

Study of anodic stripping Voltametric characteristics of the 2,4,6-Trinitrotoluene and its use in the determination of conversion efficiency in the reaction with zero-valent iron

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Abstract

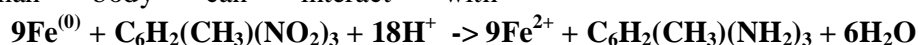
Even though many methods are available for the determination of 2,4,6-Trinitrotoluene in water, all these methods suffer from one more drawbacks. In the present work, a novel anodic stripping Voltammetric technique developed as it was simple, fast and precise, may be used in practice. In the supporting electrolyte of $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ 0.1 M with the accumulation time of 30 s, at accumulation potential of -0.9 V, the scan rate of 250mV/s, TNT has been shown a sharp peak current at $E = -0.573$ V. The factors that influence on the conversion efficiency of TNT in the sample, such as pH, accumulation of time and potential were also examined in the present method.

Keywords: 2,4,6-Trinitrotoluene, anodic stripping technique, Voltammetry, TNT and ZVI.

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1.0 Introduction

The presence of explosives such as 2,4,6-Trinitrotoluene, 2,4,6-Trinitrorezorcine, 2,4-Dinitrophenol and their residues in environment have become an emerging issue for public health. The degradation and by-products of explosives are toxic and carcinogenic chemicals. More than a century of production and extensive use of TNT have made it a major global soil and groundwater contaminant. The concentrations of TNT in the soil samples have reported from 10mg/kg to 12.000 mg/kg [1-3]. In aqueous waste streams, the TNT concentrations are as high as 70mg/L[4].The large amounts of TNT can result in liver, eye and neurological damage, besides, the products of TNT metabolism in human body can interact with



By the reaction, the initial reactant ($\text{C}_6\text{H}_2(\text{CH}_3)(\text{NO}_2)_3$) can be converted onto $\text{C}_6\text{H}_2(\text{CH}_3)(\text{NH}_2)_3$, then it can be removed from water by adsorption and biodegradation process.

Number of analytical methods has been used for determination of TNT and its derivatives [8-9] like spectrophotometry, gas chromatography and high performance liquid chromatography. In the last last few years square-wave Voltammetry has become an interesting method for analysis of explosives in air and soil, as it is very sensitive and fast [10]. There are reports that describe the usefulness of square-wave Voltametric method to determine the conversion efficiency of TNT in the reaction with zero-valent iron [12]. The application of this method has been limited when TNT concentration is very low. This article will describe the application of anodic stripping Voltametric method to determine TNT and its conversion efficiency in the reaction with

macromolecules such as DNA, causing genetic defects and cancer[5].The US- EPA (United States-Environmental Protection Agency) has set a drinking water limit of 20 $\mu\text{g/L}$ as the file time exposure limit for TNT[6-7]. The analysis of TNT from wastewater, groundwater and its application to control the treatment processes of TNT has become an important targete to prove the enhancement of treatment efficiency. Recently the removal of TNT and its derivatives from water by zero-valent iron (iron particles) has been applied to treat the industrial wastewater [11-19]. The treatment of TNT or other explosives was based on the reductive characteristics of $\text{Fe}^{(0)}$ and oxidative properties of explosives (TNT).The main reaction is as following:

ZVI in the hope of overcoming this limitation.

The content of this study is focused on the determination of TNT by anodic stripping Voltametry and main factors influencing on the conversion efficiency of TNT in the reaction with ZVI such as pH, reaction time, ZVI-mass.

2.0 Materials and methods

2.1 Apparatus

All experimental measurements were made with the polarographic analyzer model of 797 VA computrace from Metrohom with three electrodes: hanging mercury drop electrode (HMDE) as working, silver-silver chloride and platinum wire as reference and counter electrodes. All chemicals (except iron powder) used for the experiment were of reagent grade and used without further treatment. The samples of TNT (1mg/L) were prepared from solid state with distilled water. The zero-valent iron (ZVI) (>98% pure, particle size 0.25 mm and surface area 0.12 m^2/g) and NH_4Cl , NH_4OH (for the

supporting electrolyte) were used for this study.

2.2 Experimental procedure

The samples consisting of 25 mL supporting electrolyte (0.1M NH₄Cl+NH₄OH) with the

different concentrations of TNT were transferred onto electrochemical cell. Total samples in cells were desecrated by bubbling with high-purity nitrogen for 10 min.

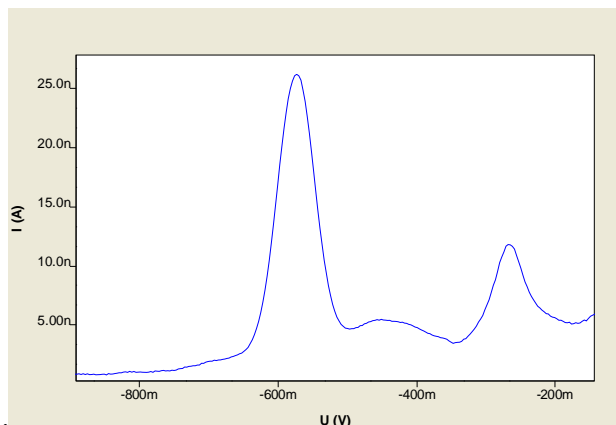


Figure-1: The anodic stripping Voltammogram of TNT in the electrolyte NH₄Cl +NH₄OH 0,1M consisting of 6,4 mg/L(TNT); acc. time =30s; acc. potential -0.9V; anodically polarized scan rate made at 250mV/s from -0.9 to - 0.1V.

The accumulation was carried out at -0.9V (while stirring) on a fresh drop of mercury and was followed by a settling period of 30 seconds. The drop was anodically polarized from -0.9 to -0.1V at scan rate of 250mV/s to obtain Voltammogram.

Batch experiments (for the reaction between TNT and ZVI) were performed in a rotary shaker at 25⁰C and 110 rpm. Solutions consisting of 200 mL of TNT solution and ZVI in the different concentrations were prepared in 250 mL Erlenmeyer flasks, pH adjusted with the diluted solution HCl or NaOH. After every 5-min-time interval, two mL of solution (surfactant) was taken and made up to 25mL with supporting electrolyte (NH₄Cl+NH₄OH, 0.1M) for the anodic stripping Voltametric analysis. The peak current heights on the Voltammogram corresponding to the TNT concentrations in the samples were used for the determination of the conversion efficiency (R%) of TNT in the reaction with ZVI. The conversion efficiency of TNT was calculated by the following expression:

$$R\% = \frac{I_p^0 - I_p^t}{I_p^0} \times 100$$

Here I_p^0, I_p^t denoted the peak heights corresponding to the TNT concentrations at initial and t-time in the reaction processes, respectively.

3.0 Results and Discussion

3.1. The anodic stripping Voltammetric current of TNT on HMDE

3.1.1. The choice of supporting electrolyte

Different supporting electrolytes such as CH₃COONa +CH₃COOH, KH₂PO₄+ NaOH, NH₄Cl and NH₄Cl + NH₄OH were

applied to the determination of TNT in the water samples respectively. The obtained results proved that there was a sharp oxidized peak of the TNT in NH₄Cl+NH₄OH, 0.1M solution. Hence, NH₄Cl+ NH₄OH 0.1M buffer was selected as supporting electrolyte for this study.

3.1.2. Anodic stripping Voltammogram of TNT

The anodic stripping Voltammogram of TNT on HMDE after 30s of accumulation at -0.90 V was presented in From Voltammogram, the sharp high peak current appeared at -0.573 V and this was proportional to the TNT concentrations (see

Figure-3) and hence the electrolyte was selected for analysis of TNT in the sample.

3.1.3. The influence of pH on peak current and peak potential

The influence of pH on peak current and peak potential was examined and presented in Table-1.

pH	$-I_{pic} (A).10^{-9}$	$-E_{1/2}(V)$
3	2.75	0.619
4	1.45	0.597
5	2.11	0.593
6	2.46	0.591
7	2.14	0.587
8	4.136	0.585
8.5	5.24	0.584
9	9.12	0.582
9.5	9.35	0.577
10	11.9	0.573
11	8.64	0.602

Table-1: Influence of pH of NH_4Cl (pH adjusted by HCl or NH_4OH solution) on peak current and peak potential. The scan rate, accumulation time and potential were $250mV/s$, 30 s acc., -0.8 V acc., respectively. $TNT = 3.2$ mg/L

The experimental data shows that the peak potential for TNT became more positive with increasing pH (Table-1) and with the pH increasing ($pH \leq 10$) the peak current increased. When pH was increased to greater than 10, the peak current decreased.

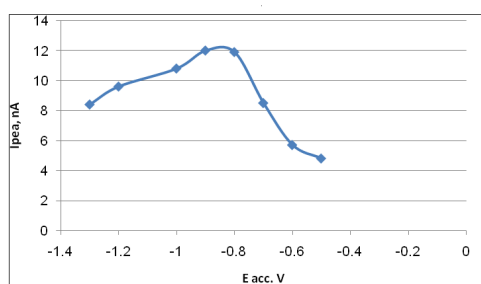


Figure-2: Influence of accumulation of potential on the peak current. $TNT=3.2mg/L$; $t_{acc}=30$ s; supporting electrolyte NH_4Cl+NH_4OH $0.1M$, scan rate $250mV/s$.

This suggested that the hydroxide ions would affect the rate of electrode reaction. Thus the $pH=10$ was selected for this study.

3.1.4. Choice of accumulation time and potential

The effect of accumulation time for 3.2mg/L NB was investigated from 0 to 120 s. Within 30 s the peak current of TNT increased with increase of accumulation time, then became constant (not shown here). The effect of accumulation potential was examined at a constant accumulation time of 30 s over the range from -1.3 to -0.5V in $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ 0.1M buffer and the data is given in Figure-2.

3.1.5. The dependence of the peak height on TNT concentrations

The anodic stripping Voltammetric currents of TNT with the different concentrations on HMDE after 30s of accumulation at -0.90 V were presented in Figure-3. The conditions for the anodic stripping Voltammetric analysis were selected with the accumulation time of 30 seconds, accumulation potential of -0.9 V, scan rate 250m V/s, supporting electrolyte $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ 0.1M, pH= 10.

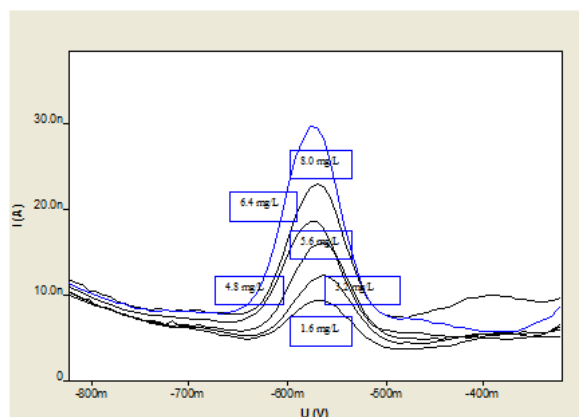


Figure-3: The anodic stripping Voltammetric currents corresponding to the TNT different concentrations.

The obtained data have shows that the peak current heights at the potentials of (-0.573 V) are proportional to the TNT concentrations in samples (see Figure-4).

The peak current height was used for determining the TNT and its conversion efficiency in reaction with ZVI

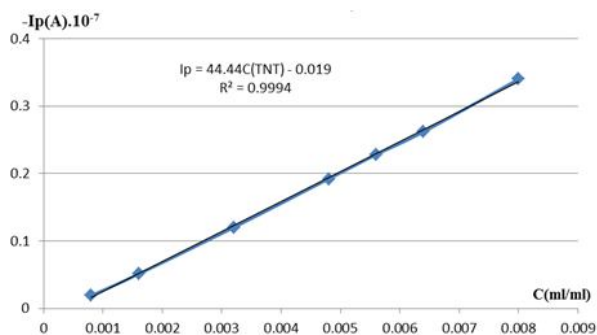


Figure-4: The plot of the peak current height versus different concentrations of TNT .

3.2 Application of the anodic stripping Voltammetric method in studying the conversion efficiency of TNT in reaction with ZVI

3.2.1 The anodic stripping Voltammetric current of TNT in sample after reaction with ZVI

The experimental data have shows that after reaction with TNT at different reaction times, the anodic stripping current of TNT consists of three peaks at the different potentials corresponding to P_A (-0.573 to -0.528V); P_B (-0.402 to -0.381V) and P_C (- 0.283 to- 0.251). The anodic stripping peak current at the potentials (-0.573 to- 0.528 V) (Peak1) that coincided with the TNT peak (Figure--1), was selected to calculate the conversion efficiency of TNT, because this peak height of TNT is sharply decreased for the reaction times, Figure-3.

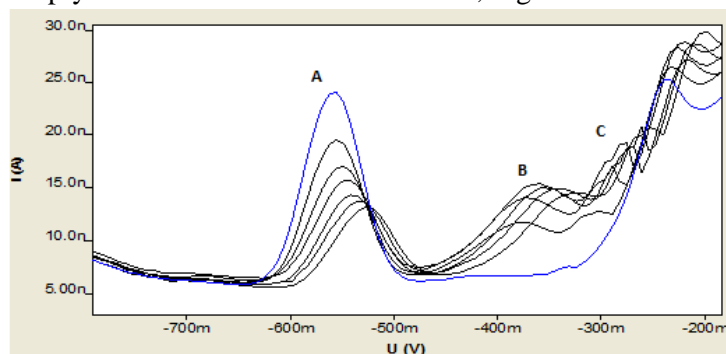


Figure-5: The anodic stripping Voltammogram of TNT after the reaction with ZVI (TNT = 3.2 mg/L, $Fe^{(0)}$ = 0.1157 g/200mL, pH= 5 for the reaction time from 5 to 30 minutes, while stirring with 110 rpm, temperature =25⁰C.

3.2.2 Factors influencing on the TNT conversion efficiency

Influence of solution pH

The experimental data shows that when the pH of reaction samples increased from 3.0 to 9.0, the TNT conversion efficiencies has decreased, Figure-4. These results suggest

that the reaction of TNT and ZVI occurred with the participant of ions H^+ to convert TNT into amine products (see above reaction).

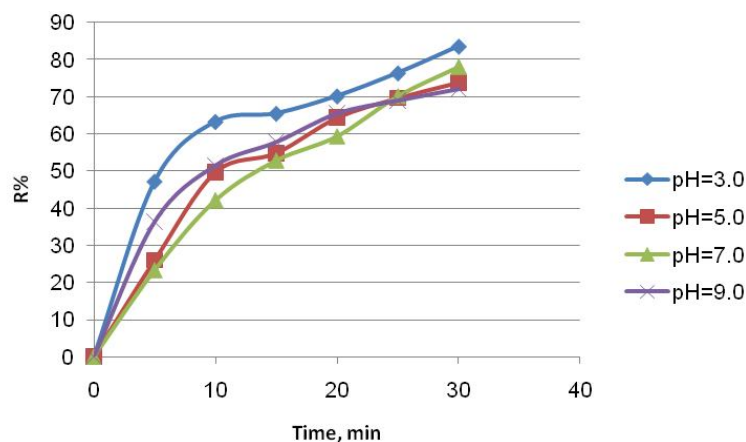


Figure-6: Influence of pH on TNT conversion efficiency versus time and pH, TNT = 3,2mg/L, $Fe^{(0)}$ = 0.1157 g/200mL, while stirring with 110 rpm, temperature =25⁰C.

Influence of ZVI mass

The experiments have been carried out with 3,2mg/L of TNT (constant) and the different ZVI mass such as 0.1157; 0.2034; 3.1012 g./200mL, pH= 3.0; reaction time from 0 to 30 minutes while stirring with 110 rpm. The obtained experimental data shows that the TNT conversion efficiency increases as the ZVI-mass increased, Figure-7.

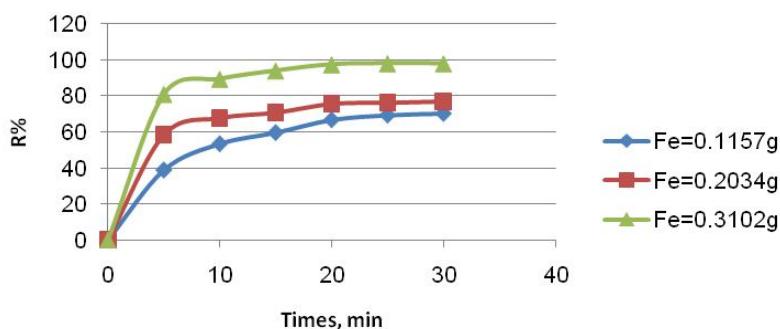


Figure-7: Influence of ZVI mass on TNT conversion efficiency, TNT=3.2mg/L, pH=5.0, reaction time from 5 to 30 min, stirring 110rpm, temperature 25⁰C.

The high conversion efficiency of TNT with high ZVI mass, besides the reduction of TNT may be due to the contribution of precipitation, adsorption onto FeOOH formed in solution, suggested by Dimitrios Vlassopoulos et al [20]. According to these authors, ZVI is a good adsorbent in environmental treatment of polluted water.

4.0 Conclusion

In the present method, a novel anodic stripping Voltammetric method was developed to determine TNT in water and its conversion efficiency in the reaction with ZVI. The method developed was simple, accurate and precise to determine TNT even at low concentration level of $4.4 \cdot 10^{-3}$ mM.

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