

OPTIMIZATION OF CYCLIC VOLTAMMETRIC PARAMETERS FOR DETERMINATION OF SUBSTITUTED ANILINE IN AQUEOUS MEDIA: APPLICATION IN REAL SAMPLE

Richa Paliwal[✉] and Rajdeep Malik

Department of Chemistry, Gurukula Kangri (Deemed to be) University, Haridwar-249404 (Uttarakhand), India

[✉]Corresponding Author: paliwalricha6@gmail.com

ABSTRACT

A new voltammetric method has been proposed to determine 2-methyl-4-nitroaniline (substituted-aniline, 2MPNA) in aqueous media. This study reports the anodic oxidation of 2MPNA in various solutions such as (A) Thiel-Schultz-Koch (TSK) buffer (100%V/V), (B) TSK buffer (80%V/V) and eight electrolytes (20%V/V) and (C) eight electrolytes (100%V/V) at the platinum electrode. The influence of parameters such as scan rate (mV/s), pH, and concentration have been observed to achieve higher voltammetric signals. Electrochemical parameters were evaluated in TSK buffer (80%V/V) and eight electrolytes (20%V/V), and one of the eight electrolytes (sodium orthophosphate: SOP) based on the ease of oxidation and higher peak current response. In SOP, the relationship between concentrations and peak currents was linear. Further, this optimized method was successfully applied to determine 2MPNA in a real sample.

Keywords: 2-methyl 4-nitroaniline, Electrochemical Kinetic, Cyclic Voltammetry, Water Treatment.

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INTRODUCTION

Substituted anilines (SAs) are aromatic amines (AAs) of substantial production and industrial value and have thus become vital environmental pollutants. AAs are detrimental to health.^{1,2} In industries, aniline, and SAs are used as precursors to prepare different products such as dyes and pigments, polymers, pharmaceuticals, isocyanates production, agricultural chemicals, and rubber processing chemicals.^{3,4} Industries release these toxic and carcinogenic anilines in water bodies as effluent. The introduction of SAs into the environment is harmful to human health.⁵ According to the research SAs pose a severe health risk; carcinogenic to human health if they percolate into certain water supplies.⁶ The US EPA (Environmental Protection Agency) has identified nitroaniline isomers as priority pollutants. They are highly toxic, potentially carcinogenic, and mutagenic and form adducts with proteins and DNA.⁷⁻⁹ Researchers have employed many alternative techniques to estimate, recover, and degrade SAs. Chromatography: HPLC; UV-VIS spectrophotometry, electrochemical methods such as polarography, voltammetry, amperometry, Fenton-oxidation, and electrochemical oxidation using various metallic electrodes are some alternative methods.¹⁰⁻¹² The electrochemical technique is the most promising for wastewater treatment. Anilines are prevalent pollutants in commercial effluents.¹³ Voltammetry is an eco-friendly and susceptible electrochemical technique that has been used to detect aniline and its derivatives.¹⁴⁻¹⁶ Cyclic voltammetry is so widespread for the redox reactions of organic compounds and has the benefits such as fast response, simplicity, low cost, eco-friendly, and convenience to operate.¹⁷ Different authors have evaluated the electrooxidation of SAs and nitro derivatives.^{18-21,30-31} No information has been published on the electrochemical oxidation of 2-methyl 4-nitroaniline (2M4NA). This work represents the voltammetric oxidation of 2M4NA at the platinum electrode in different solutions (buffer solution, the mixture of solution (buffer and different electrolytes), and electrolytes solution. Further, we optimized experimental parameters for 2M4NA determination in a real sample: tap water.

EXPERIMENTAL

Material and Methods

All compounds were of AR grade. 2M4NA (Merck) was purified using distillation for further experiments. Acetonitrile (Fisher Scientific) served as solvent. Electrolyte (0.1M): sodium orthophosphate (SOP),

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potassium hydrogen phthalate (PHP), sodium meta periodate (NaIO₄), potassium peroxodisulphate (K₂S₂O₈), tetraethylammonium bromide (TEAB): Merck, hydrochloric acid (HCl), sulphuric acid (H₂SO₄) and nitric acid (HNO₃): Fisher Scientific were used in the study. Thiel Shulz Koch (TSK) (0.1M) buffer solution (pH 8.5) (a mixture of oxalic acid, boric acid, succinic acid, and sodium sulphate (Merck)) was used as a buffer in this experiment. All solution was prepared with triple-distilled water throughout the work. The electrochemical cell is a three-electrode system; the reference (Ag/AgCl/3M KCl), the counter electrode (platinum wire), and the working electrode (platinum disc). The CV investigations were performed using an Autolab Metrohm (Metrohm AG, Netherlands) model PGSTAT 101 galvanostat/potentiostat 663 VA Stand. Alumina powder (Al₂O₃) was used to polish the platinum disc electrode before each experiment. The cyclic voltammetry measurements were carried out using five different scan rates (50-250 mV/s) at an ambient temperature (of 25±0.1°C). A digital pH meter (Systronics) was used to record pH measurements.

RESULTS AND DISCUSSION

Optimization of Parameter

Cyclic Voltammetry Study

Figure-1(A) illustrates the voltammetric behavior of 2M4NA in TSK buffer solution and TSK buffer/supporting electrolytes solution (80/20% V/V). Additionally, Figure-1(B) illustrates cyclic voltammograms (CVs) in different supporting electrolytes (100% V/V). Both figures display one sharp peak in 1mM 2M4NA in the potential window ranges of 0.5-1.115V and 0.5-1.300V, respectively. The scan rate was 50mVs⁻¹. There are no significant peaks for 2M4NA in the two solutions (buffer/H₂SO₄ and TEAB) while the overall data shows good results in the SOP solution. These results are better than the results obtained in TSK buffer/SOP solution.

Influence of Consecutive Cycles in Different Solutions

We recorded consecutive cyclic voltammograms in different solutions at different scan rates to examine the electrode stability. Figure-(2) shows that the reaction is adsorption-controlled due to the current decreases with scan numbers. Figures-2 (A), (C) and (D) show that the peak potential, E_p, value is the same during the run, so the non-conductive polymeric product obstructs the electrode surface. Therefore, the first anodic cycle is considered for results interpretation in subsequent studies.

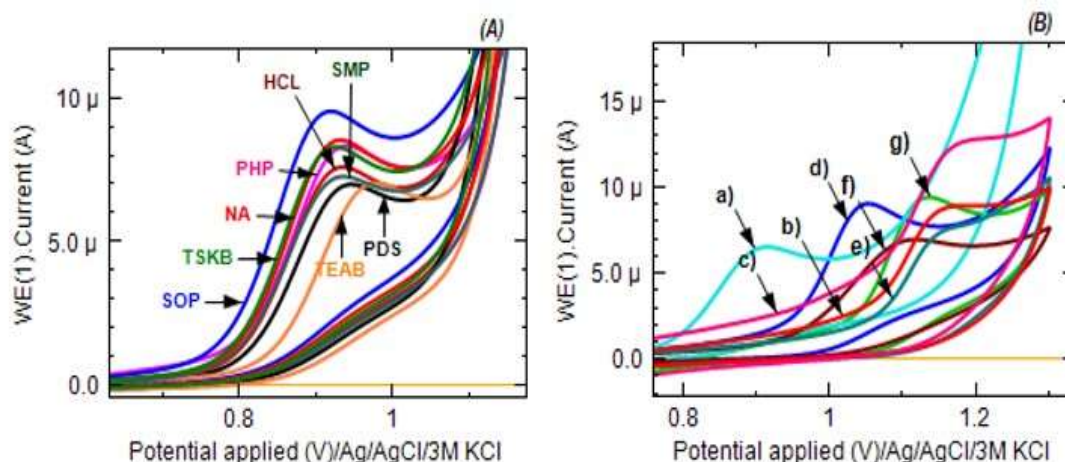


Fig.-1: (A) Showing Cyclic Voltammogram in TSK Buffer and a Mixture of Buffer/: SOP, NA, PHP, HCL, SMP, PSD, TEAB 80/20 (V/V %) (B) Showing Cyclic Voltammogram in (a) SOP, (b) H₂SO₄ (c) HNO₃ (d) PHP (e) HCl (f) periodate (g) PSD

Influence of Different Scan Rates

Figure-3 displays 2M4NA electrooxidation at a variable scan rate (50-250 mVs⁻¹). The peak potentials at different scan rates for the anodic process shift from negative to positive potential with respect to Ag/AgCl. The corresponding peak currents increase with scan rates in all solutions [except in 80% TSK Buffer/20% SOP (Fig.-3B) and 80% TSK Buffer/20% HNO₃ solution (Fig.-3G) (V/V%)].

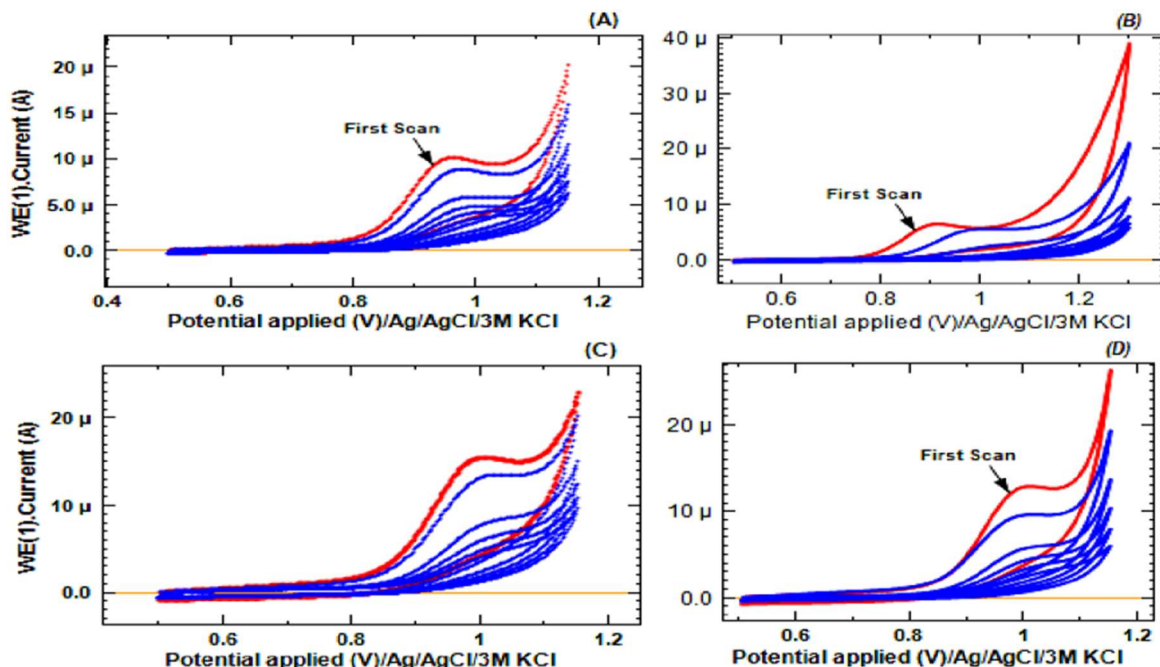


Fig.-2: 6 Consecutive Cycles in 80% Buffer + 20% (A) TEAB (100mV/s), (B) SOP (50mV/s), (C) HCL (250mV/s) (D) PSD (200mV/s)

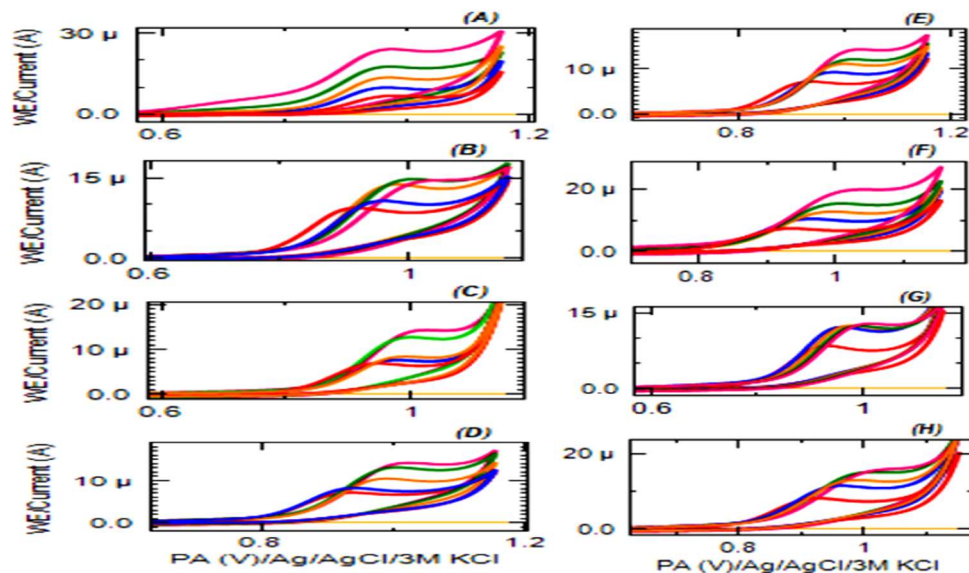


Fig.-3: Showing Cyclic Voltammograms at 50-250 mV/s Different Scan Rate (a-e) in 80% TSK Buffer + 20% (V/V%): (A) TEAB, (B) SOP, (C) PSD, (D) PHP, (E) Periodate, (F) HCl, (G) HNO₃, and (H) in 100% TSK Buffer (V/V%)

Figure-4 displays the calibration curve of peak current vs scan rate: i_p vs v and $\ln i_p$ vs $\ln v$.²² The peak current increases linearly with the square root of the scan rate, (calibration graph not shown) and is described by the following equation:

$$i_p(A) = \left\{ 41.309 \pm 5.128 \left[v (Vs^{-1})^{\frac{1}{2}} \right] \right\} mA - 3.268 \pm 1.986 mA, R = 0.977$$

$$i_p(B) = \left\{ 18.502 \pm 3.835 \left[v (Vs^{-1})^{\frac{1}{2}} \right] \right\} mA + 5.488 \pm 1.485 mA, R = 0.941$$

$$i_p(C) = \left\{ 26.108 \pm 6.543 \left[v (Vs^{-1})^{\frac{1}{2}} \right] \right\} mA - 0.132 \pm 2.534 mA, R = 0.917$$

$$ip(D) = \left\{ 25.345 \pm 3.755 \left[v (Vs^{-1})^{\frac{1}{2}} \right] \right\} mA + 1.033 \pm 1.454 mA, R = 0.969$$

$$ip(E) = \left\{ 23.441 \pm 1.440 \left[v (Vs^{-1})^{\frac{1}{2}} \right] \right\} mA + 1.737 \pm 0.558 mA, R = 0.994$$

$$ip(F) = \left\{ 38.310 \pm 4.899 \left[v (Vs^{-1})^{\frac{1}{2}} \right] \right\} mA - 1.666 \pm 1.898 mA, R = 0.976$$

$$ip(G) = \left\{ 12.170 \pm 5.306 \left[v (Vs^{-1})^{\frac{1}{2}} \right] \right\} mA + 6.791 \pm 2.055 mA, R = 0.798$$

$$ip(H) = \left\{ 24.308 \pm 2.339 \left[v (Vs^{-1})^{\frac{1}{2}} \right] \right\} mA + 3.059 \pm 0.906 mA, R = 0.986$$

This aspect suggests the process is diffusion-controlled and has a preceding chemical reaction.²³

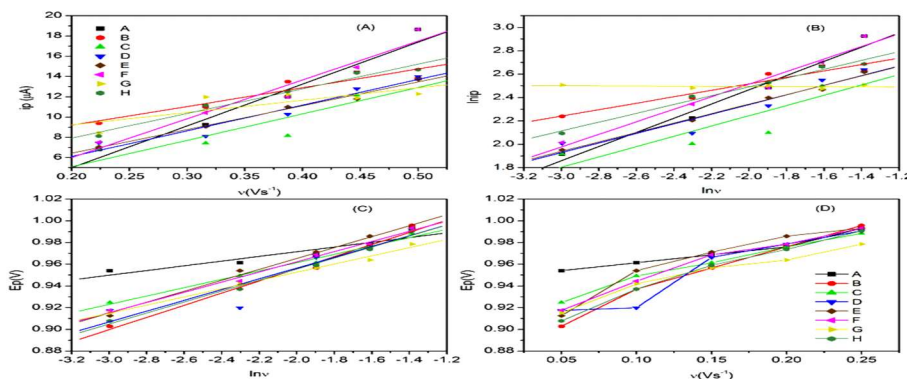


Fig.-4: Showing Calibration Graph (A) ip vs v , (B) $\ln ip$ vs $\ln v$, (C) E_p vs $\ln v$, (D) E_p vs v
Figure-4(B) illustrates that $\ln ip$ depends on $\ln v$ linearly, and the subsequent equation describes it.

$$\ln ip(A) = \{0.607 \pm 0.059 [\ln v (Vs^{-1})]\} mA + 3.681 \pm 0.125 mA, R = 0.986$$

$$\ln ip(B) = \{0.276 \pm 0.045 [\ln v (Vs^{-1})]\} mA + 3.069 \pm 0.095 mA, R = 0.963$$

$$\ln ip(C) = \{0.440 \pm 0.127 [\ln v (Vs^{-1})]\} mA + 3.124 \pm 0.269 mA, R = 0.894$$

$$\ln ip(D) = \{0.411 \pm 0.076 [\ln v (Vs^{-1})]\} mA + 3.163 \pm 0.160 mA, R = 0.953$$

$$\ln ip(E) = \{0.404 \pm 0.022 [\ln v (Vs^{-1})]\} mA + 3.151 \pm 0.047 mA, R = 0.995$$

$$\ln ip(F) = \{0.537 \pm 0.057 [\ln v (Vs^{-1})]\} mA + 3.588 \pm 0.120 mA, R = 0.984$$

$$\ln ip(G) = \{-0.004 \pm 0.014 [\ln v (Vs^{-1})]\} mA + 2.486 \pm 0.029 mA, R = -0.198$$

$$\ln ip(H) = \{0.377 \pm 0.027 [\ln v (Vs^{-1})]\} mA + 3.246 \pm 0.058 mA, R = 0.992$$

Figure-4(C) illustrates that the electrochemical process is controlled by diffusion.^{15, 24-26} The average value of αn and the value of αn were calculated according to Bard and Faulkner and Laviron equation respectively.¹⁵⁻¹⁶ The number of electrons transferred (n) was one (1) for 2MPNA in all the solutions. The value of k^0 and the electron transfer rate constant (k_{ox}) were also calculated which is a function of the applied potential.^{16, 27-28} A dependence E_p versus scan rate shows irreversibility. Standard electron potential (E^0) is also calculated (Fig.-4D). (Table-1)

Influence of Concentration of SOP and 2M4NA

Figure-5 illustrates the voltammogram of 2M4NA in different concentrations of SOP ranges 0.1-0.5M. As electrolyte concentration increases, due to high affinities between 2M4NA and species of supporting electrolyte, the peak current decreases and the peak potential switches to a positive potential value. The outcome confirms the inverse relationship between the diffusion coefficient and the solution's ionic strength. At low concentrations, a high peak current confirms the more oxidation of 2M4NA.

Influence of pH and SOP

Figure-6 shows a voltammogram of 5mM of 2M4NA at different pH (2.0-12.0) in the SOP solution. Figures-6(B) and (D) display the pH dependence of the current signal and peak potential. Anodic peak potential shifts to lower values up to pH 9.0, to the more positive potential at pH 10.0, and again attain a low value at pH 12.0 and obeys the following equation:

$$Ep(V) = 1.134 \pm 0.009 - 0.0264 \pm 0.001 \text{ pH}, R = 0.994$$

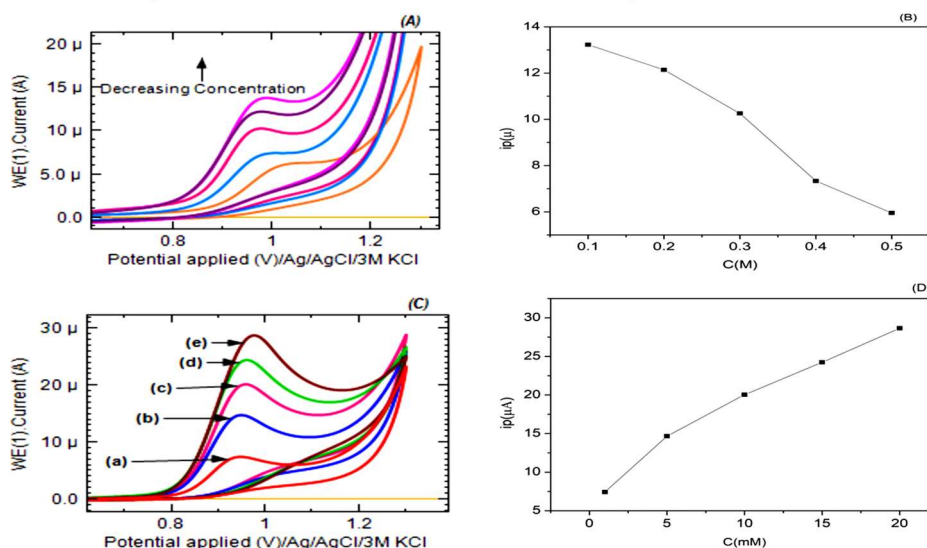


Fig.-5: (A) CVs of 5mM 2mpna in Different Conc. of SOP 0.1-0.5M at 100mv, (B) Calibration Graph of 2MPNA in Different Conc. of SOP 0.1-0.5M, (C) CVs of 1mM – 25mM 2mpna Different Conc. in 0.1M SOP at 100mV (D) Calibration Graph of Different Conc. of 2MPNA in 0.1M SOP

The slope value is close to the expected half of the theoretical value, indicating that transferred electrons are double in number that of the number of hydrogen ions.²⁹ So in this process, one proton and two electrons are involved. Initially, the increasing pH caused an increase in peak current (i_p), therefore, the significant outcome regarding sensitivity followed by a sharper response acquired at pH 7.0. Therefore, pH 7.0 was chosen as the optimum value to perform a quantitative assessment of 2M4NA.

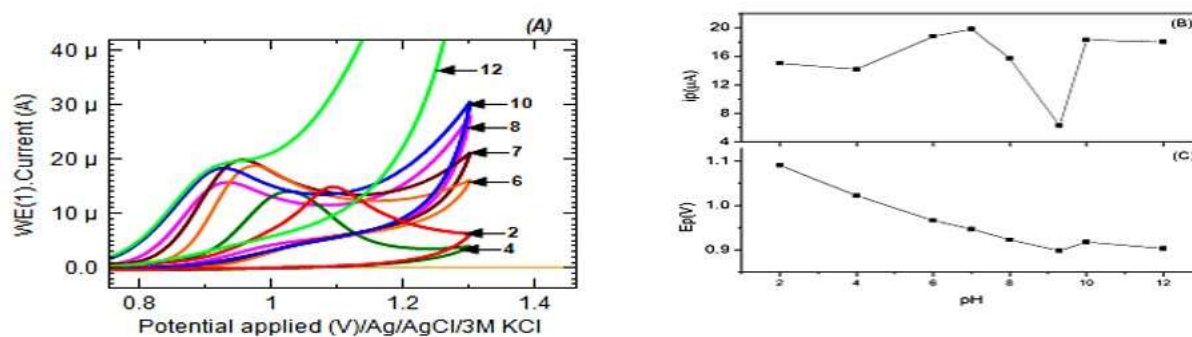


Fig.-6: (A) Voltammogram showing the effect of different pH of SOP in the Presence of 2M4NA, (B) Calibration Graph Showing a Trend of pH Against Peak Current (i_p), (C) Calibration Graph Showing a Trend of pH Against Peak Potential E_p

Validation of the Optimal Analytical Method

A linear correlation between concentrations of 2MPNA and the current signals was reported over 5mM-25mM (Fig.-7). The linearity range was found to be 5mM to 25mM. Accuracy is reported as a percentage recovery, so the average percentage value is more than 98 percent. Sensitivity is the limit of quantification and detection for the sample. LoD is a limit test that specifies above or below a specific value of an analyte. The lowest concentration of an analyte in a sample that can be accurately and precisely measured under the method's specified optimal parameters is known as the LoQ, defined as the signal-to-noise ratio; ($S/N=10$).³² According to the following calibration equation:

$$Ip(\mu A) = 0.1418 \pm 0.009 + 0.6177 \pm 0.001 C (mM), R = 0.994$$

The detection limit was 2.3mM.

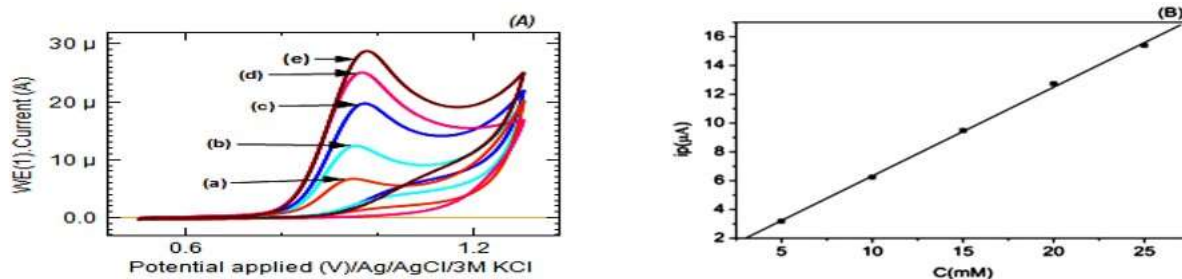


Fig.-7: (A) Voltammogram Showing Effect of Different Concentration of 2MPNA (a)-(e) 1mM, 5mM, 10mM, 15mM and 25mM Respectively in Real Sample, (B) Calibration Graph Showing Different Concentration of 2MPNA 5mM-25mM

Analytical Application of Proposed Method in Real Sample: Tap Water

The optimized method was then employed to spiked tap water. The results listed in Table-2 are satisfactorily accurate and precise. We employed the calibration graph to estimate spiked 2MPNA in the water sample. The finding results of the water sample acquired are tabulated (Table-3). Table-3 displays the RSD and SD values and the recovery was ranged from 98.7 to 102.0%.

Table-1: Kinetic Parameters of 2MPNA in Different Electrolyte

Solvent	Acetone	Range = 0.5-1.15				
Symbol	Supporting Electrolyte/0.1M	E^0 (V)	α	K^0 (cm/s)	n	Kox
	20% + 80% Buffer					
A	TEAB	0.943	0.693	1279.097	1	603.306
B	SOP	0.886	0.804	457.04	1	55.45
C	PPS	0.914	0.96	664.033	1	118.341
D	PHP	0.893	0.881	534.666	1	64.765
E	NaIO ₄	0.906	0.873	482.709	1	67.575
F	HCl	0.905	0.873	489.769	1	73.886
G	HNO ₃	0.907	0.857	661.944	1	149.007
	100%					
H	TSK Buffer	0.893	0.881	502.865	1	62.48
		Range= 0.5-1.30				
Symbol	Supporting Electrolyte/0.1M	E^0 (V)	α	K^0 (cm/s)	n	Kox
	100%					
B1	SOP	0.896	0.897	625.829	1	142.045

Table-2: Analytical Parameters and Resulted Values

Parameter	Value
Accuracy	99.914± 1.477
SE of intercept	0.197
SD of intercept	0.44
Linearity range	5.0-25.0mM
Correlation coefficient	0.998
Slope	0.617
Intercept	0.141
LOD	2.353mM
LOQ	7.130mM

Table-3: Application of the Optimal Method for Determination Of 2M4NA in Spiked Tap Water

Standard concentration (mm)	Found concentration (mm)	Recovery %
5	4.94	98.791
10	9.898	98.979
15	15.136	100.908
20	20.407	102.034
25	24.715	98.859
	\bar{x}	99.914
	SD	1.477
	RSD%	1.478

CONCLUSION

We found the oxidation process irreversible and diffusion-controlled in sodium orthophosphate (SOP) over 2.0 to 12.0 pH. This method also shows good reproducibility and a low detection limit for 2M4NA determination.

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