Using an anodic Fenton process for degradation of nitrobenzene in waste water

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Abstract

The paper deals with the degradation of nitrobenzene (NB) by advanced catalytic oxidation based on an anodic Fenton's reagent. . The degradation or the conversion of nitrobenzene in to CO_2, H_2O and other minerals was performed by electrochemical method in the electrolysis system with direct current, with the iron anode section volume of 53ml, with potential 2.5 V, consisting of EDTA (1mM), O_2 (10mg/l), Na_2SO_4 (0.1M), the graphite cathode section volume of 53ml consisting electrolyte of Na_2SO_4 (0.1M). Concentrations of NB during electrochemical degradation were monitored using high-performance liquid chromatography, (HPLC, Aligent USA). The electrochemical degradation of NB can be explained by the free radical $OH^{\bullet}$ generated during electrolysis using direct current with iron anode in presence of EDTA, oxygen in weak acid pH – solution.

Keywords: Degradation of nitrobenzene, advanced oxidation, anodic Fenton's reagent, oxygen activation.

Introduction

The destruction of aromatic compounds from groundwater and wastewater is of interest due to its biotoxic and recalcitrant properties preventing direct biological treatment. Moreover the treatment conducted at mild operating conditions is gaining more attention because of lower equipment and operation costs. The system of Fe^0 – H_2O was successfully used to reduce nitro aromatic compounds [1, 2]. In this case the nitro groups were rapidly reduced to the corresponding amines due to the presence of iron, in its zero–valent state (Fe^0) and dissolved ferrous form (Fe^{2+}) in water. The combination of zero-valent iron and H_2O_2 exhibiting both the oxidative and reductive characters has been used in the removal of organic compounds from water [3, 4]. It is known that in the case of the oxidation of the metallic iron in oxidation conditions, both ferrous iron superoxide radicals and free radicals $OH^{\bullet}$ appear to be generated, leading to degradation of contaminants. The oxygen activation at room temperature and pressure is of fundamental importance used in practice. In [5] the combination of metallic iron with ethylenediaminetetraacetic acid with atmospheric oxygen was used to completely destruct the mixture of 4-chlorophenol and pentachlorophenol under room temperature conditions. In that study, the authors proposed three possible dioxygen activation schemes: (i) a heterogeneous activation at the metallic iron surface, (ii) a homonogeneuos activation by ethylenediaminetetraacetic acid (EDTA) and finally, (iii) an heterogeneous activation producing ferryl species at the surface of the particles. The oxidative system consisting of zero-valent iron, EDTA and atmospheric oxygen was used to degrade many toxic, persistent organic compounds [6]. In practice the oxygen activation may be implemented by the some ways: chemistry, electro chemistry and photo catalysis, as follows:

- The chemical way

The oxygen activation was performed at mild conditions in the system of $Fe^{(0)}$- L - O_2 - H_2O. In this case the free radical $OH^{\cdot}$ generated from the activation has been demonstrated in the destruction of melathion [6] and EDTA [7].

The electrochemical process

An indirect electro-oxidation method with H_2O_2 electrogeneration is based on the continuous supply of this oxidant in acid medium from the two-electron reduction of oxygen gas:

$$O_2\,(g) + 2H^+ + 2e^- \rightarrow H_2O_2$$

This reaction can take part in different cathodes such as reticulated vitreous carbon [8], mercury pool, carbon felt and O_2- diffusion electrodes.[9]

When Fe^{2+} is added to the medium, the oxidizing power of electrogenerated H_2O_2 is enhanced by the production of $OH^{\cdot}$ from the classical Fenton'reaction

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^-$$

In other cases, when Fe^{3+} is added to electrolyte, in the presence of oxygen and EDTA, the ferrous iron generated in this manner at the cathode surface may produce an oxygen activation. [10]

The photo catalytic way [11].

The photo catalytic process in the system of O_2/ TiO_2/ UV leads to oxygen activation through reactions:

$$TiO_2 + hv \rightarrow e_{CB}^- + h_{VB}^+$$

$$e_{CB}^- + O_2 \rightarrow {}^{\bullet}O_2^-$$

The ${}^{\bullet}O_2^-$ can then react with H_2O to provide additional $OH^{\bullet}$, OH^- and O_2 as follows:

$$2^{\bullet}O_2^{-} + 2H_2O \rightarrow H_2O_2 + 2OH^{-} + O_2,$$
$$H_2O_2 + e^{-}_{CB} \rightarrow OH^{\bullet} + OH^{-}$$

In addition, the hydrogen peroxide generated may also react with the ferrous iron added to produce highly reactive hydroxyl radicals.

The above presentation shows that the oxygen activation due to the ferrous iron freshly generated, in acidic medium has been demonstrated. The addition of an organic ligand like EDTA to this system would enhance the efficiency of oxygen activation. This paper describes the oxygen activation process by electrochemical method using a divided cell with a graphite cathode and an iron sacrificial anode able to electrogenerate Fe^{2+}. After the addition of EDTA and atmospheric oxygen to the electrolyte (Na_2SO_4, $pH = (3 \div 4)$, the nitro aromatic compounds like nitrobenzene are simultaneously degraded during electrolysis. This is a novel study on forming free radical $OH^{\cdot}$ to degrade nitrobenzene compounds by this system.

Experimental Section

2.1. Chemicals

Nitrobenzene (NB) and EDTA were reagent grade from Merck. Anhydrous sodium sulfate, Na_2SO_4 as background electrolyte was analytical grade Fluks. Analytical grade sulfuric acid was purchased from Merck. Organic solvents and other chemicals used were analytical grade from Merck.

2.2. Apparatus and analysis procedures

All electrochemical measurements were carried out by an Autolab with PGSTAT30 (Fig.1)

Fig. 1 Instrument of electrolysis

Three electrode the system consists of (i) iron anode (working electrode), (ii) graphite rod (auxiliary electrode and (iii) Calomel electrode (reference electrode). A KNO_3 salt bridge keeps the auxiliary electrode separated from bulk solution. The employed anode and cathode have effective area of 5 cm^2. The working volume of the anodic and cathode section had the same size of 53 ml. Before electrolysis every electrode was treated with a diluted acidic solution (0.5M) to remove contaminants deposited. The solution pH was measured with a Crison 2000 pH-meter and adjusted directly by NaOH or H_2SO_4 (0.05M). The oxygen concentration in the samples is kept constant by the pure oxygen resource outside. The determination of NB compounds and their degradation products were implemented using high-performance liquid chromatography (HPLC, Aligent USA) by comparison with the retention time of the standard compounds. Aliquots of 25μl were filtered using a 0.1μm nylon membrane filter, injected into the HPLC to determine the concentration of NB compounds and degradation products, running with mobile phase of acetonitrile/water/concentrated H_3PO_4 (v/v/v) at 45/54/0.1. The separation was performed with a Sphesisorb C18 (200 x 4mm) reversed phase column at flow rate of 1.5 ml/min and column temperature of 25^0C. A UV detector was used with the wavelength set at 275 nm.

The efficiency of the degradation process or conversion of nitrobenzene during electrolysis time is calculated by the expression as follows:

$$D\ (\%) = \frac{C_0 - C_t}{C_0} 100,$$

Here: C_0, C_t, (in g/l) are the concentrations of NB at the initial and t- time respectively.

3. Results and Discussion

3.1. Degradative behavior of nitrobenzene

In the experiments electrolysis was carried out by direct current in the two-divided electrolytic cell system at 2.5 V (for anode). The anodic cell contained 53 ml of Na_2SO_4 (0.1M), NB (0.05g/l), EDTA 1mM, oxygen (10mg/l). The cathode cell contained only 53 ml of Na_2SO_4 (0.1M), medium pH of 3.5. After electrolyzing for 30 and 60 minutes, respectively the samples were taken out, and filtered for HPLC analysis. Fig. 2 and Fig 3 show the results of HPLC analysis.

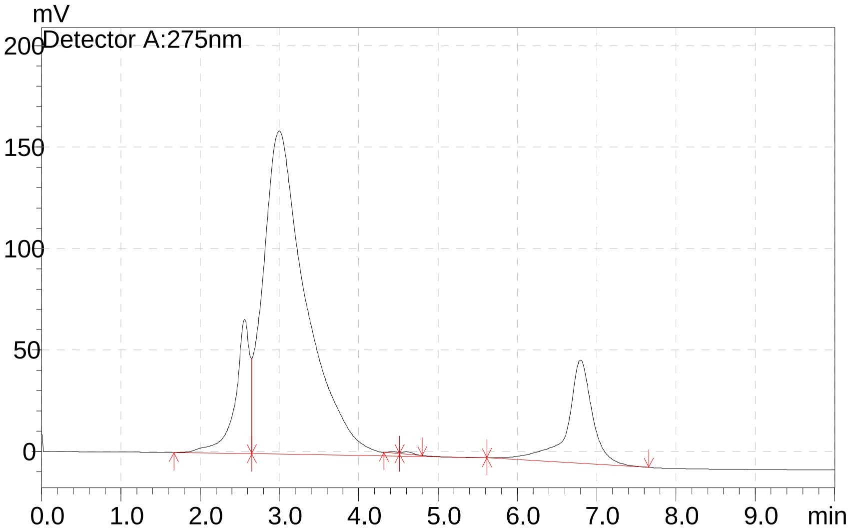


Fig. 2. Chromatogram of studied sample electrolyzed for 30minutes

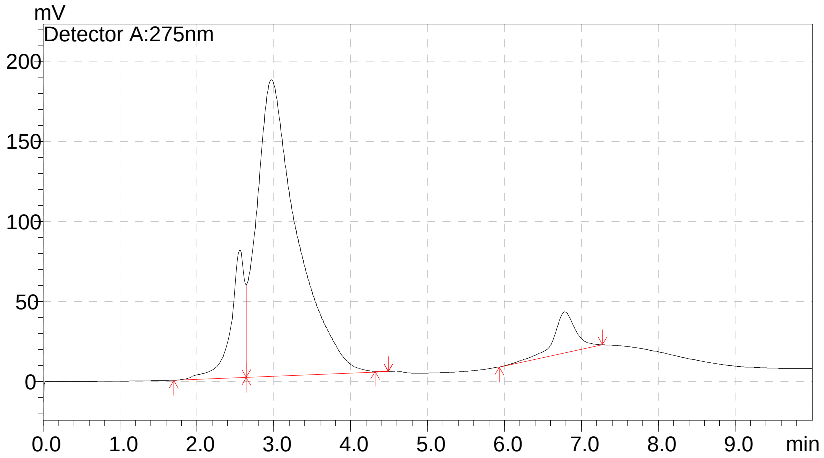


Fig. 3 Chromatogram of studied sample electrolyzed for 60 minutes

Each of the obtained chromatograms is characterized by two sharp peaks at 3.1 and 6.8 minutes. The experimental data (not shown here) tend to assure that these peaks correspond to the presence of $Fe^{(II)}$- EDTA complex and NB compound respectively. In order to increase the electrolysis time up to 30, 60, 90, 120 and 150 minutes, the peak area of $Fe^{(II)}$EDTA is kept nearly constant while the peak area of NB in the samples decreases corresponding to the percent of its conversion or oxidation increase (Table 1).

Table1. The evolution of percent of NB conversion with electrolysis time, with a direct current and the potential of 2.5 V (anodic potential), for degradation of nitrobenzene (0.05g/l), in 53ml solution of Na2SO4 (0.1M), EDTA 1mM, oxygen 10mg/l, (for anodic cell); the cathode cell contains only 53 ml of Na_2SO_4 (0.1M); solution pH constantly remains at 3.5.

Time electrolyzed (minutes)	30	60	90	120	150
Percents of conversion (%)	72.2	87.2	94.4	95.8	97.1

The characteristics of HPLC chromatogram may be explained by the following reasons:

- The appearance of $Fe^{(II)}$EDTA complex in the sample

The presence of $Fe^{(II)}EDTA$ in the samples during electrolyzing was explained by the combination between EDTA and Fe^{2+} dissolved from iron anode as follows:

Process of the iron anode dissolution

$$Fe^{(0)} \rightarrow Fe^{2+} + 2e^{-} \qquad (1).$$

Process of complex formation

$$Fe^{2+} + EDTA \rightleftarrows Fe^{(II)}EDTA \qquad (2).$$

The concentration of $Fe^{(II)}EDTA$ complex depends on the concentration of EDTA and the Fe^{2+}.The maximum concentration in sample is 1mM equaling initial EDTA concentration. This explains why the peak area of the $Fe^{(II)}$ EDTA complex is approximately constant after electrolyzing for 30 minutes.

- The oxidation or conversion of nitrobenzene

The decrease of the concentration of nitrobenzene for electrolyzed time is explained by its oxidation conversed to other compounds due to the free radical $OH^{\bullet}$ generated from the Fenton-like reaction of $Fe^{(II)}EDTA$ and oxygen in the sample. According to [12], the formation of free radical $OH^{\cdot}$ is based on the following reactions:

Reactions of intermediate formation

$$Fe^{(II)}EDTA + O_2 \rightarrow O_2\,Fe^{(II)}EDTA, \quad k_1 = 10^3\ M^{-1}s^{-1} \qquad (3).$$
$$O_2\,Fe^{(II)}EDTA \rightarrow Fe^{(III)}EDTA + O_2^{-}, \quad k_2 = 10^2\ M^{-1}s^{-1} \qquad (4)$$
$$Fe^{(II)}EDTA + O_2^{-} \rightarrow O_2^{2-}\text{-}Fe^{(III)}EDTA, \quad k_3 = 10^6\ M^{-1}s^{-1} \qquad (5)$$
$$O_2^{2-}\text{-}Fe^{(III)}EDTA + 2H^{+} \rightarrow Fe^{(III)}EDTA + H_2O_2,\ k_4 = \text{fast} \qquad (6)$$

Reaction of the free radical formation

$$Fe^{(II)}EDTA + H_2O_2 \rightarrow Fe^{(III)}EDTA + OH^{\bullet} + OH^{-},\ k_5 = 10^3\ M^{-1}s^{-1} \qquad (7).$$

Due to the concentration of $Fe^{(II)}EDTA$ complex kept constant in solution, it plays a catalyst role in this conversion reaction.

Due to the role of the $Fe^{(II)}EDTA$ catalyst for the reaction, its concentration in sample and the area of $Fe^{(II)}EDTA$ peak on chromatogram is kept nearly constant in accordance with experimental data. The free radical $OH^{\bullet}$, a strong reagent, would oxidize nitro compounds in the sample, convert them into other substances. Due to no new peak occurrence in the HPLC chromatogram, it was concluded that most of the nitrobenzene was oxidized, converted to $CO_2 + H_2O$ and other minerals.

During electrolyzing from beginning to 150 minutes, due to the low solution pH (3.5), the presence of EDTA, the sample solutions were transparent and there is no precipitation. During this time, $Fe^{(II)}$EDTA peak on chromatogram kept nearly constant, it means that there is no degradation of EDTA in the sample. The obtained experimental data have shown that if the electrolyzing time prolongs after 150 minutes, a degradation of EDTA will be appeared. This is in accordance with the previous authors [10].

3.2. Effect of applied potential

The effect of applied potential on electrolysis was studied. Table 2 shows the change in area of the nitrobenzene peak in the HPLC chromatogram for different applied potentials.

Table 2. The change of the height of the nitrobenzene peak on HPLC chromatogram versus different applied potentials: for degradation of 53ml solution of Na_2SO_4 (0.1M), NB (0.05g/l), EDTA 1mM, oxygen from air, 10mg/l, (for anodic cell); the cathode cell contains only 53 ml of Na_2SO_4 (0.1M); for 60 minutes electrolyzed, solution pH remains 3.5.

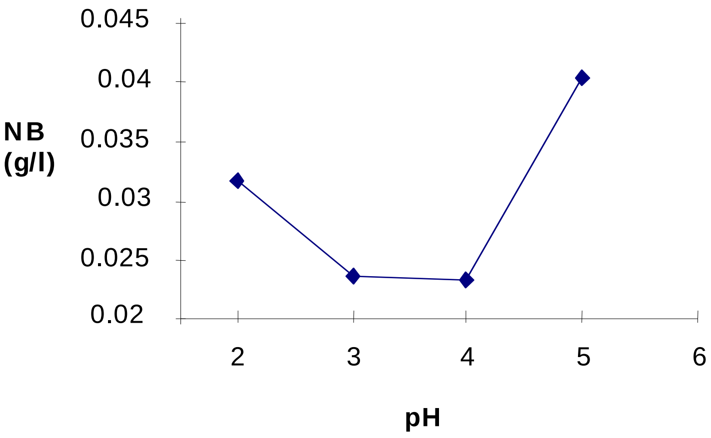
Applied potential (anode) V	0.5	1.5	2.5	3.5	4.5	6.0
Conversion percent of nitrobenzene	81.5	83.7	87.2	80.0	33.3	25.2

The table 2.indicates that at applied potentials ≥4.5 V, the conversion percent of nitrobenzene decreases. This phenomenon may result from the some intermediate products oxidized when iron anodic electrode could not take part in the reaction generating OH. Blocking of the electrode might occur for instance by iron passivity, which still may be controlled by EDTA. There is also a possibility that EDTA oxidizes as the anode potential gets strongly positive. But: these are only suppositions.

3.3. Effect of solution pH

As can be seen, the conversion of NB depends on the pH-solution. Fig.3 shows the conversion of NB versus pH-solution in system consisting of (i) anodic cell: 53 ml of nitrobenzene (0.05g/l), EDTA (1mM), Na_2SO_4 (0,1M), O_2 10 mg/l; (ii) cathode cell: 53 ml of Na_2SO_4 (0,1M); the electrolysis lasts 45min at potential 2.5 V by direct current.

Fig.3. The conversion of NB versus pH



After electrolyzing for 45 minutes, at pH range from 3 to 4, the concentration of NB has decreased from 0.05g/l to 0.023 mg/l. This indicates that the pH values of 3-4 are suitable values for the conversion reaction of NB . This is in accordance with conditions for the Fenton reagent.

3.4. Role of EDTA, oxygen for nitrobenzene conversion

The role of EDTA and oxygen for the nitrobenzene conversion has been demonstrated by the experimental data. Fig. 4 shows the obtained results for the conversion of nitrobenzene in system consisting of (i) anodic cell: 53 ml of nitrobenzene (0.05g/l), EDTA (1 mM), Na_2SO_4 (0,1M), O_2 10 mg/l; (ii) anodic cell: 53 ml of nitrobenzene (0.05g/l), EDTA (0 mM), Na_2SO_4 (0,1M), O_2 (10 mg/l), (iii) anodic cell: 53 ml of nitrobenzene (0.05g/l), EDTA (1 mM), Na_2SO_4 (0,1M), O_2 (0.1 mg/l); (iiii) cathode cell: 53 ml of Na_2SO_4 (0,1M); The time of electrolysis is 45 minutes at potential 2,5 V by direct current, pH = 3.5.

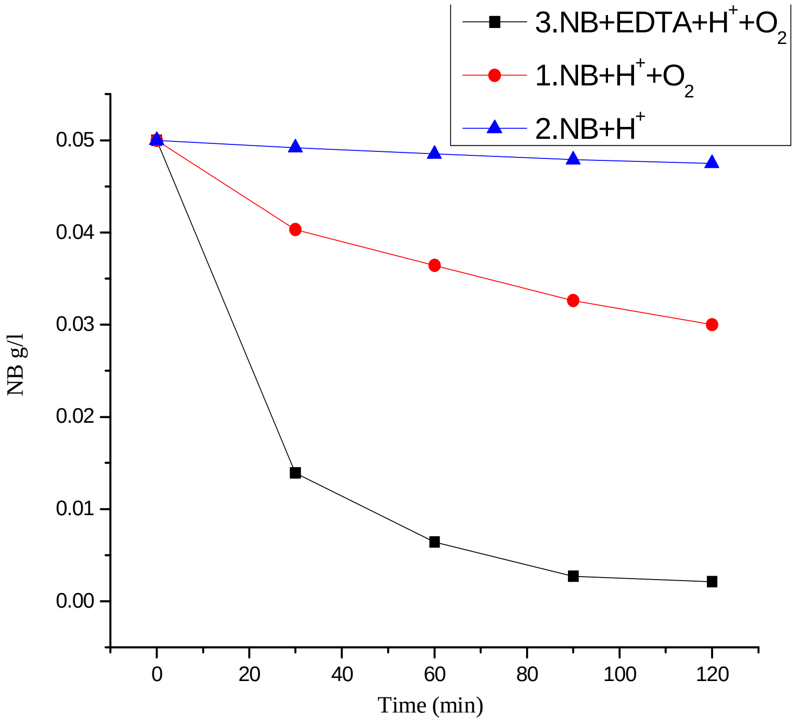


Fig.4. The influence of EDTA, O_2 on conversion of NB

The obtained experimental data have confirmed that the conversion of NB is carried out at high rate when there are simultaneously EDTA and oxygen in sample. This result is explained above and is in agreement with the reaction scheme suggested in [7].

4. Conclusion

The degradation of NB by advanced oxidative process based on an anodic Fenton's reagent is a novel method. The degradation or the conversion of nitrobenzene in to CO_2, H_2O and other minerals was performed by an electrochemical method in the electrolysis system with direct current, with the iron anodic section volume of 53ml with potential 2.5 V, consisting of EDTA (1mM), O_2 (10mg/l), Na_2SO_4 (0.1M) and the graphite cathode section volume of 53ml consisting electrolyte of Na_2SO_4 (0.1M). Concentrations of NB during electrochemical degradation were monitored with high-performance liquid chromatography, (HPLC, Aligent USA). The electrochemical degradation of NB can be explained by the free radical $OH^·$ generated during electrolysis using direct current with iron anode in presence of EDTA, oxygen and weak acid solution pH. Some kinetics parameters such as temperature, EDTA concentration, ferrous ions, NB concentration that influence on the efficiency of NB oxidation would be studied in the next article.

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