Study on the reuse of nanoscale zero-valent iron (nZVI) in a Sono–Photo–Fenton-like process for the treatment of TNT-contaminated wastewater

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ABSTRACT

This study evaluates the effectiveness of recovering and reusing nano zero-valent iron (nZVI) in the treatment of TNT-containing wastewater using the Sono-Photo-Fenton-like (SPF-like) process. Experiments were conducted under fixed optimal conditions: pH = 2.5; H_2O_2 = 40 mM; and initial TNT concentration = 50 mg/L. Results showed that recovered nZVI material maintained good catalytic activity, with TNT removal efficiency reaching over 24% after 4 consecutive reuse cycles. When dry-recovered iron material was combined with fresh nZVI at a 1:1 ratio (1.0 mM nZVI and 1.0 mM $Fe(OH)_3$), treatment efficiency reached 94.85%, while still reducing the amount of new material used by 50%. These results demonstrate the practical applicability of recovering and reusing iron in advanced oxidation systems, helping to maintain high treatment efficiency, while reducing operational costs and waste generation in the treatment of industrial wastewater containing persistent pollutants like TNT.

Keywords: Sono-Photo-Fenton-like process; nZVI; TNT; Iron recovery; Catalyst reuse.

1. INTRODUCTION

During TNT production, in addition to the main product 2,4,6-trinitrotoluene, many highly toxic nitroaromatic compounds such as mononitrotoluene, dinitrotoluene, nitrosotoluene, and sulfonated compounds are generated, which are harmful to the blood, liver, and nervous system [1, 2]. TNT production generates two main wastewater streams with different colors and chemical properties: acidic yellow wastewater and alkaline red wastewater. Among these, yellow wastewater contains many persistent nitroaromatic compounds that are difficult to biodegrade and can cause severe environmental pollution if not thoroughly treated. Existing and emerging treatment technologies include: activated carbon adsorption, alkaline hydrolysis, biological treatment, and Advanced Oxidation Processes (AOPs) such as Fenton, Photo-Fenton, and Sono-Fenton [3]. Each method has its own advantages and disadvantages; however, advanced oxidation technologies are highly regarded for their ability to thoroughly treat refractory compounds and their short reaction times, which help reduce treatment costs compared to other technologies [4]. At the implementation level, persistent iron loss (and the consequent requirement for make-up iron) together with post-treatment management of iron-laden sludge constitute key bottlenecks, thereby limiting scalability and degrading life-cycle performance of TNT wastewater treatment systems.

Advanced oxidation technologies, especially the Sono-Photo-Fenton-like (SPF) process, have demonstrated effectiveness in treating refractory pollutants by generating highly oxidizing hydroxyl radicals (•OH) [5]. However, traditional homogeneous Fenton systems using Fe^{2+} salts encounter many obstacles regarding catalyst recovery and the generation of sludge after treatment. To reduce sludge, research focuses on nanoscale zero-valent iron (nZVI) as a heterogeneous catalyst that can be recovered and reused, thereby reducing secondary waste generation. Although the potential for nZVI recovery, reuse, and reduction of secondary waste has been mentioned in some studies,

systematic research on the efficiency of nZVI recovery and reuse under experimental conditions of the SPF-like system is still limited, especially for highly contaminated TNT wastewater. Moreover, prior studies rarely quantify cycle-to-cycle activity retention under SPF-like conditions for TNT matrices, posing a methodological gap for robust techno-economic assessment.

Based on this, the present study focuses on evaluating the effectiveness of nZVI iron catalyst recovery and reuse in an SPF-like system for treating yellow wastewater containing TNT. In this study, the authors investigated TNT treatment efficiency over multiple catalyst reuse cycles, with emphasis on dry recovery methods, and analyzed the feasibility of mixing fresh and reused nZVI. The results aim to establish an efficient, cost-effective, and environmentally sustainable TNT wastewater treatment process.

2. PROBLEM

2.1. Chemicals and equipment

2.1.1. Equipment

- The experimental setup was equipped with a 15 W UV lamp (wavelength 254 nm), an ultrasonic generator, and an aeration device.

- The high-performance liquid chromatography (HPLC) system used was an HP 1100 model with a diode array detector (DAD), manufactured by Agilent (USA).

2.1.2. Chemicals

- 2,4,6 – Trinitrotoluene (crystalline, analytical grade, Xilong Scientific).

- Nanoscale zero-valent iron (nZVI) synthesized at the laboratory of the Institute for Materials, Biology and Environment.

- $Fe_2SO4.7H_2O$, $FeCl_3.6H_2O$, $CuCl_2.H_2O$ (99%, Xilong scientific, China), $NaBH_4$, NaOH, H_2SO_4 98% (Xilong scientific, China), H_2O_2 30% (Analytical reagent, China), De-ionized water (18.2 mΩ) (Milli Q).

- HPLC-grade solvents (acetonitrile, ethanol, methanol, hexane) (Merk).

2.1.3. Experimental model

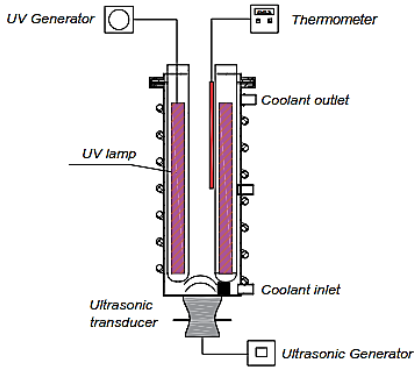


Figure 1. *Setup of the Sono-Photo-Fenton process experiment.*

Figure 1 shows the experimental model of the Sono-Photo-Fenton system. The experimental model for studying the effectiveness of the Sono-Photo-Fenton system is described in figure 1, designed based on a referenced study. A 1.0-liter reaction vessel made of 1 mm-thick Inox 304 material was used. At the bottom of the vessel, an ultrasonic transducer with 60W power and 40 kHz frequency was installed. Inside the vessel, centrally positioned, was a 15W UV lamp with a wavelength of 254 nm. To enhance the mixing process in the model, an air diffuser was used to create an upward airflow at 1 L/min with bubble sizes ranging from 0.1 - 3 mm. The system integrated temperature control and pH monitoring during the reaction.

2.2. Experimental procedure

2.2.1. Preparation of simulated wastewater

Simulated yellow wastewater for optimization experiments was prepared as follows: pure TNT was dissolved to create a standard solution and diluted with de-ionized water to achieve a concentration of 50 mg/L. The pH of the solution was adjusted to 2.5 using H_2SO_4.

2.2.2. Experiment on iron recovery after TNT treatment using SPF-like process

Experiments were conducted with an initial TNT concentration of 50 mg/L, nZVI dosage of 2 mM, H_2O_2 concentration of 40 mM, and pH = 2.5 [3]. Experiments were conducted for 30 minutes to investigate the treatment efficiency. After treatment, the pH of the solution was adjusted to 7. Iron material was recovered by washing with ethanol (99%) and vacuum filtration. SEM, XRD, and BET analyses were performed to determine the composition and properties of the recovered material. The recovered iron material was then tested for its effectiveness in treating TNT-contaminated yellow wastewater. Treatment efficiency over multiple reuse cycles was evaluated to determine the optimal number of reuse cycles.

2.2.3. Combined use of recovered iron and fresh iron for TNT treatment in SPF process

Experiment Recovered iron material and newly synthesized nZVI were added at different ratios to treat TNT-contaminated yellow wastewater via the Sono-Photo-Fenton process. The optimal mixing ratio of recovered iron and fresh nZVI was then determined to achieve maximum treatment efficiency with minimal use of new nZVI.

2.3. nZVI Recovery methods

Solid-phase nZVI recovery: SPF-like runs (50 mg/L TNT "yellow" wastewater, 40 mM H_2O_2, 2 mM nZVI) were followed by neutralization to pH 7 with NaOH. The brown iron precipitate was concentrated by decanting to ~30 mL in a 100 mL beaker and collected by Büchner filtration. The solid was washed 3× with 99% ethanol, vacuum-dried in a desiccator for 24 h, and stored under N_2 in a sealed glass vial to minimize oxidation. This recovery method was developed based on the research by Cao Guo-min et al. [6].

2.4. Method for determining TNT

Concentration in Solution TNT concentration in the solution was analyzed using a high-performance liquid chromatography (HPLC) system (Agilent, USA, 1100 Series) with a Hypersil C18 column (200 x 4 mm), a mobile phase of methanol and water (65/35), pressure of 120 bar, and pH = 7.

2.5. Method for evaluating TNT treatment efficiency

TNT treatment efficiency was calculated using the formula:

$$H\% = \frac{C_0 - C_t}{C_0}\ x\ 100\ (\%) \quad (1)$$

Where: H is the treatment efficiency, Co and Ct are the concentrations of TNT at the initial time and time t, respectively, in mg/L.

3. RESULTS AND DISCUSSION

3.1. nZVI material characteristics

3.1.1. Surface morphology and particle size of nZVI

SEM images were taken at different magnifications to evaluate the morphological characteristics and particle size of nZVI before and after treatment by the Sono-Photo-Fenton process. The initially synthesized nZVI particles were spherical with diameters ranging from 25 to 70 nm. They exhibited a relatively uniform shape and narrow size distribution. These results are

similar to the study by Ayanda et al., where nZVI particles appeared as interconnected nanospheres [7]. After undergoing the SPF-like reaction with TNT, particle aggregation was observed. This could be due to magnetic interactions between particles and the formation of chemical bonds between nZVI and TNT molecules. A portion of nZVI was oxidized to Fe_3O_4, leading to the formation of aggregates. However, the application of ultrasound broke these large clusters, creating fibrous or layered structures. The material surface after SPF treatment became more porous, with the appearance of smaller particles. This indicates that the SPF process broke down previous iron oxide clusters and created new nZVI particles. The non-uniform distribution and formation of new clusters suggest that nZVI was regenerated from iron oxides and tended to re-aggregate into smaller clusters upon reformation.

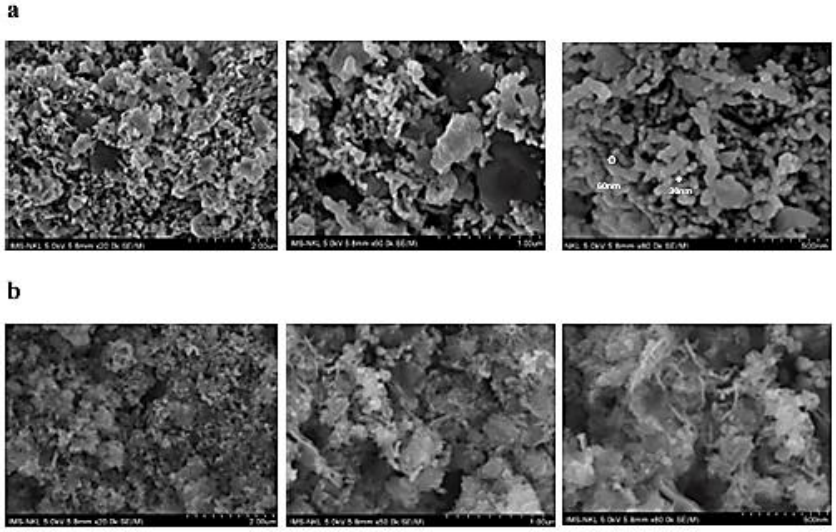
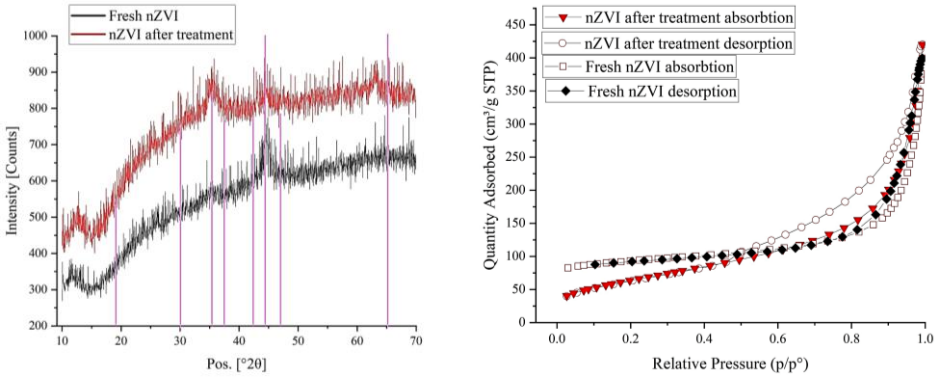


Figure 2. *SEM results of nZVI: a) Synthesized nZVI; b) nZVI after SPF.*

3.1.2. XRD images of nZVI

XRD results are shown in figure 3a. The XRD spectrum of the initially synthesized nZVI showed characteristic diffraction peaks of zero-valent iron (Fe^0), especially a peak at $2\theta \approx 44.7°$, representing the body-centered cubic (BCC) crystal structure of elemental iron [8].



a) *b)*

Figure 3. *a) XRD patterns of nZVI; b) BET results of nZVI.*

The broad peak with low intensity indicates poor crystallinity, typical of nanomaterials due to small particle size and non-uniform size distribution, as well as the presence of structural defects or amorphous regions. The XRD spectrum of nZVI after SPF treatment still showed diffraction peaks related to Fe^0 (especially a strong peak at $2\theta \approx 44.7°$). This suggests that the SPF process

not only facilitates continuous cleaning of the catalyst surface but also contributes to nZVI regeneration during the reaction. However, additional diffraction peaks corresponding to iron oxides such as hematite and magnetite were also observed. This indicates that zero-valent iron (Fe^0) was oxidized during the reaction and transformed into Fe^{2+} and Fe^{3+} forms. These results are consistent with the study by Shukla et al. [9]. Broader peaks further suggest that the regenerated Fe^0 particles have smaller sizes and different crystallinity compared to the initially synthesized nZVI, possibly due to the presence of impurities in the sample.

3.1.3. Porosity characteristics of nZVI

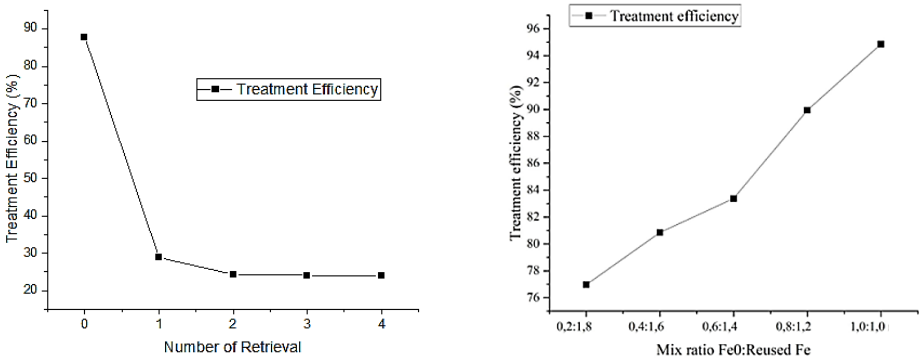
The BET analysis results shown in figure 3b reveal significant changes in the porosity of nZVI after the SPF process. The nitrogen adsorption–desorption isotherms of both the pristine and treated samples were classified as type IV according to the IUPAC classification, which is characteristic of mesoporous materials with a pronounced hysteresis loop.

For the pristine nZVI, the maximum nitrogen adsorption capacity reached approximately 250 cm^3/g STP, while the post-SPF sample exhibited values exceeding 400 cm^3/g STP. This increase reflects a remarkable improvement in the mesoporous structure and adsorption capacity of the material. The SPF process, by combining ultrasound, UV irradiation, and Fenton reactions, generated harsh local conditions (high temperature and pressure, •OH and •H radicals) that disrupted the passive oxide layers on the surface, dispersed particle agglomerates, and partially regenerated Fe^0 from iron oxides. Consequently, the active surface area and porosity of nZVI were substantially enhanced.

These findings demonstrate that the SPF process not only promotes TNT degradation but also simultaneously restructures and improves the porosity of nZVI, thereby enabling the catalyst to maintain its activity and reuse potential in subsequent cycles. The SPF-like process not only enhances the degradation of organic compounds but also contributes to the restructuring and significant improvement of surface properties. The clear increase in nitrogen adsorption capacity and the expansion of the hysteresis loop provide strong evidence that nZVI after SPF-like treatment has improved reusability and high potential for applications in environmental treatment processes.

3.2. Treatment efficiency of dry recovered material

The results of the study on the effect of recovered material on TNT degradation efficiency in the Sono-Photo-Fenton process are presented in figure 4a.



a) *b)*

Figure 4. *a) Treatment efficiency of yellow wastewater containing TNT over multiple dry recovery cycles; b) TNT removal efficiency in yellow wastewater using different mixing ratios of nZVI and dried recovered material.*

After each cycle, the material was recovered, dried, and reused with the same mass (0.112 g). The results show that TNT treatment efficiency gradually decreased with increasing reuse cycles, from 28.87% (first cycle) to 24.01% (fourth cycle).

The decrease in efficiency can be attributed to changes in the material's morphology and surface structure during reuse. Factors such as mechanical abrasion, surface saturation by intermediate products, formation of low-activity iron oxides (Fe_2O_3, Fe_3O_4), and accumulation of impurities can all reduce the ability to generate •OH radicals and adsorb TNT [10, 11]. The results indicate that the dry recovery method can maintain treatment efficiency for the first few cycles, but improvements are needed to extend the catalyst's lifespan in SPF-like systems

3.3. TNT treatment efficiency of dry recovered material combined with nZVI

To improve catalytic efficiency after reuse, dry recovered material was mixed with newly synthesized nZVI at different ratios (Fe^0:Fe^{3+}) to investigate its effect on TNT treatment efficiency in wastewater. The results show that reaction efficiency increased over time at all mixing ratios (figure 4b), with the 1.0:1.0 mM ratio yielding the highest treatment efficiency (~ 95%).

At low ratios (0.2:1.8 mM), efficiency only reached ~ 75 - 80%, indicating that the amount of nZVI was insufficient to provide electrons for effective reductive reactions. When the nZVI ratio was increased (0.4:1.6 and 0.8:1.2 mM), efficiency improved significantly (80.85% and 83.37%) due to the balance between the reductive capacity of Fe^0 and the adsorption-dispersion role of $Fe(OH)_3$.

At the 0.8:1.2 mM ratio, the removal efficiency reached nearly 90%, but the reaction rate showed little improvement compared to 0.6:1.4 mM, likely due to surface saturation or nZVI aggregation. In contrast, the 1.0:1.0 mM ratio achieved the highest efficiency (~95%) with a stable reaction rate, highlighting the synergistic role of $Fe(OH)_3$ and the importance of optimizing the Fe^0:Fe^{3+} ratio for effective and economical TNT removal.

3.4. Treatment efficiency of acidic yellow wastewater using recovered material combined with nZVI

To assess practical applicability, the study experimented with treating actual acidic yellow wastewater collected from Z factory, using different mixing ratios of nZVI and dry-recovered iron material. The results show that the sample using only nZVI (2 mM) achieved the highest treatment efficiency (58.5%), confirming the primary role of nZVI in reducing pollutants in low pH environments.

When the nZVI concentration was halved and replaced with recovered material (1:1 ratio), the efficiency decreased to 44.2%, indicating that the reused material still contributed somewhat through adsorption or precipitation mechanisms. The case of using entirely recovered iron (2 mM) achieved the lowest efficiency (30.2%), suggesting that this material cannot completely replace the role of nZVI in strong reductive reaction systems.

Furthermore, the amount of recovered material used increased with the mixing ratio, from 0 g (using only nZVI) to 0.177 g (1:1) and 0.354 g (using only recovered iron). Therefore, the 1:1 ratio could be a reasonable intermediate option between material cost and treatment efficiency, providing a basis for further optimization studies.

This significant difference (58.5% in real wastewater treatment compared to ~95% in simulated wastewater experiments) is explained by the difference in wastewater composition and complexity. The simulated wastewater was prepared from pure TNT dissolved in deionized water, resulting in a relatively clean matrix. In contrast, the real yellow wastewater from the Z factory plant contained many other stable nitroaromatic compounds such as mononitrotoluene, dinitrotoluene, nitrosotoluene, and sulfonated compounds. These substances not only act as interfering impurities but also compete with TNT in the reaction with highly reactive hydroxyl radicals (•OH), resulting in a reduction in TNT degradation efficiency. Furthermore, the presence of other organic and inorganic substances in wastewater may actually adsorb onto the nZVI catalyst surface, reducing the number of active sites, or affect the formation and stability of free radicals, thereby reducing the overall performance of the SPF-like system.

4. CONCLUSIONS

This study demonstrated the feasibility of applying a SPF-like process using nanoscale zero-valent iron (nZVI) for TNT-containing wastewater treatment. nZVI acted as a reusable heterogeneous catalyst, with dry-recovered material retaining catalytic activity over several cycles. The highest removal efficiency (~ 94.85%) was obtained at the 1:1 (mM) mixing ratio of fresh nZVI and dry-recovered material, effectively reducing the demand for a new catalyst. Tests with real wastewater further confirmed the practical potential of the process. Overall, the findings highlight the sustainability of nZVI recovery and reuse in advanced oxidation systems and provide a basis for future studies focusing on optimized dosage strategies and pilot-scale validation.

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TÓM TẮT

Nghiên cứu thu hồi và tái sử dụng vật liệu sắt (nZVI) trong hệ Sono-Photo-Fenton-like để xử lý nước thải chứa TNT

Nghiên cứu này đánh giá hiệu quả của việc thu hồi và tái sử dụng nano sắt hóa trị không (nZVI) trong xử lý nước thải chứa TNT bằng quá trình Sono-Photo-Fenton-like (SPF-like). Thí nghiệm được tiến hành trong điều kiện tối ưu cố định: pH = 2,5; H_2O_2 = 40 mM; và nồng độ TNT ban đầu = 50 mg/L. Kết quả cho thấy vật liệu nZVI sau thu hồi vẫn duy trì được hoạt tính xúc tác tốt, với hiệu suất loại bỏ TNT đạt trên 24% sau 4 chu kỳ tái sử dụng liên tiếp. Khi vật liệu sắt thu hồi khô được kết hợp với nZVI mới theo tỷ lệ 1:1 (1,0 mM nZVI và 1,0 mM $Fe(OH)_3$), hiệu suất xử lý đạt 94,85%, đồng thời giảm 50% lượng vật liệu mới cần sử dụng. Những kết quả này chứng minh tính khả thi trong việc thu hồi và tái sử dụng sắt trong các hệ thống oxy hóa nâng cao, góp phần duy trì hiệu suất xử lý cao, đồng thời giảm chi phí vận hành và lượng chất thải phát sinh trong xử lý nước thải công nghiệp có chứa các chất ô nhiễm bền vững như TNT.

Từ khóa: Sono-Photo-Fenton-like; nZVI; TNT; Thu hồi sắt.