DEGRADATION OF BENZALDEHYDE IN AQUEOUS MEDIA BY CYCLIC VOLTAMMETRY TECHNIQUE

JASVINDER KAUR[1]*, RAJDEEP MALIK [2] AND DUSHYANT GANGWAR [3]

Department of Chemistry, Gurukula Kangri (Deemed to be University), Haridwar 249 404, (Uttarakhand) India

ABSTRACT

Benzaldehyde has been used as a precursor in various industrial products such as medicines, cosmetic, fragrance, dye etc. Released effluents from these industries contaminate water. It is an environmental concern that the degradation of these products is necessitated. In this work, electrochemical degradation of benzaldehyde was investigated in aqueous medium at different scan rate on a platinum electrode by using environment friendly, cyclic voltammetry technique. Also, Evaluate the Kinetic and electrochemical parameters such as standard heterogeneous rate constant (k^o, $2.5857 \times 10^3 s^{-1}$), anodic electron transfer rate constant (k_{ox}, $2.8398 \times 10^3 s^{-1}$), electron transfer coefficient of reaction (α, 0.426), formal potential (E^0, 1.0392 V) and linearity under the influence of scan rate.

KEY WORDS : Benzaldehyde, Water treatment, Cyclic voltammetry, Kinetic parameters, Electro-oxidation, Platinum electrode

INTRODUCTION

Aromatic aldehydes (AAs) are toxic pollutants in aquatic, soil and terrestrial ecosystems which cause critical health hazard (Asadollahi-Baboli, 2013). Benzaldehyde (BA) is the utmost commercially useful member of aromatic aldehydes (AAs) (Abdu *et al.*, 2017). It is used as a precursor in many industries such as dyes, medicines, cosmetic, fragrance etc (Abdu *et al.*, 2017; Kunjapur *et al.*, 2015). BA is frequently used as a bacteriostatic agent or as one of the ingredients in various liquid medicinal checking of its content in medicine is important as after oxidation it converts into toxic benzaldehyde (Baranowska *et al.*, 2014). Recently it is suspected that benzaldehyde is carcinogenic (Jin *et al.,* 1998; Pettersen *et al.*, 1983; Andersen, 2006). Also, high concentration of benzaldehyde in Na-diclofenac pharmaceutical injection causes adverse neurotoxic side-effects (Kazemifard *et al.*, 2003). Additionaly, benzaldehyde may lead degeneration and demyelination of nerve fibers (Kazemifard *et al.*, 2002). Benzaldehyde induced genotoxic effect it was noticed in *Drosophila melanogaster* (Demir *et al.*, 2008) it also induces renal tubular necrosis in mice (Kluwe *et al.*, 1983). Many methods also have been reported to determine or degrade these toxic; liquid chromatography (HPLC) and derivative UV spectrophotometry (Di Pietra *et al.*, 1987) Capillary gas chromatography (Kazemifard *et al.*, 2003). Continuous increase of pollutants in water bodies has necessitated the need to develop cost-effective methods for their removal (Rasalingam *et al.*, 2014). Voltammetry is an eco-friendly method to investigate pollutants and other compounds and it is widely used for the determination of kinetics and mechanism of reaction (Nicholson *et al.,* 1964). It has many advantages, like low detection limit, rapid response, excellent reproducibility, simplicity and low cost (Sharma *et al.*, 2009). Electrochemical and polarography reduction of benzaldehyde at mercury electrode have also been reported (Lopez *et al.*, 2001; Tokuoka, 1935). Researchers have also studied electrochemical behavior of benzaldehyde at polycrystalline platinum (Planes *et al.*, 2003). However to our best knowledge benzaldehyde have

not yet been investigated in aqueous solvent using these parameters.

MATERIALS AND METHODS

Material and solutions

Analytical grade chemicals such as perchloric acid ($HClO_4$), ethanol and BA (Merck) were used to carry out the experiment. Aqueous solution of BA was prepared in 50% ethanol. $HClO_4$ used as supporting electrolyte. All solutions were freshly prepared in triple distlled water.

Apparatus

An Autolab model PGSTAT 101 potentiostat/ galvanostat 663 VA Stand (Metrohm AG, Netherlands) was used to perform Cyclic Voltammetry (CV) technique. In this technique electrochemical cell along with three electrode system.Pt disc electrode (PE) (0.031 cm^2) acted as working electrode (WE), Ag/AgCl/3M KCl electrode as the reference electrode and a Pt wire acted as the counter electrode. In preparation for investigation, working electrode was polished with alumina powder (particle size 0.05 mm) on a cloth polishing pad and washed with triple distilled water.All experiments were carried out at room temperature.

RESULTS AND DISCUSSION

In the present work,the cyclic voltammetry technique was used for benzaldehyde electrochemical behaviour. The cyclic voltammetry experiment was performed with in the scan potential window range from +0.4V to +1.6V at the 10mVs^{-1} -100mVs^{-1} different scan rate in a voltammetric cell with the BA solution (10mM) in presence of $HClO_4$ as supporting electrolyte. Kinetic parameters were determined by the peak current (Ip) under the influence of scan rate (v). A linear relationship was established between Ip and v, and between Ep and v.CV of benzaldehyde displayed only one anodic peak at the v=10 mVs^{-1} (Figure 1b). This peak indicates that the irreversible reaction was occurred on the platinum electrode surface.

Influence of scan rate

The influence of different scan rate on BA analyzed by using cyclic voltammetry method (Figure 2). The peak current (Ip) and peak potentials (Ep) were
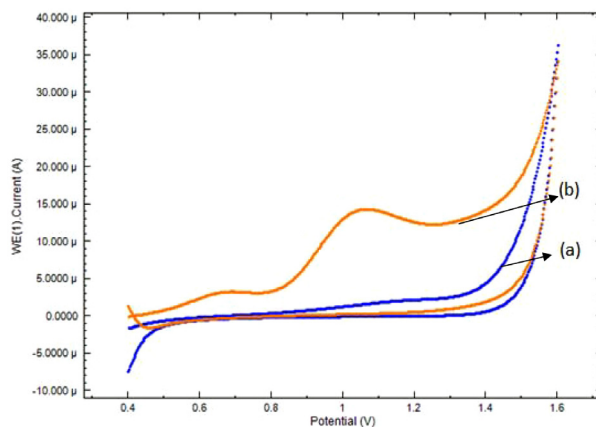
Fig. 1. **S**uccessive cyclic voltammogram (CV) of platinum electrode (PE) **(a)** with $HClO_4$ in Absence of Benzaldehyde **(b)** containing BA (10 mM)

determined for the first scan of BA electro-oxidation at different san rate. On scanning the reverse direction there was no cathodic peak showed.
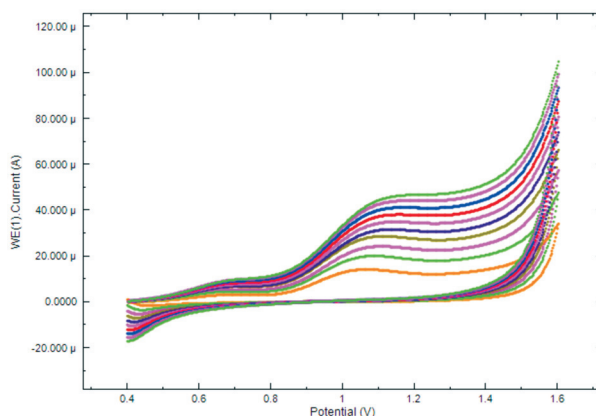
Fig. 2. CVs of PE with BA at different scan rates: 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mVs^{-1}

For electrochemical reaction rate,the reversibility controls by adsorption and diffusion and it depends on two factors: Ip on v$^{1/2}$ and log Ip on log v (Nicholson, 1965). (Figure 3a, b). If origin of the coordinates is not intercepted by the linear fit (Figure 3a), the electrode process is diffusion control and proceeded by chemical reaction (Wudarska et al., 2013). At various scan rate (v) ranging from 0.01to 0.1Vs^{-1}, peak current (Ip) depends linearly on the square root of v (equation below):

Ip(µA)=139.07v$^{1/2}$ (V$^{1/2}$ s$^{-1/2}$) - 0.0711 (r=0.999)

Alternatively, linear relationship was observed between log Ip and log v (Figure 3 b) corresponding to the equation.
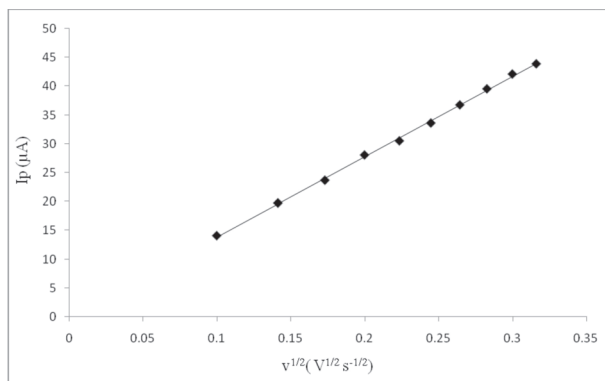
log Ip (µA)=0.49 log v(Vs^{-1})+2.137 (r=0.999)

Fig. 3a. Ip vs $v^{1/2}$

The slope value of this linear fit (Figure 3b) is 0.49. It was close to theortical expected value of 0.5 for purely diffusion controlled current (Gowda *et al.*, 2012) with which confirms that the electro-oxidation of BA was fully diffusion controlled reaction. With an increase in scan rate, the peak potential was observed in the range 0.01-0.1Vs^{-1} as shown in (Figure 3 c). The relationship can be expressed as:

$$Ep(V)=0.056 \log v(Vs^{-1})+ 1.146 \ (r=0.994)$$

For irreversible electrode process laviron equation (Laviron, 1979) is given below to define E_p:
$$E_p= E^O +(2.303RT/\alpha nF) \log (RTk^0/\alpha nF) + (2.303RT/\alpha nF) \log v$$

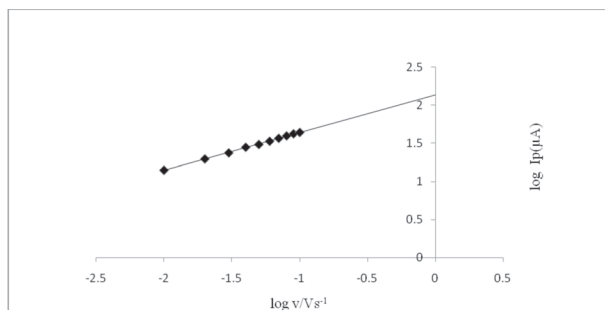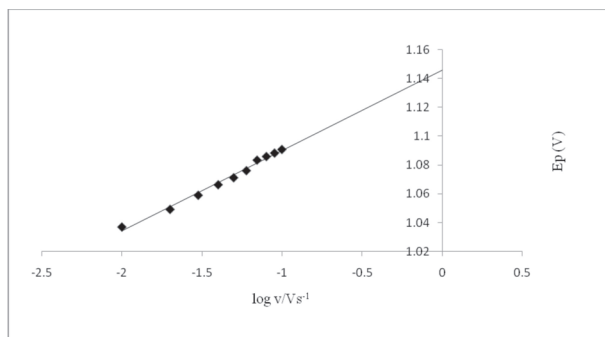Where E^0 is the formal standard redox potential, α is the transfer coefficent, n is the number of electron transferred, k^0 is the standard heterogeneous rate constant of the reaction, v is the scan rate. Thus from the slop of plot Ep vs log v, the value of αn can be easily calculated as 1.05. α can be expressed by Bard and Faulkner (Allen *et al.*, 2001) as:

$$\alpha = 47.7/(Ep–Ep_{1/2}) \ mV$$

Where $Ep_{1/2}$ is the potential at half –peak current. So the average value of electron transfer coefficient of reaction (α) calculted as 0.426. Further, the number of the transferred electron (n) was calculated from the αn value as $2.46 \approx 2$ in the BA electro-oxidation. The value of 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 Ep 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 1.0392 and 2.5857 $\times 10^3 s^{-1}$ respectively. The electron transfer rate constant (k_{ox}) can be calculated from the equation.

$$k_{ox} = k^o \times \exp \{-(1-\alpha)nF(E-E^o)/RT\}$$

So the, k_{ox} was obtained as $2.8398 \times 10^3 s^{-1}$

CONCLUSION

The aim of this research was to degrade, benzaldehyde with the help of eco friendly cyclic voltammetry technique. With an increase the scan rate, the degradation of benzaldehyde is fast and It was found that benzaldehyde displayed irreversible involving two electron transfer, diffusion controlled reaction.

REFERENCES

Abdu, M.S., Aska, A.S., Faruq, U.Z., Dangoggo, S.M. and Ali, A.U 2017. Determination of Activation Energy for the Catalytic Oxidation of Toluene to Benzaldehyde using chromium (Vi) Oxide/Hydrogen Peroxide Oxidant System. *Journal of Applied Chemistry.* 10 (9) : 28-31

Allen, J. B. and Larry, R. F. 2001. *Electrochemical Methods Fundamentals and Applications.* John Wiley & Sons.

Andersen, A. 2006. Fina l report on the safety assessment of benzaldehyde. *International Journal of Toxicology.* 25 : 11

Asadollahi-Baboli, M. 2013. Straightforward MIAQSTR evaluation of environmental toxicities of aromatic aldehydes to Tetrahymena pyriformis. *SAR and*

Fig. 3b. log Ip vs log v

Fig. 3c. Ep vs log v

QSAR in Environmental Research. 24 (12) : 1041-1050.

Baranowska, I., Wojciechowska, I., Solarz, N. and Krutysza, E. 2014. Determination of preservatives in cosmetics, cleaning agents and pharmaceuticals using fast liquid chromatography. *Journal of Chromatographic Science.* 52 (1) : 88-94.

Demir, E., Kocaoglu, S. and Kaya, B. 2008. Genotoxicity testing of four benzyl derivatives in the Drosophila wing spot test. *Food and Chemical Toxicology.* 46 (3): 1034-1041.

Di Pietra, A. M., Cavrini, V. and Raggi, M. A. 1987. Determination of benzaldehyde traces in benzyl alcohol by liquid chromatography (HPLC) and derivative UV spectrophotometry. *International Journal of Pharmaceutics.* 35 (1-2) : 13-20.

Fotouhi, L., Fatollahzadeh, M. and Heravi, M.M. 2012. Electrochemical behavior and voltammetric determination of sulfaguanidine at a glassy carbon electrode modified with a multi-walled carbon nanotube. *Int. J. Electrochem. Sci.* 7 *:* 3919-3928

Gowda, J. I. and Nandibewoor, S. T. 2012. Electrochemical behavior of 4-aminophenazone drug at a graphite pencil electrode and its application in real samples. *Industrial & Engineering Chemistry Research.* 51 (49) : 15936-15941.

Jin ,L., Dai, J., Guo, P., Wang, L., Wei, Z. and Zhang, Z. 1998. Quantitative structure-toxicity relationships for benzaldehydes to Daphnia magna. *Chemosphere.* 37 (1) : 79-85.

Kazemifard, A.G., Moore, D.E. and Mohammadi, A. 2002. Polarographic determination of benzaldehyde in benzyl alcohol and sodium diclofenac injection formulations. *Journal of Pharmaceutical and Biomedical Analysis.* 30 (2) : 257-262.

Kazemifard, A. G., Moore, D. E., Mohammadi, A. and Kebriyaeezadeh, A. 2003. Capillary gas chromatography determination of benzaldehyde arising from benzyl alcohol used as preservative in injectable formulations. *Journal of Pharmaceutical and Biomedical Analysis.* 31 (4) : 685-691.

Kissinger, P.T. and Heineman, W.R. 1983. Cyclic voltammetry. *Journal of Chemical Education.* 60 (9): 702.

Kluwe, W. M., Montgomery, C.A., Giles, H.D. and Prejean, J.D. 1983. Encephalopathy in rats and nephropathy in rats and mice after subchronic oral exposure to benzaldehyde. *Food and Chemical Toxicology.* 21 (3) : 245-250.

Kunjapur, A.M. and Prather, K.L. 2015. Microbial engineering for aldehyde synthesis. *Applied and Environmental Microbiology.* 81 (6) : 1892-1901.

Laviron, E. 1979. General expression of the linear potential sweep voltammogram in the case   of diffusionless electrochemical systems. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry.* 101 (1) : 19-28.

López, L.J.M., Mochón, M. C., Sánchez, J.C.J., López, M.A.B. and Pérez, A.G. 2001. Electrochemical reduction of benzaldehyde as its Girard-P derivative at the mercury electrode and differential-pulse polographic determination of benzaldehyde. *Microchimica Acta.* 137 (1-2) : 19-24

Nicholson, R. S. 1965. Theory and application of cyclic voltammetry for measurement of electrode reaction kinetics. *Analytical Chemistry.* 37(11) : 1351-1355.

Nicholson, R. S. and Shain, I. 1964. Theory of stationary electrode polarography. Single scan and cyclic methods applied to reversible, irreversible, and kinetic systems. *Analytical Chemistry.* 36 (4) : 706-723.

Pettersen, E. O., Rønning, Ø. W., Nome, O. and Oftebro, R. 1983. Effects of benzaldehyde on protein metabolism of human cells cultivated in vitro. *European Journal of Cancer and Clinical Oncology.* 19 (7) : 935-940.

Planes, G. A., Moran, E., Rodriguez, J. L., Barbero, C. and Pastor, E. 2003. Electrochemical behavior of benzaldehyde on polycrystalline platinum. An in situ FTIR and DEMS study. *Langmuir.* 19 (21) : 8899-8906.

Sharma, S., Kumari, M. and Sharma, D. K. 2009. Electroreduction of 4-nitrobenzaldehyde in basic medium at Different Electrodes. *Nature and Science.* 7 (3) : 84-98.

Tokuoka, M. 1935. Polarographic studies with the dropping mercury kathode. Part LII. The electroreduction of benzaldehyde. *Collection of Czechoslovak Chemical Communications.* 7 : 392-403

Wudarska, E., Chrzescijanska, E., Kusmierek, E. and Rynkowski, J. 2013. Voltammetric studies of acetylsalicylic acid electrooxidation at platinum electrode. *Electrochimica Acta.* 93 : 189-194.

Wu, Y., Ji, X. and Hu, S. 2004. Studies on electrochemical oxidation of azithromycin and its interaction with bovine serum albumin. *Bioelectrochemistry.* 64 (1): 91-97.