Electrochemical behaviour of 1,2,4-triazole and benzotriazole at glassy carbon electrode in acidic media

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ABSTRACT

Electrochemical investigations of 1,2,4-triazole and benzotriazole in aqueous acidic media has been carried out by cyclic voltammetric measurements. Cyclic voltammetric experiments were carried on glassy carbon (GC) working electrode. Effect of potential scan rate, pH of the solution and use of different surfactant on the electrochemical behavior has been investigated. Single reduction wave was observed for 1,2,4-triazole due to the reduction of N = N moiety and no oxidation peak was observed in the reverse scan. In case of benzotriazole one clear reduction peak was observed in the cathodic scan and no anodic peak was seen. Effect of pH, sweep rate, analyte concentrations and the presence of different surfactants on the reduction peak current was evaluated. Electro-reduction processes of both the compounds were found to be diffusion controlled in nature. The plausible mechanism for the electroreduction process was proposed. Electrochemical property of two compounds was also studied under hydrodynamic conditions using glassy carbon rotating disc electrode.
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INTRODUCTION

Use of pesticides in agricultural production and the negative environmental impacts associated with these compounds has led to the development of different electroanalytical techniques[1-7] and studying the electrokinetics of such compounds. Electrochemical methods are applied in toxicological, ecotoxicological and environmental regulations due to the applicability over a wide concentration range[8] using techniques starting from coulometry, cyclic voltammetry to differential pulse voltammetry.

The basic building block of the compound, 1,2,4-Triazole has got very wide varieties of applications, most notably, it is used as antifungal in the form of fluconazole and itraconazole. There are many derivatives of triazole used as the corrosion inhibitor in the corrosion inhibition of steel and copper[9-11]. In some of our recent reports we have used benzotriazole as the corrosion inhibitor in acidic media[10,11] and the mechanism of the inhibition have been reported. Electrosorption and polymerization of triazoles at the electrode-electrolyte interface using brass and gold electrode have been discussed in some of the recent studies[12-14]. Triazoles can

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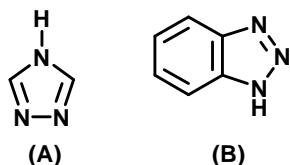
Chart 1 : Chemical structure of (A) 1,2,4 triazole and (B) benzotriazole

Chart 2 : Proposed scheme of the electroreduction process of benzotriazole

present in different tautomeric forms, effect of such tautomeric forms on the electrochemical property of triazoles. On gold electrode surface triazole produces two redox peaks, the pre-peak before the diffusion controlled peak was attributed to be due to the adsorption of triazole on gold surface.

In the present study the two compounds studied are belonging to the triazole group and they are used for many similar purposes. The chemical moiety of the two compounds are same (triazole ring) but the chemical identity of the two compounds are differed by the introduction of a benzene ring in benzotriazole, which is absent in triazole. Therefore it is very interesting and important to see the redox behavior of 1,2,4-triazole and benzotriazole in aqueous media and compare their behaviour. In the present study, electrochemical property of two triazoles has been studied in aqueous solution using glassy carbon as the working electrode. Effect of pH, sweep rate and effect of different surfactants on the reduction process of the two compounds has been investigated. Electroreduction behaviour has also been investigated under hydrodynamic conditions using rotating disc electrode.

## EXPERIMENTAL

Reagents and chemicals

Triazoles were purchased from Merck and used as obtained. Cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl sulphate (SDS) and Triton X-100 were obtained from Merck and used without further purification. All other reagents used in the present study were of analytical reagent grade. All solutions were prepared using double distilled and de-ionized water. Britton-Robinson buffer was used to adjust the pH of the supporting electrolyte solution at the wide range of pH's from 2 to 12. It was prepared by mixing 1:1:1 ratio of 0.04M boric acid (H_3BO_3), phosphoric acid (H_3PO_4) and acetic acid (CH_3COOH).

Instrumentation and apparatus

Cyclic voltammetric experiments were carried out
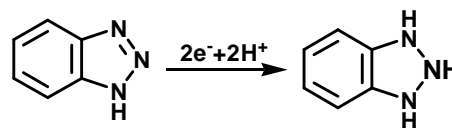
using a three-electrode configuration consisting of a glassy carbon (disk, 3 mm diameter) as a working, Pt foil as the counter and saturated calomel electrode (SCE) as the reference electrode. All potentials reported are related to this reference electrode. The electrochemical measurements were performed using an EcoChemie make Potentiostat/Galvanostat Autolab-100 and the analysis was made by GPES-4.9 software. The glassy carbon electrode was polished with 0.3μm alumina powder and then rinsed with distilled water before use. All the experiments were performed at room temperature. Prior to the electrochemical scan solutions were purged with nitrogen for 15 min. In cyclic voltammetric measurements the applied potential was scanned from 0V to -1.6V with respect to SCE. Rotating disc electrode (RDE) experiments were carried out using the PINE electrode assembly with pine speed control system connected to the AUTOLAB 100 potentiostat. The RDE used in this investigation was carried out using the glassy carbon as the working electrode attached with the PINE electrode assembly. In all the tables the spread in the data points were presented as the 2 sigma (2s) from 3 repeated current measurements.

RESULTS AND DISCUSSION

Cyclic voltammetric scans of 1,2,4-triazole at a concentration of 2×10^{-3} M in aqueous acid media using HCl as the supporting electrolyte, with a sweep rate of 0.05mV s^{-1} at glassy carbon electrode was obtained and shown in figure 1. In case of 1,2,4-triazole, a single cathodic wave and no anodic peak was appeared at the experimental potential window. From the chemical structure and cyclic voltammograms of the investigated compounds it is indicated that the peak at around 1.5V vs. SCE was due to reduction of azo group present in the molecule. In case of benzotriazole one reduction peak was obtained at -1.48V and no anodic peak in the reverse scan was seen (Figure 2).

Effect of the concentration of the compounds

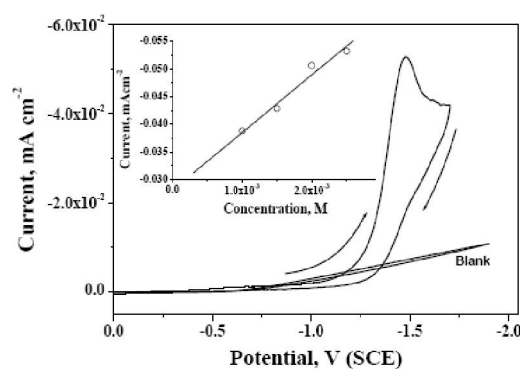The observed reduction peak current was found
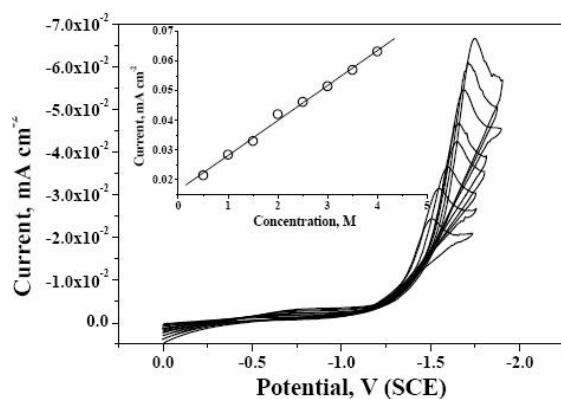
Figure 1 : Cyclic voltammogram of 1 mM 1,2,4-triazole at glassy carbon electrode in aqueous acidic media, pH = 3.1, Inset: Plot of concentration versus cathodic peak current on reduction of 1,2,4-triazole at GCE
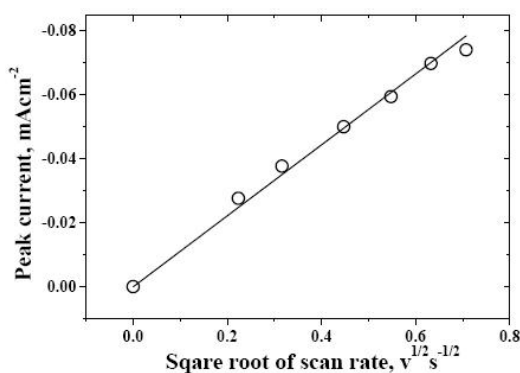
Figure 3 : Plot of square root of scan rate verses peak current on reduction of 1 mM 1,2,4-triazole at pH 3.1 on GCE

to increase linearly with the concentration of triazole at the concentration range of 0.5×10^{-3} to 4×10^{-3}M in 50×10^{-3}M in HCl solution as shown in the TABLE 1. The scan rate was kept at 0.05 Vs^{-1} for this study of obtaining the concentration dependence on the reduction peak current. This linear increase in the reduction current with concentration indicates the electroreduction process to be diffusion controlled in nature. The peak current value of triazole (Figure 1) follows the regression equation of $I = 0.1644 + 0.1175$ C with standard deviation (SD) of 0.109 and correlation coefficient R = 0.995. Here the current, I is expressed in mAcm^{-2} and concentration, C in mML^{-1} unit. The peak potential was found to be shifted from -1.5V to -1.75V with the addition of higher concentration of triazole. The change in peak potential with the addition of analyte concentration indicates irreversible nature of the electrochemical process. There can also be the possibility of aggregation of the triazole molecules at higher concentration, which may lead to the shifting of the potentials to more negative values.

Figure 2 : Cyclic voltammogram of 1mM benzotriazole at glassy carbon electrode in aqueous acidic media pH=2.85, Cyclic voltammogram of the blank solution is also shown. Inset: Plot of concentration versus cathodic peak current of the peak on reduction of benzotriazole at GCE

TABLE 1 : The change in the peak potential and the peak current of 1,2,4-triazole with the change in concentration

1,2,4-triazole	Reduction peak	
Concentration mM	Potential E_{pc}(V) ±0.02(V)	Current i_{pc}(mAcm^{-2}) ±0.005 (mA cm^{-2})
0.5	-1.51	-0.034
1.0	-1.54	-0.037
1.5	-1.60	-0.039
2.0	-1.65	-0.047
2.5	-1.66	-0.052
3.0	-1.70	-0.057
3.5	-1.72	-0.059
4.0	-1.75	-0.062

In case for benzotriazole the peak current values increase linearly with the concentration as shown in the inset of figure 2 and the data points were shown in TABLE 2. The peak current values of benzotriazole (Figure 2B) follow the regression equation of $I = 0.281 + 0.105$ C with standard deviation (SD) of 0.123 and correlation coefficient R = 0.992. Here the current, I is expressed in mAcm^{-2} and concentration, C in mML^{-1} unit. The peak potential of benzotriazole does not shift any significantly with the increase in the concentration of benzotriazole.

When the electrochemical behavior of two compounds were compared it was observed that the peak potential undergo a cathodic shift in case of 1,2,4-triazole with increase in the concentration, the peak potential of benzotriazole remains unchanged. The shift in the peak potential is indicative of the irreversible nature of the electro-reduction process of 1,2,4-triazole, however, there is also a possibility of intermolecular interaction between triazole molecules, which might shift

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TABLE 2 : The change in the peak potential and the peak current of benzotriazole with the change in concentration

Benzotriazole	Reduction peak	
Concentration mM	Potential $E_{pc}(V)\pm0.02(V)$	Current i_{pc} (mAcm^{-2}) ±0.005(mA cm^{-2})
0.5	-1.48	-0.033
1.0	-1.48	-0.039
1.5	-1.49	-0.041
2.0	-1.49	-0.051
2.5	-1.49	-0.053

TABLE 3 : Effect of scan rate on reduction of 1,2,4-triazole at glassy carbon electrode, pH = 3.1

1,2,4-triazole	Reduction peak	
Scan rate	Potential-E_{pc} (V) ±0.02 (V)	Current i_{pc} (mA cm^{-2}) ±0.005 (mA cm^{-2})
50	-1.54	-0.038
100	-1.54	-0.042
200	-1.57	-0.050
300	-1.59	-0.059
400	-1.62	-0.069
500	-1.64	-0.072

the peak potential towards more cathodic potentials. Similar type of intermolecular interaction as that in triazoles is minimized in case of benzotriazole due to the presence of a benzene ring, which might repel each other and oppose any kind of intermolecular interaction. Additionally benzotriazole being aromatic compound is expected to be more stable compared to 1,2,4-triazole so the comparative possibility of polymerization would be less in benzotriazole.

Effect of scan rate

The effect of scan rates on the electrochemical behavior of 1,2,4-triazole and benzotriazole has been studied in aqueous-hydrochloric acid media. The peak currents were measured at a varying scan rates from 10-500mV s^{-1}, the results are tabulated in TABLE 3. It is observed that in the case of 1,2,4-triazole the peak current increases with increase in the potential scan rates. The peak current values when plotted with respect to the square root of scan rates, results in a straight line plot as seen in figure 3, which indicate that the process is diffusion controlled in nature[15,16]. The data points were fitted using Randle Sevcik's equation as.

$$I_p = (2.69\times10^5)n^{3/2}AD^{1/2}v^{1/2}C \qquad (1)$$

where I_p is the peak current in Amp, n is the number of electron, A is the area of the electrode in cm^2, D is the diffusion coefficient of the species in cm^{2}s^{-1}, v is the scan rate in Vs^{-1} and C is concentration of the species in Mcm^{-3}. The constant 2.69×10^5 was obtained from the numerical relation between (E-E$_{1/2}$) and $\sqrt{\pi\chi(\sigma t)}$ for a reversible electrochemical process with (E-E$_{1/2}$)n value of -28.50 V at 25°C[15]. It is observed that the experimental data points are fitted well with the straight line equation passing through origin and the with correlation coefficient r as 0.996. Thus, the electroreduction process of 1,2,4-triazole is found to be diffusion controlled in nature. The reduction peak potential shifted from -

1.54V to -1.64V with increase in the scan rates, which indicates the irreversible nature of the electrochemical process. For the reactions that are 'slow' (so called quasi-reversible or irreversible electron transfer reactions) the voltage applied does result in the generation of the concentrations at the electrode surface predicted by the Nernst equation. This happens because the kinetics of the reaction is 'slow' and thus the equilibrium is not established rapidly as comparison to the voltage scan rate. In this kind of situation the overall form of the voltammogram remains similar to the reversible system but position of the current maximum, peak potential shifts depending upon the reduction rate constant and also the applied voltage scan rates. This occurs because the current takes more time to respond to the applied voltage than the reversible case[15].

Similarly in case of benzotriazole the cathodic peak current increases with the increase in the scan rates. The peak current values were found to be proportional to the square root of the scan rate and also follow the equation (1) (plots not shown) thereby indicating the diffusion controlled electrochemical process.

Effect of pH

Effect of pH on the reduction behaviour of 1,2,4-triazole and benzotriazole was studied by varying the pH from 2 to 9.2 using B-R buffer medium. In case of 1,2,4-triazole as the pH increases from 2 to 9.2, the cathodic peak potential was found to shift towards more negative values and also a slight decrease in peak current was observed, which confirms that the 1,2,4-triazole is more electrochemically active at pH 3.1 (Figure 4A). Statistical information in the experimental result was obtained from 5 independent measurements and 2 times of the standard deviation (2s) was presented as the error bar in the plot. The peak current also decreased drastically above pH 3.15 and no peak was observed
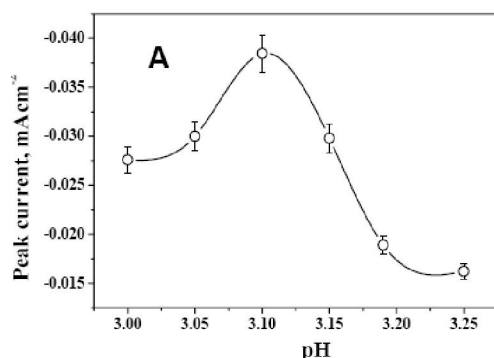
Figure 4A : Plot of pH verses peak current on reduction of 1 mM 1,2,4-triazole at GCE
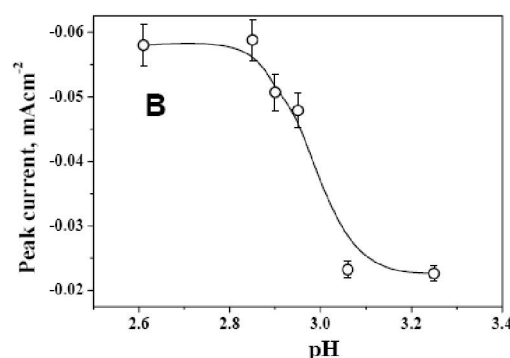

Figure 4B : Plot of pH versus cathodic peak current on reduction of 1mM benzotriazole at GCE

TABLE 4 : Effect of variation of surfactants with 1,2,4-tiazole, Scan rate: 50 mVs^{-1} concentration of the compound 1×10^{-3} M. The 2 sigma spread in potential is ±0.02 (V), and to the current is ±0.005 (mA cm^{-2})

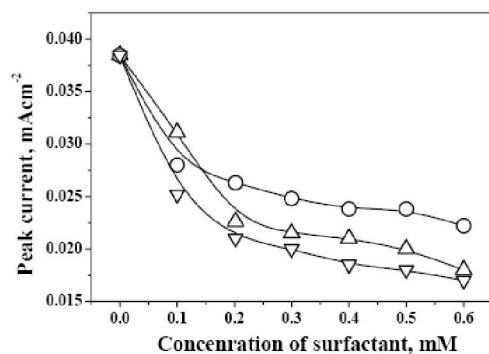| Concentration of surfactant in mM	CTAB		SDS		Triton X-100	
	E_{pc} (V)	i_{pc} (mAcm^{-2})	E_{pc} (V)	i_{pc} (mAcm^{-2})	E_{pc} (V)	i_{pc} (mAcm^{-2})
0.0	-1.52	-0.038	-1.52	-0.038	-1.52	-0.038
0.1	-1.52	-0.031	-1.53	-0.025	-1.52	-0.026
0.2	-1.54	-0.022	-1.55	-0.021	-1.52	-0.026
0.3	-1.57	-0.021	-1.58	-0.020	-1.52	-0.025
0.4	-1.59	-0.021	-1.61	-0.018	-1.52	-0.024
0.5	-1.62	-0.020	-1.65	-0.018	-1.50	-0.024
0.6	-1.68	-0.018	-1.70	-0.017	-1.47	-0.022

Figure 5 : Effect of different surfactants on the voltammetric peak of 1 mM 1,2,4 triazole (O) TX100, (Δ) CTAB (∇) SDS on GCE at pH 3.1

above pH 4. This implies that as the pH increases the reduction becomes more difficult which indicates involvement of proton in the reduction process and the reduction of both molecules is very sensitive to the pH of the medium. Similarly in case of benzotriazole, as seen from Figure 4B the peak current remains high at pH up to 2.8, beyond that the peak current decreases sharply. Therefore the observations indicate that pH has a very significant role in the electroreduction process of both 1,2,4-triazole and benzotriazole. Based on the present observation and reported literature a scheme of the electroreduction process of 1,2,4-triazole has been proposed[17] which, is presented in Chart 2.

Electrochemical behavior in surfactant media

Keeping the concentration of 1,2,4-triazole at 1×10^{-3}M, pH 2.3 in B-R buffer with a scan rate 50 mVs^{-1}, the voltammograms were recorded by increasing the concentration of three different surfactants from 1×10^{-5}M to 610^{-5} M. The observed change in the current with increase in the surfactant concentration is shown in figure 5.

In the case of anionic surfactant, sodium dodecyl sulfate (SDS), the peak current decreases with increase

in the addition of SDS and peak potentials shifted to the negative direction. Different factors affect the surfactant adsorption on solid/liquid interface[15]. Apart from this, it is also claimed that at higher concentrations of SDS, the repulsive forces among the surfactant molecules adsorbed at the interface of the solid (adsorbent)-solution are more effective[18]. By increasing the concentration of the surfactant, more and more surfactant gets adsorbed at the surface of the electrode resulting in the decrease in the cathodic current and also the peak potential was shifted towards more negative direction. This might be due to the change in the heterogeneous kinetics of the electron transfer process between the electrode surface and molecules in the interfacial region affected by the adsorbed surfactant materials as the microstructure and the active sites on the electrode surface was damaged.

In the case of cationic surfactant CTAB, the peak potential does not change with the increase in concentration of CTAB (up to 6.0×10^{-5} M) but the peak current decreases as the concentration of CTAB increases. The decrease in the peak current could be due to the
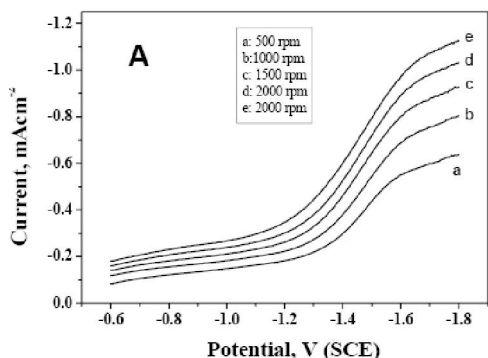
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Figure 6A : Voltammogram of 1 mM 1,2,4-triazole under hydrodynamic conditions on GCE with different rotation speed. Solution pH was maintained at 3.1
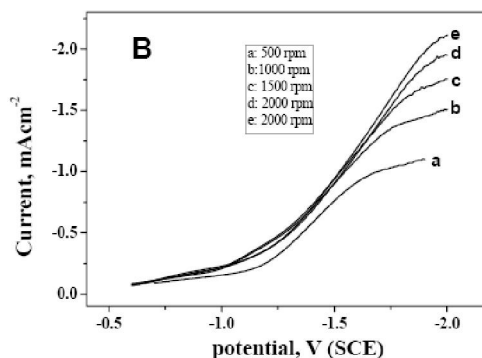
Figure 6B : Voltammogram of 1mM benzotriazole under hydrodynamic conditions with different rotation speed on GCE. Solution pH was maintained at 2.85
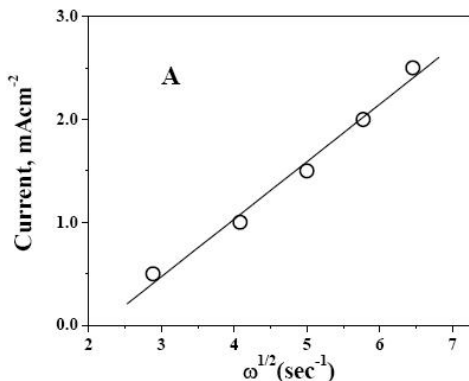
Figure 7A : Levich plot of 1,2,4 triazole for hydrodynamic voltammetry

Figure 7B : Levich plot of benzotriazole for hydrodynamic voltammetry

slower diffusion of the electroactive species as a result of higher viscosity of the medium. The cathodic peak was not observed at the higher concentration of CTAB. This indicates the saturation capacity[19] of the electrode for adsorption of the cationic surfactant due to the electrostatic interaction between the adsorbent and the surfactant, the decrease in current values can be seen from TABLE 4. The nonionic surfactant Triton X-100 affect the electrochemical behavior of 1,2,4-triazole similar to that of CTAB. The peak potential, E_{pc}, remains unchanged but the peak current, i_{pa} decreased with increase in concentration of TX100.

Rotating disc electrode (RDE) study

RDE experiments were carried out using the PINE electrode assembly with pine speed control system connected to the AUTOLAB 100 potentiostat. Voltammograms were recorded with varying rotation speed from 500 rpm to 2500 rpm. The saturation in the reduction current is seen beyond -1.6 V in both the cases however with increase in the rotation speed there is a shift in the potential towards the negative direction (Figure 6A and 6B). The limiting current value increases
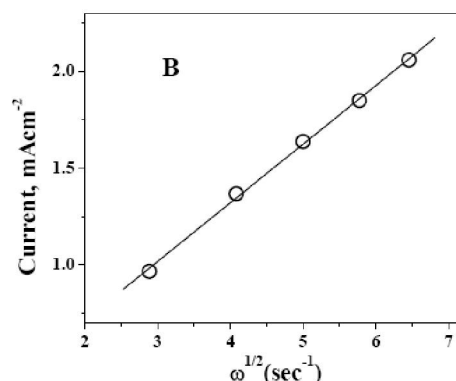
with increase in the rotation speed. Variation in the limiting current and the corresponding potential with the change in rotation speed for 1,2,4 triazole and benzotriazole are reported in TABLE 5 and table 6 respectively.

Plot of the limiting current with respect to the angular rotation frequency is plotted in figure 7 A and 7B. The data points were found to fit well with linear function passing through the origin. Therefore the correlation between the limiting current density (i_l) with the angular frequency ω found to follow the Levich relation as;

$$i_l = 0.62 \, n \, FAD^{2/3} \nu^{-1/6} \omega^{1/2} C \qquad (2)$$

where n is the number of electron, F is Faraday constant, D is the diffusion coefficient in $cm^2 s^{-1}$ ν is the kinematic viscosity (i.e., viscosity of the solution divided by its density) in this case it is considered to be $0.01 cm^2 s^{-1}$. The constant 0.62 is the Levich constant for totally mass transfer-limited conditions at the rotating disc electrode[15]. Using the Levich equation the diffusion coefficient for 1,2,4-triazole is obtained as $19.1 \times 10^{-6} \, cm^2 s^{-1}$ and for benzotriazole it is obtained as $7.5 \times 10^{-6} \, cm^2 s^{-1}$.

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TABLE 5 : RDE results of 1,2,4-triazole scan rate 50 mVs⁻¹

Rotation speed (rpm)	Current, i_l (mAcm⁻²) ±0.06 (mA cm⁻²)
500	-0.54
1000	-0.68
1500	-0.81
2000	-0.92
2500	-1.05

TABLE 6 : RDE results of 1,2,4-triazole scan rate 50 mV/s

Rotation speed (rpm)	Current, i_l (mA cm⁻²) ±0.06 (mA cm⁻²)
500	-0.97
1000	-1.37
1500	-1.64
2000	-1.85
2500	-2.06

The diffusion coefficient of triazole is found to be higher than benzotriazole; this is due to smaller size of triazole compared to benzotriazole.

Interestingly it was observed that the hydrodynamic voltammogram in case of benzotriazole was comparatively steeper than 1,2,4-triazole. Benzotriazole is a bulkier molecule than 1,2,4-triazole therefore with increase in rotation speed the change in the current is more pronounced in benzotriazole than 1,2,4-traizole which was resulted the steeper hydrodynamic voltammogram. Additionally it was also observed that the half-wave potentials of the hydrodynamic voltammograms were found to be more positive in the both benzotriazole and 1,2,4 triazole than the peak potential of the cyclic voltammogram obtained under static conditions. This might be due to the lesser possibility of adsorption of triazole species at the electrode surface under hydrodynamic conditions which otherwise present under static conditions resulted in the increased surface resistance and peak shifting towards negative direction.

CONCLUSION

Cyclic voltammetric investigations were carried out for 1,2,4-triazole and benzotriazole. Peak potential was found to shift to more positive value with increase in the acidity of the medium, indicating easier reduction due to the involvement of proton in the reduction process.

Cathodic peak current was found to increase linearly with square root of sweep rate and also with concentration of electroactive species. This suggests that overall electrode process is diffusion controlled and irreversible in nature. Diffusion coefficients of 1,2,4- triazole and benzotriazole were calculated from the RDE voltammetry.

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