



A Reliable Cyclic Voltammetry Technique for the Degradation of Salicylaldehyde: Electrode Kinetics

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ABSTRACT

Salicylaldehyde (SA) is used in numerous biological, pharmaceutical and industrial applications. Releasing effluents from these industries contaminates water. So the degradation of salicylaldehyde is necessitated. The electrochemical degradation of salicylaldehyde in buffered media was studied using the eco-friendly cyclic voltammetry (CV) technique on a platinum electrode at different scan rates. Kinetic and electrochemical parameters were evaluated for the reaction such as standard heterogeneous rate constant (k^0 , $2.468 \times 10^3 \text{ s}^{-1}$), anodic electron transfer rate constant (k_{ox} , $2.507 \times 10^3 \text{ s}^{-1}$), electron transfer coefficient of reaction (α , 0.673), and formal potential (E^0 , 1.0937) under the influence of scan rate. The nature of the reaction is found to be diffusion controlled. The concentration study in the range of 1 mM to 4 mM was calibrated. The limit of detection and the limit of quantification were calculated to be 0.0031 mM and 0.0103 mM respectively.

INTRODUCTION

Salicylaldehyde (SA) is used in numerous industrial, chemical and pharmaceutical fields such as dyes, fragrances, essential oils, drugs and biological applications (Alasmi & Merza 2017). It is mainly used for the production of coumarin. In addition salicylaldehyde is used as a precursor for aspirin. The Saligenin process is the main process for the production of salicylaldehyde (Pouramini & Moradi 2012). Also, it is naturally found in tomatoes, cinnamon, grapes, coffee, tea, and dairy products. Due to the extensive uses of salicylaldehyde, it becomes an organic pollutant and finds its path into the aqueous system through pharmaceutical and industrial fields (Wang et al. 2014). Several methods previously used for the degradation of salicylaldehyde such as colorimetric (Nonoyama et al. 1987), differential pulse polarographic (López et al. 1996), uv/spectroscopy (Matyasovszky et al. 2009), spectroelectrochemistry (Wang et al. 2014), cyclic and normal pulse voltammetry (Kiss et al. 2019), electrochemical (Kiss & Kunsági-Máté 2019) and also salicylaldehyde is determined in natural and treated water by applying GC-MS (Crompton 1999). In recent years, the increase of contaminants in water bodies has necessitated the need to develop cost-effective methods for their removal or degradation (Rasalingam et al. 2014). The electroanalytical technique is used for monitoring and trace level detection of pollutants in water (Martinez-Huitle & Ferro 2006). It

is a powerful analytical technique with high sensitivity, accuracy, precision, rapid response and low operating cost, which is used in the pharmaceutical industry, metal industry and environmental applications (Farghaly et al. 2014, Chatterjee 2017). Currently, voltammetry is well renowned and eco-friendly technique to investigate pollutants and other compounds (Nicholson & Shain 1964). It is widely employed for the determination and kinetic mechanism of the reaction (Allen & Larry 2001, Compton & Banks 2018). In the voltammetric technique, a platinum electrode (solid electrode) is usually a working electrode. Platinum is the most suitable choice of inert electrode for electroanalysis (Monk 2001) because it gives appropriate electron-transfer kinetics and a large anodic potential window range (Wang 2000).

In this work, we reported electro-oxidation of salicylaldehyde in aqueous media using the cyclic voltammetry technique. However, to the best of our knowledge salicylaldehyde has not yet been investigated in an aqueous solvent using these parameters.

MATERIALS AND METHODS

Materials

Salicylaldehyde was obtained from Sigma- Aldrich and used without further purification. A stock solution of SA was prepared in 30 % ethanol. Britton-Robinson (BR) buffer was

prepared with 0.04 M boric, phosphoric and acetic acids and 0.1 M KCl as the supporting electrolyte. All other chemicals used were of analytical grade. All solutions were prepared with doubled distilled water.

Instrumentation

An Autolab model PGSTAT 101 potentiostat/galvanostat 663 VA Stand (Metrohm AG, Netherlands) was used to perform the cyclic voltammetry (CV) technique. Electrochemical cell along with three-electrode setup is used in this technique. Pt disc electrode (PE) (0.031 cm^2) acted as working electrode (WE), Ag/AgCl/3M KCl electrode act as the reference electrode, and Pt wire acted as the counter electrode. The solution pH calculation was done using Elico LI 120 pH meter (Elico Ltd., India). In preparation for investigation, the working electrode was polished with alumina powder (particle size 0.05 mm) on a cloth polishing pad and washed with doubled distilled water. All the experiments have been performed at an ambient temperature of $25 \pm 1^\circ\text{C}$.

RESULTS AND DISCUSSION

Effect of pH

The electro-oxidation of 10 mM was studied over the pH range of 2.2-11.0 in Britton- Robinson (BR) buffer solution by cyclic voltammetry (Fig.1). However, the finest peak was observed on pH 2.2 (Acidic medium). Hence further experiment was performed in this range.

Cyclic Voltammetry Experiment of Salicylaldehyde (SA)

The electrochemical behavior of SA was recorded on the platinum electrode, using a cyclic voltammetry technique. The cyclic voltammogram was obtained for 10 mM SA at a scan rate of 20 mVs^{-1} , which shows a well-defined anodic peak at Pt electrode from potential window range +0.7 to +1.3 V Fig. 2(b). This peak indicates that the irreversible reaction occurred on the platinum electrode surface. On scanning the reverse direction there was no cathodic peak shown.

Influence of Scan Rate

The influence of scan rate on SA is examined at Pt electrode by using cyclic voltammetry method with different scan rates ranging from 20 mVs^{-1} - 90 mVs^{-1} (Fig. 3). As the scan rate was increased, the peak current (I_{pa}) for oxidation of SA was also increased.

The reversibility of electrochemical reaction rate is controlled by adsorption and diffusion, and it is dependent on two factors: I_p on $V^{1/2}$ and $\log I_p$ on $\log v$ (Nicholson 1965) (Fig. 3(a) and Fig. 3(b)). If the origin of the coordinates is not intercepted by the linear fit (Fig. 3(a)), the electrode process is diffusion-controlled and proceeded by chemical reaction (Wudarska et al.2013). At various scan rates (v) ranging from 0.02 to 0.09 Vs^{-1} , peak current(I_p) depends linearly on the square root of v (equation below):

$$I_p(\mu\text{A})= 147.32v^{1/2} (\text{V}^{1/2}\text{s}^{-1/2}) - 5.8517 (\text{r}=0.988)$$

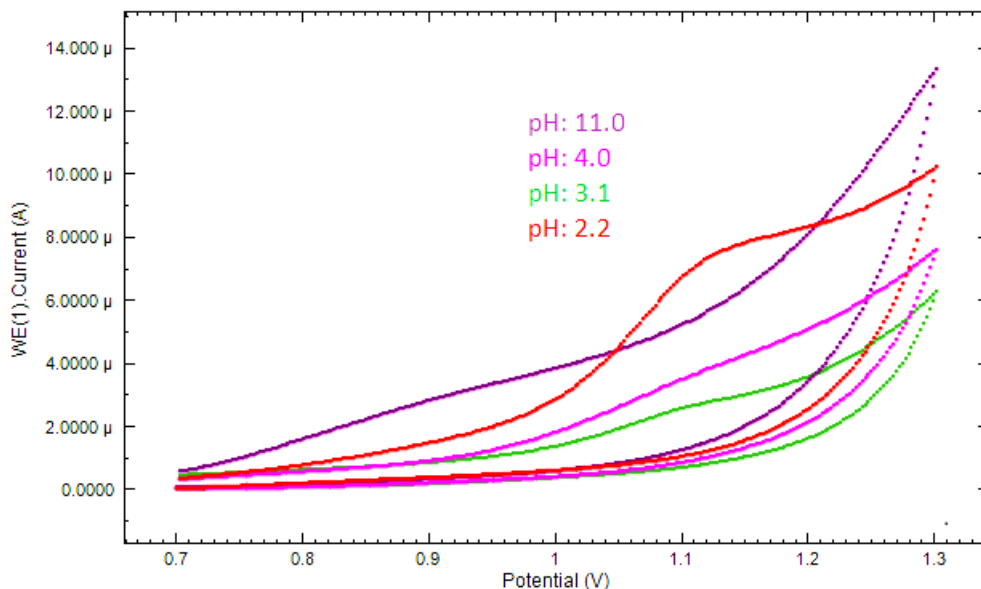


Fig. 1: Cyclic voltammograms of 10 mM SA at different pH values (a) 11.0, (b) 2.2, (c) 4.0, (d) 3.1

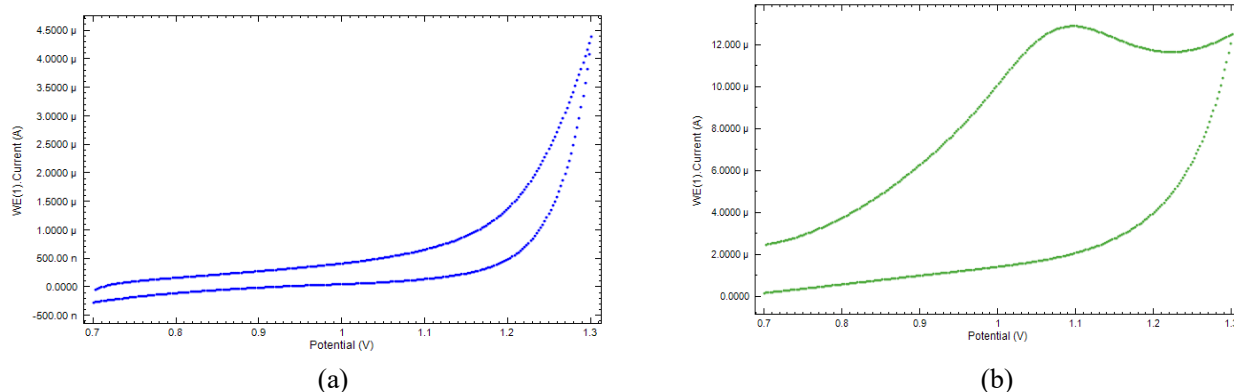


Fig. 2: Cyclic voltammogram for 10 mM SA on Pt electrode in 0.04 M BR buffer. (a) Blank (b) SA at scan rate (v) = 20 mVs^{-1}

Alternatively, a linear relationship was observed between $\log I_p$ and $\log v$ (Fig. 3(b)) corresponding to the equation.

$$\log I_p (\mu\text{A}) = 0.63 \log v (\text{Vs}^{-1}) + 2.2593 \quad (r=0.986)$$

The slope value of this linear fit (Fig. 3(b)) is 0.63. Therefore, according to Bard and Faulkner, and others (Allen & Ferry 2001), this process is only controlled by diffusion, which confirms that the electro-oxidation of SA was a diffusion-controlled reaction. With an increase in scan rate, the peak potential was observed in the range 0.02-0.09 Vs^{-1} as shown in Fig. 3(c). The relationship can be expressed as:

$$E_p (\text{V}) = 0.0468 \log v (\text{Vs}^{-1}) + 1.1768 \quad (r=0.970)$$

For irreversible electrode process, Laviron (1979) equation is given below to define E_p :

$$E_p = E^0 + (2.303RT / \alpha nF) \log(RT k^0 / \alpha nF) + (2.303RT / \alpha nF) \log v$$

Where E^0 is the formal standard redox potential, α is the transfer coefficient, n is the number of electrons transferred, k^0 is the standard heterogeneous rate constant of the reaction, and v is the scan rate. Thus, from the slope of the plot E_p vs $\log v$, the value of αn can be easily calculated as

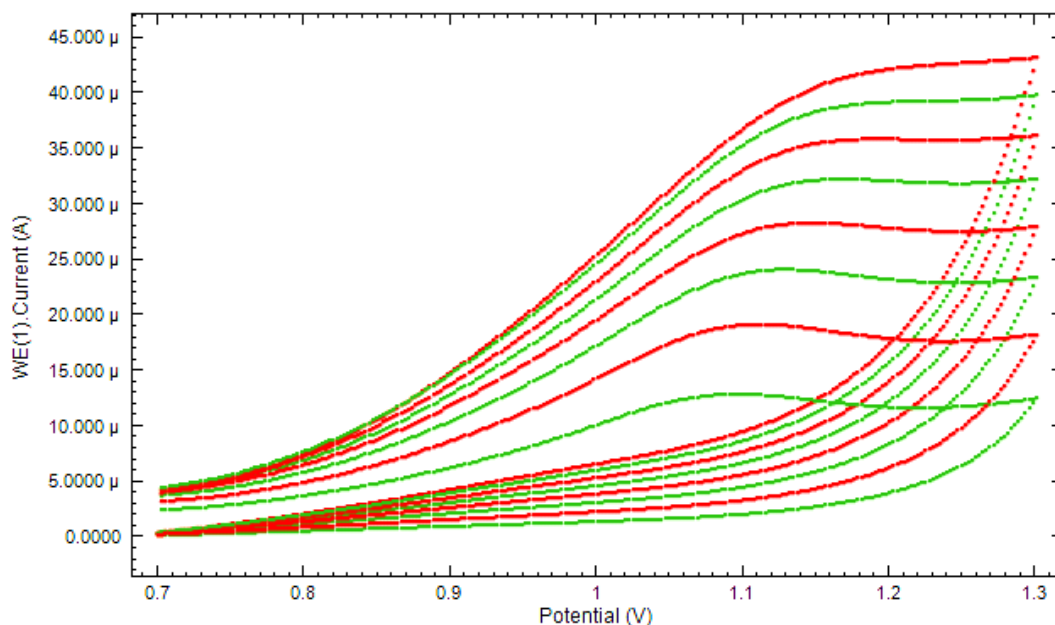
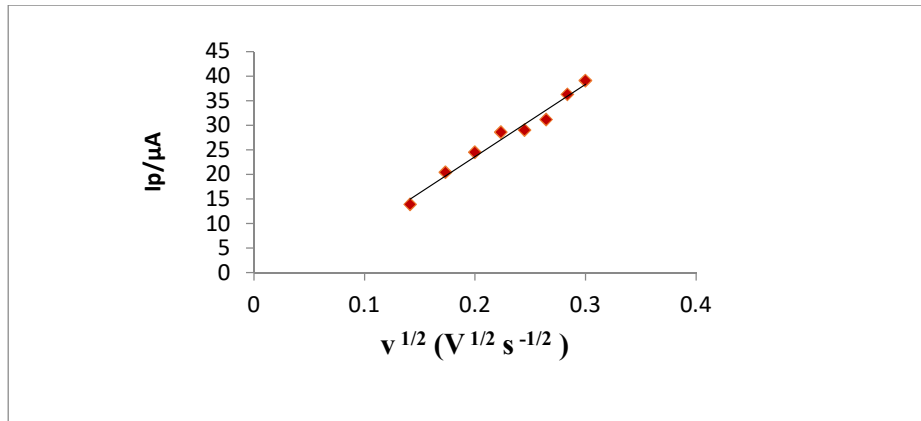
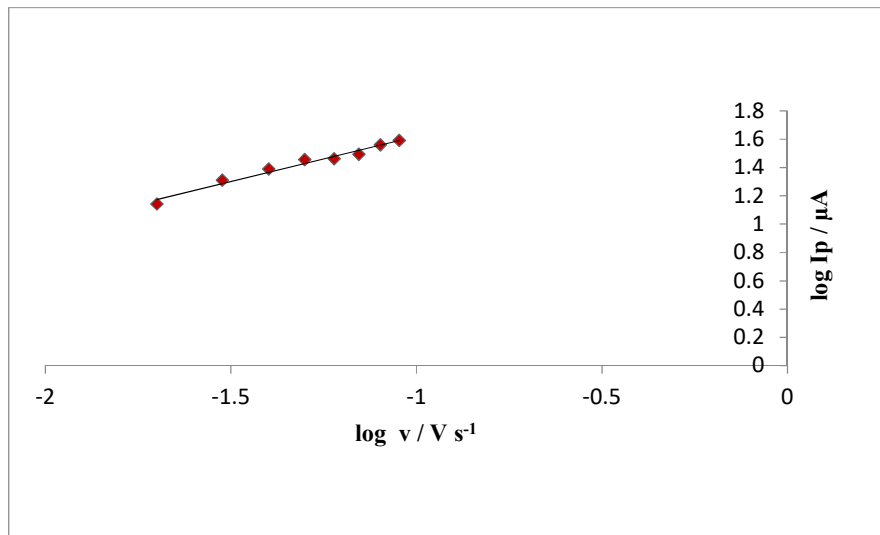
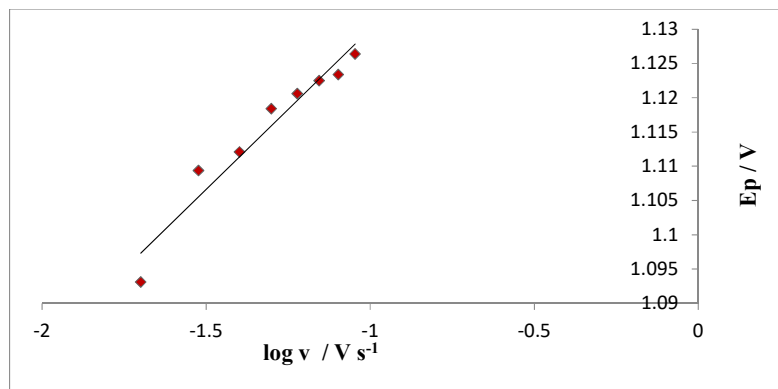


Fig. 3: Cyclic voltammograms of 10 mM SA at different scan rates 20, 30, 40, 50, 60, 70, 80, and 90 mVs^{-1} .

Fig. 3(a): I_{pa} vs $v^{1/2}$ Fig. 3(b): $\log I_{pa}$ vs $\log v$ Fig. 3(c): E_p vs $\log v$

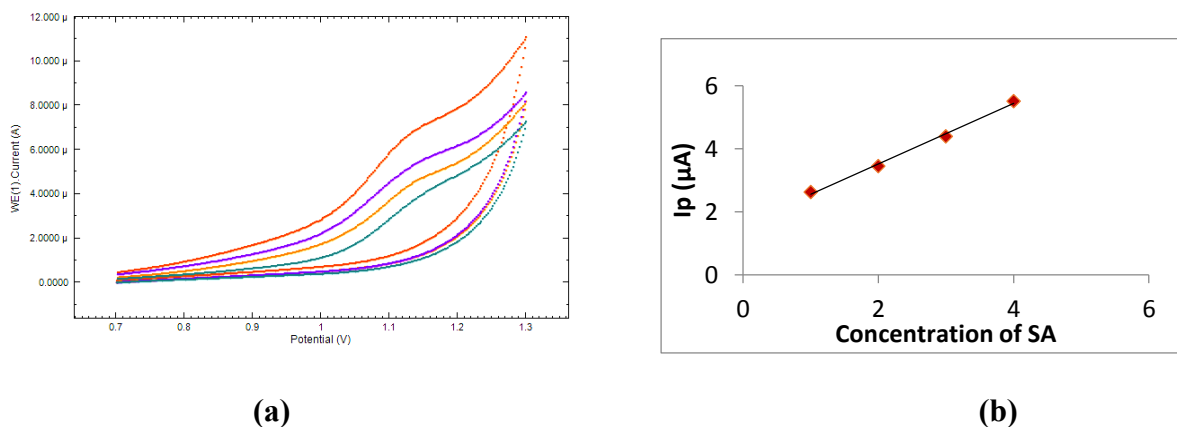


Fig. 4: (a) Cyclic voltammograms with increasing concentration of SA in pH 2.2 buffer solution on a platinum electrode with SA concentration: (i) 1.0, (ii) 2.0, (iii) 3.0, (iv) 4.0 mM (b) Plot of peak current versus concentration of SA.

1.26. In our system taking $R=8.314 \text{ JK}^{-1}\text{mol}^{-1}$, $T=298 \text{ K}$, and $F=96480 \text{ C mol}^{-1}$.

α can be expressed by Bard and Faulkner (Allen & Ferry 2001) as:

$$\alpha = \frac{47.7}{E_p - E_{p/2}} \text{ mV}$$

Where $E_{p/2}$ is the potential at half-peak current. So, the average value of the electron transfer coefficient of reaction (α) was calculated as 0.673. Further, the number of the transferred electron (n) was calculated from the αn value as 1.88~2 in the SA electro-oxidation. The value of the standard heterogeneous rate constant (k^0) can be calculated by knowing the value of the formal potential (E^0) (from the intercept of the plot E_p versus v by extrapolating to the vertical axis at $v=0$) (Fotouhi et al. 2012, Wu et al. 2004). The formal potential (E^0) and the standard heterogeneous rate constant (k^0) for the reaction were obtained as 1.0937 and $2.468 \times 10^3 \text{ s}^{-1}$ respectively. The electron transfer rate constant (k_{ox}) can be calculated from the equation (Benschoten et al. 1983).

$$k_{ox} = k^0 \times \exp \{ - (1 - \alpha) n F (E - E^0) / (RT) \}$$

So the, k_{ox} was obtained as $2.507 \times 10^3 \text{ s}^{-1}$

Effect of Concentration

The effect of varying concentrations of SA was also studied at Pt electrode in 0.04 M BR buffer, pH 2.2 at the scan rate of 10 mVs^{-1} . With increasing concentrations of SA, the cyclic voltammogram revealed that the peak current was linearly increasing as shown in Fig. 4(a). A linear SA calibration curve was obtained in the range from 1 mM to 4 mM (Fig. 4(b)). The linear equation was

$$I_{pa} (\mu\text{A}) = 0.9625 C + 1.5947 \quad (r=0.9977)$$

The limit of detection (LOD) (Rageh et al. 2015) and limit of quantification (LOQ) (Harisha et al. 2018) were 0.0031 mM and 0.0103 mM respectively. It was calculated by the below equations.

$$\text{LOD} = 3 \text{ s/m}$$

$$\text{LOQ} = 10 \text{ s/m}$$

Where m is the slope of the calibration plot and s is the standard deviation of the peak current of three blank measurements.

Table 1: Comparison of potential window range, concentration, and limit of detection (LOD) obtained for salicylaldehyde using the proposed method with the previously reported methods.

S.No	Method	Potential window range	Concentration range	LOD	References
1	Uv/ Vis Spectroscopy	–	30 ppm	–	(Matyasovszky et al. 2009)
2	Spectroelectrochemistry	- 0.4 to 1.2 V	100 μm	–	(Wang et al. 2014)
3	Electrochemical	0 to 3 V	10 mM	–	(Kiss & Kunsági-Máté 2019)
4	Photoelectrochemical	-0.4 to 1.2 V	30 ppm	–	(Tian et al. 2009)
5	Cyclic voltammetry	0.7 to 1.3 V	1-4 mM	0.0031 mM	Present work

CONCLUSION

The aim of this research was to degrade toxic salicylaldehyde with the help of an eco-friendly cyclic voltammetry technique. Salicylaldehyde was discovered to have an irreversible two-electron transfer, diffusion-controlled reaction. This work will help in the clinical and safety development of the environment.

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