VOLTAMMETRY STUDY OF THE 2,4,6 -TRINITROTOLUENE CONVERSION INTO THE AMINE COMPOUNDS USING ZERO-VALENT IRON

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abstract: The paper describes the use of voltammetry in monitoring the reductive process of 2,4,6 Trinitrotoluene(TNT) to amine compounds by zero-valent Iron. This method let us to determine simultaneously the reduction of TNT and the increase of Fe^{2+} concentrations in the samples. The method may be applied to determine quickly the efficiency of the conversion process of TNT, the role of zero-valent iron, and its efficiency in the reductive process. The factors such as pH, TNT concentration, reaction times and Fe(0) mass influencing on the conversion process into amine compounds have been studied.

key words: voltammetry; 2,4,6- Trinitrotoluene; Zero-valent Iron; Reduction of TNT.

1. Introduction

The degradation of nitro aromatic compounds, especially 2,4,6-Trinitrotoluene (TNT) is of interest because they are recalcitrant environmental contaminants resulting from munitions, insecticides, herbicides pharmaceuticals and dyes manufacturing. They also may be formed in the environment from aromatic contaminants in the atmosphere [1]. Degradation of TNT has been implemented by many methods such as incineration, electrochemical reductions, using hydrogen as a reducing agent and using zero-valent metals as reducing agent like metallic iron particles [2,3]. Using zero-valent iron to convert TNT into triamine toluene (TAT) is an interest problem studied in the work [4]. An important thing suggested finding out the methods to quickly evaluate the efficiency of the substrate conversion into final products. In the present work a reduction or conversion of TNT into amine compounds (TAT) by metallic iron particles has been studied. As known the overall reaction of TNT with $Fe^{(0)}$ is as follows:

$$TNT + 9\ Fe^{(0)} + 18\ H^+ \longrightarrow TAT + 9\ Fe^{2+} + 6\ H_2O. \tag{1}$$

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As known TNT and Fe^{2+} concentrations may be evaluated by voltammetry [5]. By this method the decreasing of TNT amount and the increasing ferrous concentrations in the samples are easily determined simultaneously. Besides, the advantage of this method is to determine the efficiency of metallic iron particles used for the reduction of TNT to form TAT.

2. Experimental part

Chemicals

TNT compound was obtained in high purity from Merck Company. The stock solutions of TNT (5 mM) were prepared in distilled water. Iron powder (99.9% purity), with the grain size (mostly $\leq$ 60 mesh) was purchased from China. The trace impurities of iron powder are 0.02% C; 0.008%S; 0.003% Si; 0.002%P; 0.002% Mn.

The sodium acetate buffer 0.01M was used as the reaction medium for the reduction of TNT by $Fe^{(0)}$.

Iron pretreatment

Prior to use, the $Fe^{(0)}$ grains were treated in 10% HCl (v/v) for 10 min to remove surface oxides or other contaminants. The cleaned metal was washed four times with distilled water to remove residual acidity or chloride remaining after the acid treatment.

Model reaction systems

A capped 250-ml glass bottle filled with 100 ml of sample consisting of sodium acetate buffer 0.01M, TNT (5mM) and 10g $Fe^{(0)}$/l was used for the experiments. The glass bottle was placed in an electric shaker which maximized contact between TNT and $Fe^{(0)}$. The concentration change of TNT and the increase of Fe^{2+} in the samples were determined by square wave voltammetry on electrochemical trace analyzer (Princeton Applied Research) with M394 analytical Voltammetry software. The hanging drop mercury electrode was used for the working electrode. The 2nd electrode used is the Ag- electrode. The 3rd electrode configuration is Pt - wire. Usually 1ml of the sample is taken out after every interval of 10mim for the reaction and added to 9 ml of supporting electrolyte (0.1M KCl, 0.1M acetate buffer) in a 10-ml volumetric flask for voltammetry analysis. The measurements were set up with the following parameters: initial potential of –0.2V, the final potential of –1.6 V. Prior to voltammetry analysis, each sample was bulled with nitrogen for 5 min to remove oxygen.

Calculation method

There is a lot of factors which influence on the rate of the reduction reaction between TNT and $Fe^{(0)}$ such as pH, concentration of TNT, $Fe^{(0)}$ mass, temperature, dissolved oxygen, anion adsorption. In this paper we have presented the influence of TNT concentration, $Fe^{(0)}$-mass, dissolved oxygen only. These influences of these factors were calculated by the relative change of TNT and the efficiency of $Fe^{(0)}$ used for the reaction.

The change of TNT vs. the time reaction as follows:

$$\%TNT = \frac{I_c^t}{I_c^0} \cdot 100 , \tag{2}$$

with I_c^0, I_c^t are the peak height of voltammetry wave corresponding to the concentrations of TNT at the initial time and time t, at the potential of $-1,32$ V.

From equation (1), and the application of the calculation [5] the role or efficiency of the metallic iron taken part in the reduction process is expressed by the expression:

$$E_{Fe} = \frac{Fe(LT)}{Fe(TT)} = \frac{I_c^0 - I_c^t}{9} \cdot \frac{1}{I_{Fe}^t} \cdot 100 \tag{3}$$

Here I_c^0, I_c^t, I_{Fe}^t are the peak height of voltammetry wave corresponding to the concentrations of TNT at the initial time and time t and the concentration of Fe^{2+} in the time t respectively. $Fe(LT)$, $Fe(TT)$ are the concentration of Fe^{2+} determined by theoretic and experimental data.

3. Results and discussion

3.1. The voltammetry square wave of TNT and Fe^{2+}

The voltammetry square wave of TNT and Fe^{2+} in the sample is given in the Fig.1.
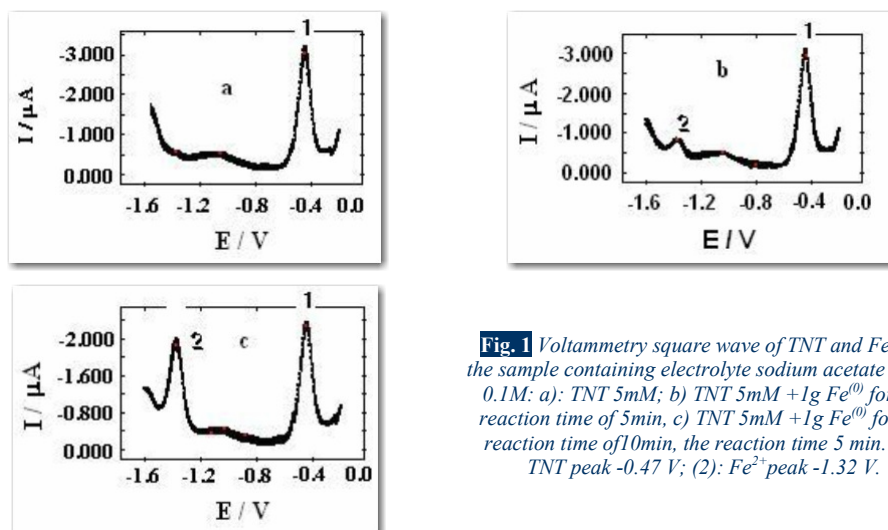

Fig. 1 *Voltammetry square wave of TNT and Fe^{2+} in the sample containing electrolyte sodium acetate buffer 0.1M: a): TNT 5mM; b) TNT 5mM +1g $Fe^{(0)}$ for the reaction time of 5min, c) TNT 5mM +1g $Fe^{(0)}$ for the reaction time of 10min, the reaction time 5 min. (1): TNT peak -0.47 V; (2): Fe^{2+} peak -1.32 V.*

By these waves the concentrations of TNT and Fe^{2+} are determined by the addition method. The experimental data have shown that concentrations of TNT in the range of 5÷100 ppm and the concentrations of $Fe^{2+} \geq 10$ ppm are easy may be determined by this method.

During the reaction between TNT and $Fe^{(0)}$ the voltammetry analysis has suggested only two peaks corresponding to TNT (–0.47V) and to Fe^{2+} (–1.32V). The conversion of TNT into final compound may implement by some steps such as:

$$TNT \rightarrow MAT \rightarrow DAT \rightarrow TAT \qquad (4)$$

Here MAT, DAT noted monoamine toluene, diamine toluene.

Beside these compounds, in the sample may find out nitroso or hydroxylamine toluene. In the weak acid medium, all intermediate compounds may give a commune square wave peak like TNT at the potential of –0.47V due to the reduction potentials of these compounds were very close [6]. This lets us use the peak height at the potential of –0.47 V to evaluate the conversion of TNT into TAT. The Fe^{2+} concentration in the samples is evaluated by the peak height at the potential of –1.32 V.

3.2. Concentration time profile of TNT

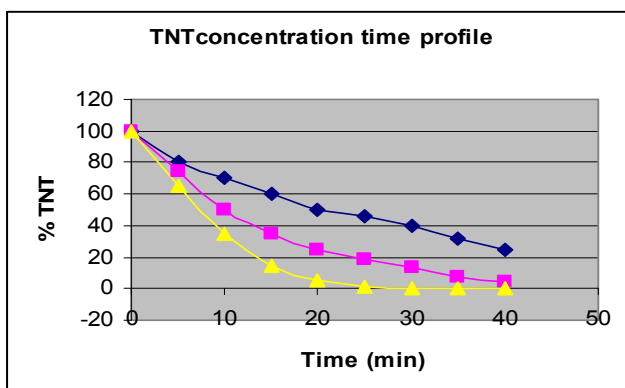The relative decrease of TNT concentration during the reaction in the samples is presented in the Fig.2.

Fig. 2 *TNT concentration time profile*
Samples of 100ml acetate buffer containing 1g Fe, pH= 4.5 and 12mg TNT (1); 8mg (2) TNT; 5mg TNT (3).

The experimental data have shown that at the constant Fe mass, the relative percent part of TNT concentration in the sample decreased during reaction and depends on the initial concentrations of TNT. When the initial TNT concentration is 12mg/100ml, after 40 min proceed, its relative percent part in the sample reached by 25%, while for the initial TNT concentration of 5mg/100ml, this relative percent part is near zero for the same conditions. These results are in concordance with the theory of the heterogeneous reaction and the work [5]. Due to this reason the reduction of TNT by $Fe^{(0)}$ would be applied suitably when concentration of TNT in the samples is low. In practice the zero-valent iron has been used for the treatment of the TNT contaminated ground water [6].

Studying the reaction kinetics of reduction process of the organic compounds (like TNT, aniline blue dye) using zero – valent iron the authors [6,7] have suggested that reaction rate law follows the expression:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = -\frac{V_m C}{K_{1/2} + C} , \tag{5}$$

Here C noted TNT concentration, mM, V_m (mM min^{-1}) is the maximum reaction rate for a particular experiment and $K_{1/2}$(mM), defined as C at $V_m/2$ reflects the affinity of the metal surface for the organic reactant. $K_{1/2}$ is roughly constant a particular substrate, presumably because all iron tends to be coated with similar oxides but, V_m varies due to different concentration of reactive sites. The $K_{1/2}$ and V_m would be determined by the plot of the dependence of the initial reaction rate on the different initial concentration of TNT and different Fe$^{(0)}$ mass. The experimental plot of the initial reaction rate vs. TNT concentrations is presented in Fig. 3.
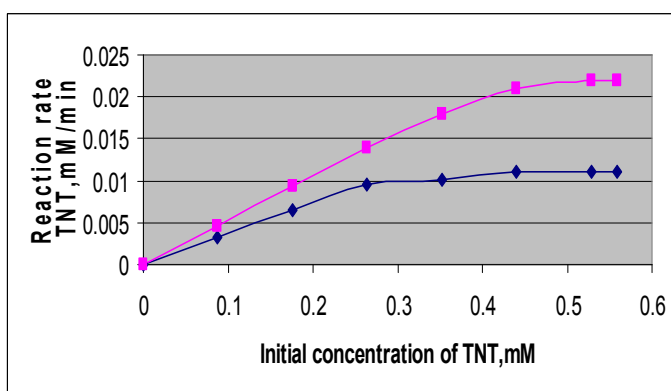

Fig. 3 *The dependence of the reaction rate vs. initial TNT concentration at the different mass of Fe(0):*
1. Fe(0) mass = 0.5g/100ml.
2. Fe(0)mass = 1.0 g/100ml.

By the experimental plots the values of V_m and $K_{1/2}$ were determined. V_m = 0.0105 mM min^{-1} (when Fe$^{(0)}$ =0.5g/100ml); 0.0221mM min^{-1} (when Fe$^{(0)}$ =1.0g/100ml); corresponding the $K_{1/2}$ = 0.0191 mM.

The obtained experimental lot is fitted with the expression (4). This has suggested again the reduction of TNT using Fe$^{(0)}$ would suitable when TNT concentration in the sample is low.

3.3. The role of zero - valent iron in the reduction of TNT

The zero – valent iron is a donor electron agent in reductive reaction of TNT (reaction 1). Since concentration of Fe^{2+} and TNT can be determined simultaneously using square voltammetry wave, it may let us determine the indirectly the efficiency (E) of the use of Fe$^{(0)}$ in the reduction of TNT by the expression [5]:

$$E = \frac{\text{moles of } Fe^{2+} \text{ theoretically required}}{\text{moles of } Fe^{2+} \text{ actually consumed}} \tag{6}$$

Basing the equation 1, the moles of Fe^{2+} theoretically required may determined through the TNT concentration converted into TAT divided by 9, the expression became as follows:

$$E = \frac{I_{TNT}^0 - I_{TNT}^t}{9I_{Fe^{2+}}^t} \cdot 100 \qquad (7)$$

Here I_{TNT}^0, I_{TNT}^t, $I_{Fe^{2+}}^t$ are the peak height of the voltammetry wave corresponding to the TNT concentration at the initial and t-time, Fe^{2+} concentration at t-time.

The efficiency of TNT reduction by $Fe^{(0)}$ has determined in the both cases with the presence of oxygen (2×10^{-4}M) or absence of oxygen, it presented in Table 1.

Table 1 *The efficiency of the $Fe^{(0)}$ - use in TNT reduction*

Nr.	Reaction time, min	$Fe^{(0)}$g/L	TNT,mg/L	E % (With O_2)	E% (Without O_2)
1	0	10	100	0	0
2	15	10	100	8	20
3	30	10	100	16	32
4	45	10	100	20	45
5	60	10	100	32	55

The experimental data have shown that the efficiency of using $Fe^{(0)}$ for the reduction of TNT in the presence of oxygen is much lower than the case of oxygen absence. It is evidence that oxidation of $Fe^{(0)}$ by oxygen is a major side reaction to reduction of TNT, that low efficiencies can be attributed to the oxidation of $Fe^{(0)}$ by oxygen. Beside the oxidation by oxygen, the re-oxidation of intermediates such as hydroxylamine – toluene to nitroso – toluene can also cause more $Fe^{(0)}$ to be consumed [5]. Hence, one may conclude that $Fe^{(0)}$ is suitably applied for the reduction of TNT or other substrates presented in groundwater, where the oxygen concentration is low.

4. Conclusion

The reduction of TNT by zero-valent iron may proceed with some steps to aniline toluene. The TNT, its intermediates and Fe^{2+} concentrations are determined using the peak height at the potential of –0.47V and –1.32V respectively By voltammetry method (square wave technique) the efficiency of TNT conversion and the efficiency of $Fe^{(0)}$ use for the reductive process were determined. The experimental data shown that reaction rate of the TNT conversion into TAT depended on the initial TNT concentrations, fitted with the expression $\frac{dC}{dt} = -\frac{V_m C}{K_{1/2} + C}$. The efficiencies of $Fe^{(0)}$ utilization in the reductive process of

TNT may be evaluated by the expression $E = \frac{I_{TNT}^0 - I_{TNT}^t}{9I_{Fe^{2+}}^t} \cdot 100$, which is influenced by the

presence of oxygen in the sample. The low efficiencies may be attributed to the oxidation of $Fe^{(0)}$ by oxygen.

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