

## Reduction of Nitrobenzene in Aqueous Media by Fe-Al Bimetallic Material

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### Abstract

Nitrobenzene is a toxic agent, that must be treated before discharging to environmental media. One of the methods to treat nitrobenzene is its reduction into amine compounds with zero-valent iron. During the reduction, the iron surface can appear as a passive film that decreases the nitrobenzene reduction. To overcome this phenomenon, many novel materials such as zero-valent bimetallics like Pd-Fe, Cu-Fe, and Cu-Al have recently been shown to have enhanced reactivity toward destroying passive layers compared to ZVI. In this study, Fe-Al powder was used for nitrobenzene reduction. Optimal conditions for nitrobenzene to amine products, such as the ratio of Fe/Al, pH, and reaction time were established.

**Keywords:** Binary metal Fe-Al, nitrobenzene, reduction with Fe-Al. amine compounds.

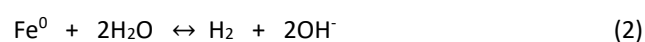
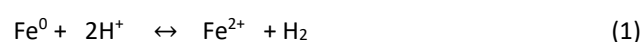
### 1. Introduction

Wastewater contaminated by nitroaromatic organic compounds has gained great attention that causes many diseases to the environment and human health. Nitrobenzene (NB) has been considered a priority control contaminant by American Environment Protection Agency [1]. Therefore, wastewater containing NB must be treated before being discharged into around environment [2,3]. So, it is necessary to find a novel and effective technology for the degradation of NB from wastewater. Nitrobenzene from wastewater has been reduced by zero-valent iron (ZVI) particles that transform NB to the final reduced product triaminobenzene [4]. During oxidation, the iron surface should be passivated by an iron oxide or hydroxide layer leading to a decrease in the rate of reaction with NB [5]. To overcome this phenomenon, many novel materials such as zero-valent bimetallics like Pd/Fe, Cu/Fe, and Cu/Al have recently been shown to have enhanced reactivity toward destroying passive layers compared to ZVI. [6]. Bimetallic particles consist of two types of zero-valent Fe/Al metals, at the same time, allowed to increase the rate of the reduction reaction of the nitro group significantly is going to be the aim of our paper.

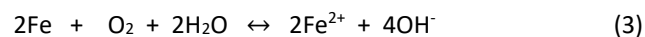
#### 1.1 Background

##### Oxidation of Fe<sup>0</sup>

ZVI oxidation from water by many substances is an electrochemical corrosion process in which oxidation of Fe<sup>0</sup> to Fe<sup>2+</sup> is an anodic half-reaction. The cathodic half-reaction involves many available electron acceptors like H<sup>+</sup>, H<sub>2</sub>O, O<sub>2</sub> or nitro group (-NO<sub>2</sub>). The ZVI corrosion in the anoxic pure aqueous phase as a system of Fe<sup>0</sup>- H<sub>2</sub>O consists of the following reactions, [7,8]:



The ZVI corrosion in aerobic aqueous phase as a system of Fe<sup>0</sup> - H<sub>2</sub>O - O<sub>2</sub> consists of the following reaction:



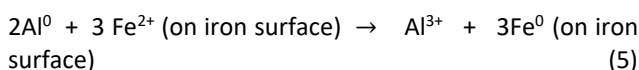
The accumulation of hydroxide Fe<sup>0</sup>- in situ triggered precipitation Fe<sup>2+</sup> along with the deposition of insoluble mineral species on the metal surface led to the loss of iron reactivity.

Bimetallic particles consist of two types of zero-valent metals as aluminum – iron (ZVA and ZVI) in aqueous exhibiting an advantage in the reduction of chloro and nitroaromatic compounds. The ZVI corrosion in the aqueous phase as a system of Fe<sup>0</sup> - H<sub>2</sub>O - Al<sup>0</sup> has an interesting character which operates as electrochemical cells. The metal Fe has electrode potential of Fe<sup>2+</sup>/Fe<sup>0</sup>, (-0.44 V) higher than Al<sup>3+</sup>/Al<sup>0</sup>, (-1.67 V) that can form a lot of electrochemical cells on the Fe/Al bimetallic particles, in which iron plays the role of anode and aluminum as a cathode [6, 9]. The metal iron can reduce organic compounds as follows:

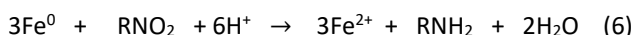
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and then



By this way, ZVI may be considered as a constant source donating electrons for the acceptor from aqueous. In this study, we apply the bimetallic zero-valent Fe/Al particles consisting of a core metal (aluminum) and a second metal (iron) for reduction of NB from water. The reaction between Al/Fe with NB denoted ( $\text{RNO}_2$ ) is presented as following:

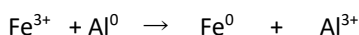


The bimetallic Fe/Al particles are used in which metal Al as an electron source prevents the precipitation of iron corrosion layer at the  $\text{Fe}^0$  surface and thus enhances the surface reactivity of iron.

## 2. Experimental part

### 2.1 Chemicals

All chemicals used for this study are analytical grade. Nitrobenzene solution (ACS Sigma – Aldrich, reagent,  $\geq 99.0\%$ , molecular weight, 123,11) was purchased in Vietnam. A commercially aluminum particle (99.5%, about 20 micrometers. Bimetallic Fe-Al particles used for this study were prepared according to the method published in [6, 9], using the zero-valent aluminum powder (ZVAl) and ferric chloride as precursors in a fume hood under ambient conditions, according to the reaction:



The  $\text{Fe}^0$  from this reaction was deposited onto  $\text{Al}^0$  - surface. They were then washed with deionized water, filtration, and dried in a vacuum. The Fe, Al in the samples were determined by an inductively coupled plasma-optical emission spectrometry (ICP-OES). The ratio of Fe/Al was calculated as follows

$$\text{Fe/Al} = (\text{Applied Fe content} - \text{Residual Fe content}) / (\text{Applied Al content} - \text{Residual Al content}).$$

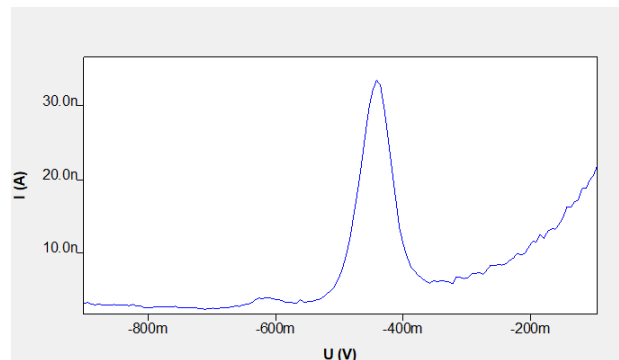
Through the experiments, the  $\text{Fe}^0/\text{Al}^0$  particle results involved 0.5, 1.2, 2.1, 2.5, and 2.8 g Fe/1g Al. These particles were used for this study.

### 2.2. Analytical method

- The pH solution was monitored using a Toledo pH meter.
- Analysis of NB concentration by anodic stripping Voltammetric method

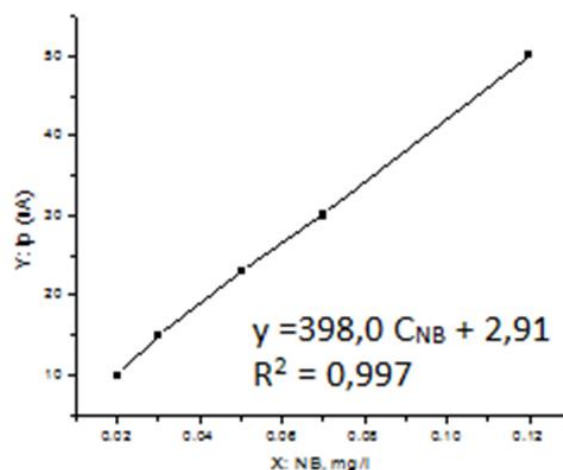
The concentration of NB was determined by anodic stripping Voltammetry with a mercury hanging drop

electrode (HMDE) using Metrohm 797 VA computrace, as published in our previous paper [4]. The solution consisting of NB in acid acetic-sodium acetate buffer 0.1 M as electrolyte was removed oxygen for 60 s by  $\text{N}_2$  gas, then pre-concentrated onto HMDE for 60 s at a potential of -0.90 V, then an anodic stripping Voltammetric current was determined in the potential as being from -0.4090 to -0.10 V. The current peak height appeared at -0.442 V, Figure 1, being proportional to the NB concentration that is used for the analysis of this compound.



**Fig. 1** Voltammogram of NB on HMDE, NB conc. 10 mg/L, acetate buffer, pH = 4.0, preconcentrated time for 60s.

The NB concentration from samples was determined with the following plot.



**Fig.2** Calibration plot of nitrobenzene

### 2.3. Reduction of NB by batch experiment

All experiments were conducted under the protection of  $\text{N}_2$ (g). The initial of NB and ZVI-Al particles were 80 mg/L and 1.0 g/L with different ratios of  $\text{Fe}^0/\text{Al}^0$ , at various initial pH values. The solutions were continuously stirred with a mechanical stirrer, in a batch of 200 mL. The pH of all solutions was adjusted with 0.1 M NaOH or  $\text{H}_2\text{SO}_4$ . Samples of a certain volume of solution collected from each reaction vessel at regular time intervals were filtered to determine the concentration of NB remained. The NB

concentrations for the reaction time were analyzed Voltammetry method.

### 3. Results and discussion

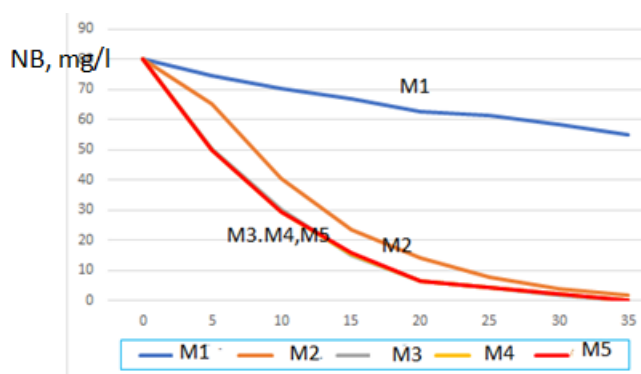
#### 3.1. The degradation of NB in a ZVAI - ZVI water system

The degradation kinetic curve of NB in the system of ZVI-ZVAI consists of different ratios of (Fe<sup>0</sup>/1gAl<sup>0</sup>). The binary metallic ZVAI-ZVI consists of different ratios between Fe<sup>0</sup> and Al<sup>0</sup> that influence the kinetic curve of NB. The NB degradation rate is increased with the increase of Fe<sup>0</sup> amount in ZVAI-ZVI, and then reaches a near-constant value, presented in Table 1. And Figure 1, corresponds to C<sub>NB</sub> initial concentration of 80 mg/L.

**Table 1.** The NB degradation dependence on the time and ratios of Fe<sup>0</sup> /1gAl<sup>0</sup>, M1, M2, M3, M4, M5 are samples involving Fe<sup>0</sup> amounts of 0.5, 1.2, 2.1, 2.5, 2.8 g/1g Al<sup>0</sup>, pH =3, respectively, NB initial of 80 mg/L in a 500 mL- batch involved 200 mL sample.

Reaction time, min	0	5	10	15	20	25	30	35
C <sub>NB</sub> /M1	80	74.5	70.1	66.6	62.5	61.4	58.3	55.2
C <sub>NB</sub> /M2	80	65.3	40.7	23.7	14.1	7.8	4.2	1.8
C <sub>NB</sub> /M3	80	50.3	30.2	15.1	6.5	4.5	2.1	0.3
C <sub>NB</sub> /M4	80	50	29.5	15.7	6.6	4.5	2.2	0.3
C <sub>NB</sub> /M5	80	50.1	29.7	15.8	6.7	4.5	2.2	0.3

and the Figure 1.



**Fig.3** Influence of Fe amount/1g Al on NB degradation, at pH = 3, at the different samples M1, M2, M3, M4, M5.

The findings showed that concentrations of NB decreased when the reaction time increased from 0 to 35 min, but at a different rate, depending on the amount of Fe<sup>0</sup>.

From Table 1, the findings showed that when the Fe<sup>0</sup> in ZVAI powders increases from 0.5 to 2.1 g Fe<sup>0</sup>/1gAl<sup>0</sup> corresponding to M<sub>1</sub>, M<sub>2</sub>, M<sub>3</sub> the NB concentration decreases from 80 to 6.5 mg/L and then reaches rear-constant values, for 20 min, although the Fe<sup>0</sup> continuously increases to 2.8 mg/1gAl<sup>0</sup>. This phenomeum would be explained by the Fe<sup>0</sup> saturated aluminum surface reducing the reaction between aluminum and Fe<sup>2+</sup>as suggested in

the paper [6]. Therefore the ratio of ZVI/Al powder with 2.1 g Fe/1 g Al was selected as optimum for the other experiments.

#### 3.2 Influence of NB initial concentration on its degradation rate by ZVAI - ZVI powder

The experiments were carried out with NB concentrations selected as 20, 40, and 80 g/L, in the batch of 500 mL contained 200 mL of the sample with 2.1g Fe/1g Al. The average rate of NB degradation was measured for a time of 5 min from the beginning. The results were presented in Table 2.

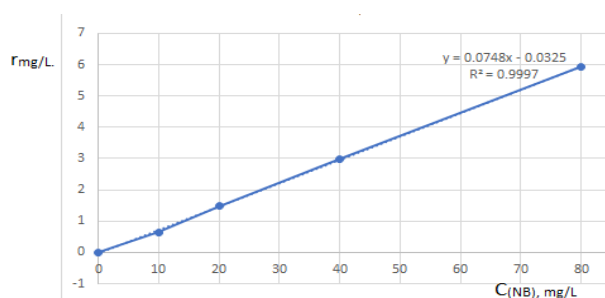
**Table 2.** The average rate of NB degradation for 5 min from the beginning

C <sub>NB</sub> initial, mg/L	0	10	20	40	80
R <sub>Average rate,mg/L.min</sub>	0	0.65	1.48	2.98	5.94

The results in Table 2 showed that the initial average rate of NB degradation by the ZVA-ZVI system, (at the constant dosage of the powder), increases with the increased initial NB concentrations. The initial degradation rate of NB can be expressed by the following expression and figure 2, [10]:

$$dC_{NB} / dt = k_{obs}C_{NB}$$

Here, C<sub>NB</sub> is considered as the initial concentration; k<sub>obs</sub> is the observed reaction rate coefficient, 1/ min.



**Fig. 4.** The dependence of the reaction rate on the initial NB concentration.

At the constant ZVAI/ZVI dosage, the reaction rate of the NB degradation is fitted with the first-order kinetics. This reaction equation is considered a simple equation of Langmuir-Hinshelwood applied for surface adsorption reaction where the limiting step is adsorption/desorption [ 10 ].

This is due to the at beginning reaction there are non-intermediate reaction products. The k<sub>obs</sub> observed is 0.0748 1/min.

#### 3.3 Influence of pH on the NB reduction by ZVAI/ZVI powders

The influence of pH on the reduction of NB by ZVI-ZVAI power is presented in table 3.

**Table 3.** Influence of pH on the NB reduction by ZVI-ZVAL powders 80 mg/L NB, 2.1 g Fe/1g Al, reaction time 20 min, in a reaction batch involving 200 mL sample.

pH	2.0	3.0	4.0	5.0	6.0	7.0	8.0
NB, mg/L	5.2	6.5	7.4	10.5	25.7	39.2	56.8

The obtained results indicated that the reduction reaction between NB and ZVI-ZVAL was the favorite in the acid medium. It means that ions  $H^+$  participate in the reduction reaction of NB (reaction 7).

#### 3.4. Recycling and reuse of Fe/Al bimetallic particles

The effectiveness of the NB reduction reaction is strongly influenced by the activated iron surface and the formation of by-production on the iron surface. In this study, Fe(III), Al(III) hydroxides may deposit on the surface of bimetal and form passivating films, which could hinder the reduction reaction. The experiments (not shown here) showed that these passivating films can be removed by acid medium, pH = 2 for 5 times then the bimetal was continuously effectively used for further experiments.

#### Conclusion

In this paper, the application of a binary metal particle Fe-Al to the reduction of nitrobenzene from the water was studied in detail. The reduction of nitrobenzene was evaluated by the nitrobenzene remaining for the reaction time, by the voltammetric method. The reduction of nitrobenzene depended on the presence of metallic iron deposited on the Al surface, pH, and reaction time. The optimal experimental conditions for the reduction of nitrobenzene were determined such as the ratio of Fe/Al (metal) is 2.1g Fe/1g Al, pH =3.0, reaction time = 20 min.

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