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Voltammetry Study of the 2,4,6-Trinitrotoluene Conversion into the Amine Compounds Using Zero-Valent Iron

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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 to simultaneously determine the reduction of TNT and the increase of Fe^{2+} concentrations in the samples. The method may be applied to establish 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: Polarography, 2,4,6-Trinitrotoluene, Reduction, Zero-valent iron.

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 may also be formed in the environment from aromatic contaminants in the atmosphere[1]. Degradation of TNT has been implemented by such methods as incineration, electrochemical reductions, hydrogen as a reducing agent and zero-valent metals as reducing agent like metallic iron particles[2,3]. Using zero-valent iron to convert TNT into triamine toluene (TAT) is the subject of the several studies[4]. One advantage of the method is to quickly evaluate the efficiency of the substrate conversion into final products. In the present work a reduction or conversion of TNT into amino compound (TAT) by metallic iron particles has been studied. As known the overall reaction of TNT with $Fe^{(0)}$ is as follows:

$$TNT + 9Fe^{(0)} + 18H^+ \longrightarrow TAT + 9Fe^{2+} + 6H_2O \qquad (1)$$
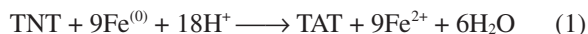
As known TNT and Fe^{2+} may be evaluated by voltammetry[5]. By this method the decreasing TNT amount and the increasing ferrous concentrations in the samples are easily determined simultaneously. Besides, the advantage of this method is to determine the efficiency of metallic iron particles used for the reduction of TNT to form TAT.

EXPERIMENTAL

2,4,6-Trinitrotoluene (TNT) compound was obtained in high purity from Merck Company. The stock solution of TNT (5 mM) was prepared in distilled water. Iron powder (99.9 % purity), with the grain size (mostly ≤ 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 0.01 M was used for 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 was be filled with 100 mL of sample with sodium acetate buffer 0.01 M, TNT (5 mM) and 10 g $Fe^{(0)}$/L were 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 2-electrode used is the Ag-electrode. The 3-electrode configuration is Pt-wire. Usually 1 mL of the sample is taken out after every interval of 10 min for the reaction and added to 9 mL of supporting electrolyte (0.1 M KCl, 0.1 M acetate buffer) in a 10-mL volumetric flask for voltammetry analysis. The measurements were set up with the following parameters: initial potential of -0.2 V, the final potential of -1.6 V. Prior to voltammetry analysis, each sample was filled with nitrogen for 5 min to remove oxygen.

Calculation method: Many factors influence 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. The influences of these factors was 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:

$$TNT\,(\%) = \frac{I_c^t}{I_c^0} 100 \qquad (2)$$

with I_c^0, I_c^t are the peak height of voltammetry wave corresponding to the concentrations of TNT in the initial and time t, at the potential of -1.32 V.

From eqn. 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 following equation:

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

here I_c^0, I_c^t, I_{Fe}^t are the peak height of voltammetry wave corresponding to the concentrations of TNT in the initial 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.

RESULTS AND DISCUSSION

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. From 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 appeared to be easily determined by this method.

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

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

here MAT, DAT noted monoamine toluene, diamine toluene.

Beside these compounds, in the sample nitroso or hydroxylamine toluene may be found. In the medium weak acid, all intermediate compounds may cause a commune square wave peak like TNT at the potential of -0.47 V because 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.

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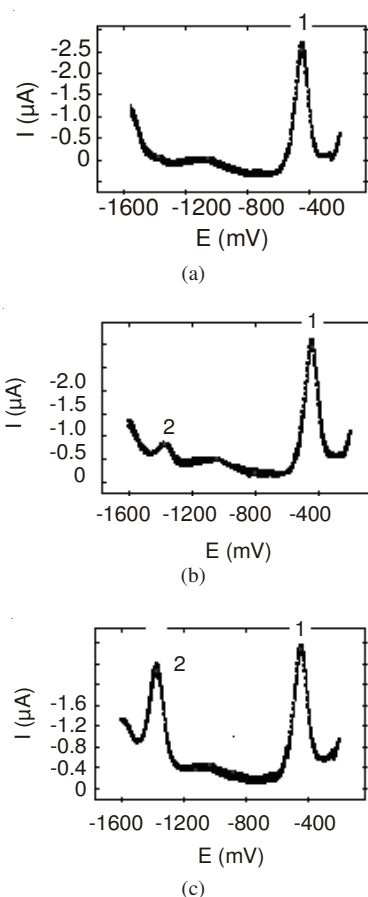

Fig. 1. Voltammetry square wave of TNT and Fe^{2+} in the sample containing electrolyte sodium acetate buffer 0.1 M: (a): TNT 5 mM; (b) TNT 5 mM + 1 g $Fe^{(0)}$ for the reaction time of 5 min, (c) TNT 5 mM + 1 g $Fe^{(0)}$ for the reaction time of 10 min, the reaction time 5 min (1): TNT peak -0.47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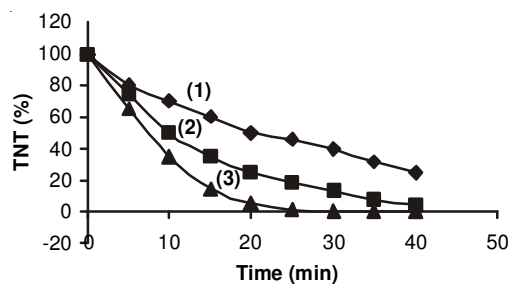

Fig. 2. 2,4,6-Trinitrotoluene concentration time profile samples of 100 mL acetate buffer containing 1 g Fe, pH = 4.5 and 12 mg TNT (1); 8 mg (2) TNT; 5 mg TNT (3)

The experimental data have shown that at the Fe mass constant, the relative per cent part of TNT concentration in the sample decreased during reaction and depended on the initial concentrations of TNT. When the initial TNT concentration is 12 mg/100 mL, after 40 min, its relative per cent part in the sample reached by 25 %, while for the initial TNT concentration of 5 mg/100 mL, this relative per cent part is near zero in the same conditions. These results are in concordance with the theory heterogeneous reaction and the studies[5]. Due to this reason the reduction of TNT by $Fe^{(0)}$ would be applied appropriately 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].

Studies on the reaction kinetics of reduction process of the organic compounds (like TNT, aniline blue dye) using zero-valent iron, Martin and Tashdjian[6] have suggested the reaction rate law in the expression as follows:

$$\frac{dC}{dt} = -\frac{V_m C}{K_{1/2} + C} \quad (5)$$

where C is the 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 concen-tration 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.
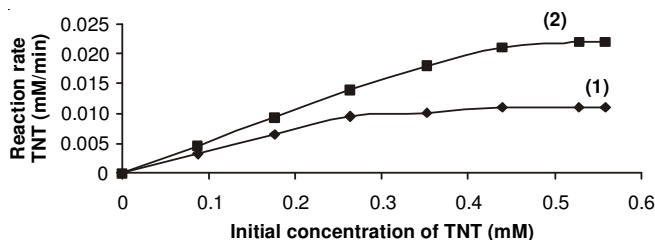

Fig. 3. Dependence of the reaction rate *vs.* initial TNT concentration at the different mass of Fe$^{(0)}$: (1) Fe$^{(0)}$ mass = 0.5 g/100 mL, (2) Fe$^{(0)}$ mass = 1.0 g/100 mL

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

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

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 indirectly the efficiency (E) of the use of Fe$^{(0)}$ in the reduction of TNT by the expression[5]:

$$E = \frac{\text{Moles of Fe}^{2+} \text{ theoretically required}}{\text{Moles of Fe}^{2+} \text{ actually consumed}} \quad (6)$$

Based on the eqn. 1, the moles of Fe^{2+} theoretically required may determined through the TNT concentration converted into TAT divided by 9, the expression (6) became as follows:

$$E = \frac{I^0_{TNT} - I^t_{TNT}}{9 I^t_{Fe^{2+}}} 100 \quad (7)$$

here I^0_{TNT}, I^t_{TNT}, $I^t_{Fe^{2+}}$ 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 (Table-1).

TABLE-1
EFFICIENCY OF THE Fe$^{(0)}$-USE IN
2,4,6-TRINITROTOLUENE REDUCTION

No.	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 in case of without oxygen. It is evident that the 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.

Conclusion

The reduction of TNT by zero-valent iron may proceed with some steps to aniline toluene. The 2,4,6-trinitrotoluene, its intermediates and Fe^{2+} concentrations are determined using the peak height at the potential of -0.47 and -1.32 V, respectively by votlammetry 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 $\dfrac{dC}{dt} = -\dfrac{V_m C}{K_{1/2} + C}$. The efficiencies of Fe$^{(0)}$ using in the reductive process of TNT which may be evaluated by the expression $E = \dfrac{I^0_{TNT} - I^t_{TNT}}{9 I^t_{Fe^{2+}}} \times 100$, are 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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