behaviour of Reactive Blue 49 was studied from 1.0 to 13.0 at scan rate 50 mV/s. The maximum peak current response was found in pH 7.0. The cyclic voltammogram of RB 49 was reveled one anodic peak and one cathodic peak at potential around 731 mV and –846 mV vs Ag/AgCl. A systematic study of the experimental parameters that affect the anodic stripping voltammetric response was carried out. Maximum peak current conditions were arrived. Calibration curve was made under the maximum peak current conditions. The concentration range studied for the determination of 250 to 700 ppb. The lower limit of detection is 200 ppb for GC and 100 ppb for Graphine and the RSD 2.2% and 1.8% respectively. The suitability of this method for the quantisation of dye in textile industries effluents was also ascertained.

## 1. Introduction

In our country, textiles industry is one of the largest contributors to India's exports. At the same time this textile sector is considered as the most polluting sector by among the different human activities [1-3]. Every year million tons of dyes are produced all around the world. Due to the large volume of water consumption in textile industry, the production of huge volumes of wastewaters is unavoidable [4]. During the production of dyes, up to 50% of the dyes are lost which are disposed out in the effluents [5-7]. Dyes cause a lot of problems i.e. skin allergies, skin irritations, cancer, mutation, etc. Therefore the dye present in the effluents are needed to be removed before the effluent is discharged to the environment.

Dye is a coloured compound containing chromophore and auxochrome groups. While chromophore is responsible for dye colour and auxochrome group is responsible for dye-fibre reaction. Dyes are classified as various types such as acidic dye, basic dye, direct dye, azo dye, disperse dye, vat dye, mordant dye, and reactive dye, etc., [8, 9].

Among the various types of dyes, reactive dyes have been identified as the most problematic compounds in textile effluents as they are difficult to remove due to their high waer solubility and low exhaustion [10]. Most of the reactive dyes contain azo group as the chromophore, followed by the anthraquinone group. Reactive Blue 49 contains anthraquinone as the chromophore. Due to the long life of colour, cotton and silk can be dyed with this type of dye.

Dye present in the industrial effluents is generally removed by physical or chemical processes (i.e. adsorption, chemical transformation, incineration, electrocoagulation, photocatalysis or ozonation) and biological or enzymatic treatment. These methods are effective but rather costly [11].

Over the past 10 years, the electrochemical techniques are becoming an alternative wastewater treatment method and replacing the conventional processes, because many industrial processes produce toxic wastewaters, which are not easily biodegradable and requiring costly physical or physicochemical pretreatments [12-14].

The purpose of this work is to study the electrochemical behavior of an anthraquinone reactive dye, Reactive Blue 49 dye on glassy carbon and graphene modified glassy carbon electrode in order to evaluate some possibilities for destroying reactive dye based on anthraquinone groups in aqueous solution by electrochemical technology.

## 2. Experimental Methods

All reagents were of AR grade purchased commercially. The stock solution of Reactive Blue 49 was prepared by dissolving the substances in double distilled water purified from SG purification system. The supporting electrolyte (pHs) solutions were also prepared by same water. The pH values of the buffer solutions were measured by Hanna HI 2211 pH/ORP meter.

The electrochemical studies were carried out in exploratory and determination mode on a software connected CH Instruments Electrochemical Workstation (model CH 650C). The cell was made of glass, having a capacity of 15 mL and the Teflon made cell top was comprised of three separate holes for the insertion of electrodes viz. working electrode (Glassy Carbon, Graphene modified GCE), counter electrode(platinum foil) and reference electrode (Saturated calomel) . The cell setup is kept in a Ch Instrument Picoamp Booster and Faraday cage. The cell top also has the purging and blanketing facilities of nitrogen gas with separate tubes to remove oxygen gas. This setup enables to maintain an inert atmosphere above the sample solution throughout the experiment.

The surface of the glassy carbon electrode is apt to be contaminated by surface-active substances and other compounds. Thus the effective surface area and other properties may be changed. Hence, it is necessary to treat the electrode before use, if a good reproducibility is required. Well-known and accepted procedures for the treatment of glassy carbon electrode were adopted. First the electrode was washed with water-ethanol-ammonia mixture followed by ethanol-ammonia, ethanol-acetic acid and ethyl acetate-ethanol mixture. It was then washed with distilled water and trichloro ethylene. With this method, oxides and surface-active substances and organic compounds were removed from the electrode surface. When electrode surface seriously contaminated, the most effective and, at the same time the simplest way employed for the renewal of the surface was to remove a layer of it by rubbing with 0.05 μM of fine

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powder of γ-$Al_2O_3$. After rubbing, the electrode was wiped with a filter paper and then rinsed with water. The fine particles of alumina adsorbed on glassy carbon electrode were removed by ultrasonication in the presence of water. Then, the electrode was thoroughly degreased with trichoro ethylene and washed with deionized water and acetone.

### *2.1 Modification of the Electrodes*

A GCE (3 mm diameter) was polished using 1.0 and 0.05 mm alumina slurry and rinsed thoroughly with Milli- Q water. Ultrasonic agitation for 30 min of 2.0 mg of purchased nanostructured graphene in 2 mL of water gave a homogeneous solution. 20 μL of this solution was placed on the GCE surface. The electrode was then dried at room temperature to obtain a graphene modified GCE.

## 3. Results and Discussion

### *3.1 Electrochemical Studies*

#### *3.1.1 Effect of pH*

The cyclic voltammetric of RB49 was studied at different scan rates, concentrations and pH using glassy carbon electrode (GCE), graphene modified GCE and the respective cyclic voltammograms were recorded. The effect of pH was studied by measuring and comparing the peak potentials and current.

The influence of pH on CV of 200 ppm RB49 at 100 mV/sec scan rate was studied. RB49 exhibit characteristic response in the acidic, neutral and basic pH media. The studies were carried out in the pH region 1.0 to 13.0. In all the pH range 1.0 – 13.0 one anodic peak and one cathodic peak in the reverse scan were observed. In all these cases, the intense and sharp anodic peak appeared in the region 700-900 mV. Due to the high current, the anodic peak in the above region was considered for comparisons. The plot of peak current versus pH was given in Fig. 1. From the figure, it is clear that the anodic current decreased with increase in pH upto pH 4.0 then increases upto pH 7.0 and then slowly decreased in basic medium. This indicates that the rate of oxidation of RB49 is decreased in basic pH. It is concluded that pH 7.0 is the most suitable pH for analytical studies due to maximum peak current. The Fig. 2 represents the peak potential versus pH plot. The peak potential increases with increase in pH upto 7.0 again decreased in basic media suggesting that the oxidation is facilitated in neutral media. The energy required for the oxidation decreases with increase in pH. The lowest oxidation potential i.e. minimum energy requirement is seen at pH 7.0. Facilitation of oxidation at basic pH due to the availability of lesser proton is a common expectation for anodic reaction of organics.

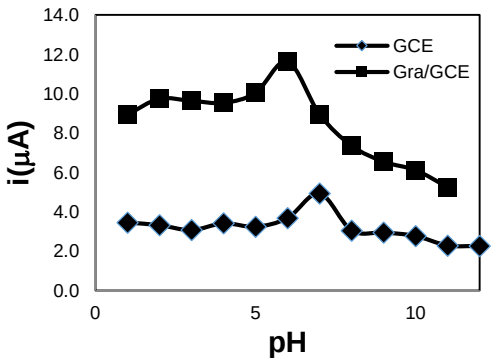


**Fig. 1** Curve of peak current vs pH

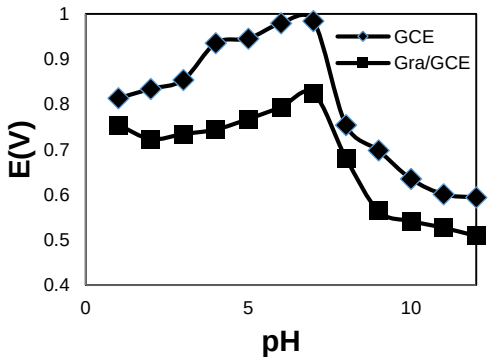


**Fig. 2** Curve of peak potential vs pH

#### *3.1.2 Effect of Scan Rate and Concentration*

The scan rate was varied from 25 to 500 mV/s at the four representative pH and the cyclic voltammograms were recorded for 200 ppm RB49. The plots of peak current versus scan rate, square root of scan rate and the logarithmic plot of current versus scan rate were made. The concentration of the substrate was varied from 50 to 300 ppm at a constant scan rate 100 mV/s. The plot of current versus concentration of RB49 was made. The electrochemical behaviour of RB49 on GCE and graphene modified GCE.

The cyclic voltammetric behaviour of RB49 at pH 7.0 on glassy carbon electrode and graphene modified GCE at a scan rate 100 mV/s was given in Figs. 3 and 4. One anodic peak at 780 mV and one cathodic peak at –718 mV in the reverse scan were noticed.

The anodic peak potential shifts anodically with the increase in scan rate. The anodic peak current versus scan rate plot resulted in a slightly curved line whereas the current versus square root of scan rate plot resulted in a straight line with $R^2$ value 0.9929. The logarithmic plot of current versus scan rate is a straight line with slope value 0.4965. This anodic peak didn't show any reversible peak in the reverse scan. No characteristic peak satisfying the criteria for reversibility was noticed. The Epa versus log υ plot was made. This plot resulted in a straight line and the αn value was calculated from the slope of the linear plot. The fractional value of α (0.545) indicates the oxidation of RB49 to be irreversible. All the above facts revealed that the oxidation of RB49 at pH 7.0 was irreversible and adsorption-controlled. The anodic peak potential and current resulted in the increasing trend with increase in concentration. The peak current versus concentration plot is linearity.

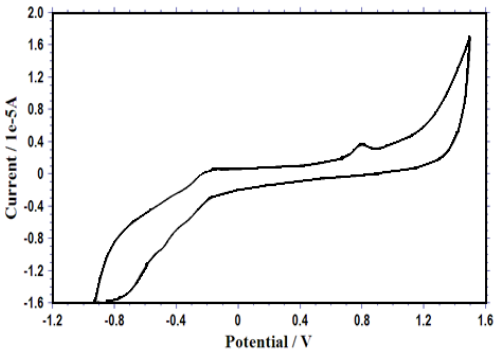


**Fig. 3** Cyclic voltammetric behavior of 200 ppm RB 49 on GCE at the scan rate 100 mV/s in pH 7.0

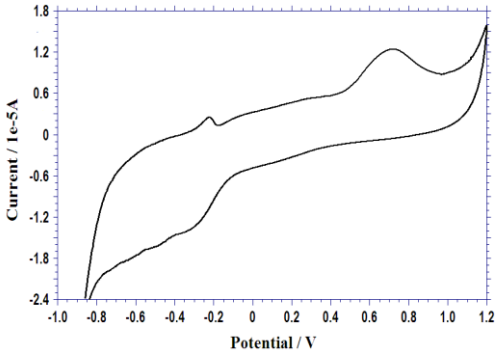


**Fig. 4** Cyclic voltammetric behavior of 200 ppm RB 49 on Graphene/GCE at the scan rate 100 mV/s in pH 7.0

### *3.2 Differential Pulse Stripping Voltammetry*

Having chosen the best pH (pH 7.0) trial experiments on GCE and modified GCE were carried out to optimize various parameters with the solution containing 300 ppb RB 49. The adsorptive stripping voltammetry of RB 49 was carried out on plain GCE and modified GCE at a positive potential and the stripping peak potential was close to the anodic oxidation potential observed in CV studies. This suggests the adsorptive accumulation and anodic stripping of the substrate. The factors affecting the electrode process were optimized and discussed as follows. Generally adsorptive stripping voltammetry involves two major steps. The analyte molecules were first accumulated by adsorption on the electrode surface from the bulk and then the accumulated molecules were stripped out giving specific signals. Hence, optimization of accumulation potential was done in the first part by fixing other parameters as in default setup. The effect of accumulation potential was studied by varying it from –800 to 500 mV. Maximum peak current was observed at 500 mV and it was fixed as the maximum peak current accumulation potential. The anion of the dye

adsorbed easily at a positive potential due to electrostatic attraction. The effect of deposition time on the stripping signal in the range 20 to 100 sec was studied and the peak current reached maximum value at 80 seconds. The initial scan potential is another important parameter as it confirms the non-faradaic nature of the pre concentration step. It also controls both the peak potential and peak current in the stripping voltammogram. The influence of initial potential on the peak current was studied by varying from –800 to 400 mV. Better response was observed at –800 mV. The pulse height was varied from 25 to 200 mV and the maximum value was obtained at 150 mV. The effect of pulse width was studied in between 25 to 200 msec and was found that maximum peak current was at 75 msec. Effect of scan increment was studied by varying it from 2 to 20 mV. The peak current was linearly dependent on the scan increment up to 17 mV. The maximum peak current was observed at the scan increment 17 mV and hence it was chosen as the best and optimized scan increment. After fixing the above parameters the peak current response on scan rate was also studied. The scan rate was varied from 20 to 120 mV/s. Highly resolved stripping response with maximum peak current was obtained at the scan rate 40 mV/s. Hence, it was taken as the optimum scan rate for studying the effect of the concentration.

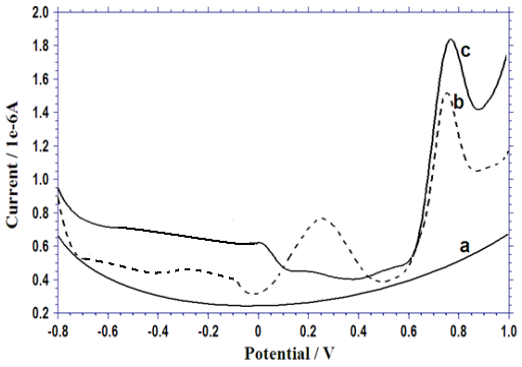


**Fig. 5** Differential pulse voltammetric behavior of a) Buffer on GCE b) 300 ppb RB 49 on GCE and b) 300 ppb RB 49 on Graphene/GCE under optimum experimental condition

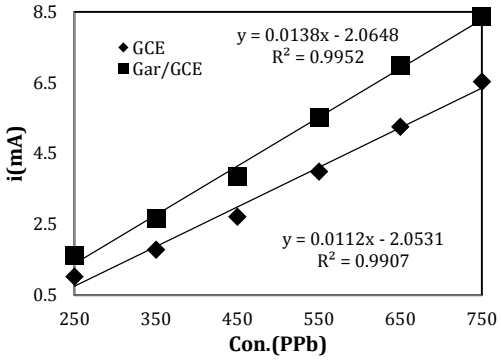


**Fig. 6** Calibration plot of behavior of RB 49 on GCE and Graphene/GCE under optimum experimental condition

*3.3 Analytical Characteristics*

The dependence of peak current on concentration was studied under the above fixed optimum parameters. The studies were carried out on glassy carbon electrode, and Graphene/GCE. One anodic peak is observed in both cases. A representative voltamogram is presented in Fig. 5. Experimental results showed that the peak current increased with increase in concentration of RB49 on both electrodes and calibration plots arrived for both electrodes are given Fig. 6. The concentration range studied for the determination of 250 to 700 ppb. The lower limit of detection is 200 ppb for GC and 100 ppb for graphine. The reproducibility of the stripping signal was realized in terms of relative standard deviation for ten identical measurements carried out at a concentration level of 300 ppb and the RSD values were 2.2% for GCE and 1.8% Graphene/GCE.

## 4. Conclusion

The cyclic voltammogaram of RB 49 is exhibits one anodic and one cathodic peak on GCE and modified GCE. The modified GCE shows good responds to RB49 in all pH media. But pH 7.0 presented higher peak current behavior it is selected for best pH for further studies. From DPSV grapheme coated GCE showed the lower level of detection 100 ppb than GC electrodes. This may be due higher accumulation of the dye on modified surface because of the correct pores available on the surface to accommodate the dye molecule.

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