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# Treatment of wastewater from the flocculation process of waste cutting fluid by zerovalent iron catalyst

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### ABSTRACT

Waste cutting fluids are considered as hazardous wastes because they contain numerous different components causing environmental problems. Normally, a flocculation method is applied to treat preliminarily. However, the output wastewater still needs treating further to meet the national standards of industrial wastewater before disposal. So, this research reports the secondary treatment stage of the waste cutting fluid collected from an industrial factory in Vietnam using zero valent iron (ZVI) catalyst. This catalyst was synthesized via a redox reaction between sodium borohydride (NaBH4) and ferric chloride (FeCl3). Key factors affecting the quality of the ZVI particles such as the concentration of the NaBH<sub>4</sub> reductant, reaction temperature, and dropping rate were investigated systematically. At the optimum synthesis conditions, viz. the NaBH<sub>4</sub> concentration of 0.2 M, reaction temperature of 25 °C and the dropping rate of 3 ml/min, the synthesized ZVI exhibited a narrow range of particle size distribution with a mean size of 3.9 µm, followed by a high surface area, and good catalytic activity. As a catalyst for secondary treatment of the waste cutting fluid, the synthesized ZVI demonstrated a moderate chemical oxygen demand (COD) removal performance of  $\sim$  49%, corresponding to COD reduction for from 4023 mg/l to about 2059 mg/l.

### Introduction

Cutting fluids are widely used in metalworking industries for lubrication, refrigeration and evacuation of filings. The composition of the cutting fluids is variable depending on the requirement of mechanical processes in which they are used. The main components present in the cutting fluids include a refrigerant (water), lubricants (mineral oils, vegetal oils, and synthetic oils), tensioactives (anionics, non-ionics), inhibitors for corrosion (amines, borates, nitrides, etc.), humectants/stabilizers, biocides, additives of high pressure and antifoaming compounds [1]. Therefore, the used cutting fluids are considered as hazardous wastes, and their disposal is required under controlling.

Many methods are used to treat the used cutting fluids including both traditional and modern methods. The traditional treatment methods such as evaporation, phase separation, and filtration [2], pose relatively low treatment efficiency and normally produce secondary contaminants. Whilst, the modern methods, for instance hydrothermal oxidation [2], and ozone treatment [3] have been recently investigated and demonstrated good results. However, utilization of the harsh treatment conditions related to high pressures or plasma beams leads to difficulty in the practical application deployment of these modern methods.

In our previous work [4], we investigated treatment of cutting oil-in-water emulsion by combining flocculation and Fenton oxidation. Particularly, the flocculation was proceeded with Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> agent. The obtained results showed outstanding treatment performance with the high chemical oxygen demand (COD) removal efficiency up to 97.2%. Unfortunately, this COD parameter of the water recovered after treatment was still much higher than the national standard of treated wastewater [5]. Thus, it is extremely necessary to conduct further treatment to attain the recovered water whose quality meet the demand before discharge in the natural environment.

Zero-valent iron (ZVI) is one of metallic reducing agents used the most commonly for the treatment of toxic pollutants from wastewater, and remediation of contaminated land and groundwater [6], because of its ready availability, low cost, and high reactivity [7]. Owing to the reductive activity, convenient transport, and high adsorption efficiency, the ZVI particles show good performance in extraction of various heavy metals from wastewater, for examples Cr (VI) [8, 9], Pb (II) [10], Se [11], Te [12]. On the other hand, ZVI particles also possess a significant surface area-to-weight ratio, which leads to a large density of reactive sites and contaminant removal capacity. Once injected into the groundwater, ZVI reacts with various contaminants as well as other constituents in groundwater to form iron oxides and other iron-bearing minerals. In very recent years, ZVI has been successfully employed for dechlorination of a variety of chlorinated hydrocarbons [13-15], or dye oxidation in aqueous phase as well [16]. This illustrates the great application potential of ZVI in treatment of both organic and inorganic contaminants.

In the present work, with the aim of thorough treatment of the used cutting fluid originated from of Samsung Electronics Vietnam Thai Nguyen factory, we propose the utilization of ZVI as catalyst for the secondary treatment stage. In specific, the wastewater obtained from the used cutting fluid after flocculation pretreatment stage was treated further with ZVI. Herein, the ZVI catalyst was synthesized by a simple chemical method. To optimize the secondary treatment process using the ZVI catalyst, the synthesis conditions of the ZVI particles including NaBH4 concentration, dropping rate and reaction temperature

were tested. In addition, other factors such as pH of wastewater, catalyst content and treatment time were also investigated to determine the optimum conditions of wastewater treatment when using the ZVI catalyst.

### Experimental

### Preparation of the ZVI catalysts

Zero-valent iron particles were prepared via the chemical method based on the redox reaction as below [17, 18]:

 $2FeCl_3 + 6NaBH_4 + 18H_2O \rightarrow 2Fe + 21H_2\uparrow +$ 

Firstly, an aqueous solution of 0.1 M FeCl<sub>3</sub> (China) was into a two-necks round bottom flask. After that, a solution of NaBH<sub>4</sub> (China) with the concentration of x M (x = 0.05, 0.1, 0.2, 0.4) was added dropwise under constantly stirring at 2000 rpm in the N<sub>2</sub> gas atmosphere. Herein, the molar ratio of NaBH<sub>4</sub>/FeCl<sub>3</sub> was 3.5. The blackish ZVI product was then filtered and washed with absolute ethanol several times before being preserved in ethanol. During synthesis process, the dropping rate of the NaBH<sub>4</sub> solution was controlled at various values of 1-7 ml/min, and the reaction temperature was adjusted from 15 to 50 °C.

### Characterizarions of the ZVI catalysts

The crystalline phase of catalysts were characterized by powder X-ray diffraction (XRD) using a D8 Advance Bruker instrument with Cu K $\alpha$  radiation ( $\lambda$  = 0.15406 nm). Lazer diffraction particle size analyzer LA-950-HORIBA was used to determine the particle-size distribution (PSD) of the obtained ZVI samples. The morphology was investigated by an optical microscope under the light source as Halogen/ LED.

## Pretreatment of the used cutting fluid by the flocculation method

The waste cutting fluid collected from Samsung Electronics Vietnam Thai Nguyen Co., Ltd. was preliminarily treated by flocculation according to the optimized procedure as previously reported [4]. In detail, a certain amount of aqueous 35 wt.% Al2(SO4)3 (China) solution was added slowly into a beaker containing about 200 ml of the waste cutting fluid under constant stirring so that the concentration of Al2(SO4)3 reached 2 g/l. Simultaneously, the pH of the mixture was adjusted to pH 5 by using 1 M NaOH or

0.5 M H<sub>2</sub>SO<sub>4</sub> (Merck) solution so that the flocculation phenomenon occurred. After that, the oil and the sludge were separated from water with a separating funnel. The wastewater after filtration was aerated for 30 minutes at a pressure of 5 bar with a flow rate of 5 mL/min, followed by re-filtration prior to COD measurement and subsequent treatment with the ZVI catalyst.

### Secondary treatment of the waste cutting fluid using the ZVI catalyst

The wastewater obtained from used cutting fluid after preliminary treatment by flocculation was collected into a container, followed by pH adjustment with 1 M NaOH or 0.5 M H<sub>2</sub>SO<sub>4</sub> solution (pH = 3 -8). Subsequently, a given amount of the ZVI catalyst (5 – 30 mg/l) was added. After a stirring duration of 15-90 minutes, the mixture was filtered to separate the remaining oil from aqueous suspension. Finally, the suspension was continuously filtered to remove the ZVI solid prior to testing COD. The total treatment process for the waste cutting fluid can be described as Scheme 1.



Scheme 1: Treatment process of the waste cutting fluid using the ZVI catalyst

COD with the unit of measurement mg/l is the quantity of oxygen required to oxidize the organic compounds in a wastewater sample. In this work, the organic compounds were oxidized by K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at a reflux temperature of 148 °C for 120 minutes. AgNO<sub>3</sub> was used as a catalyst and HgSO<sub>4</sub> was added to prevent the effect of chloride substances. The excess K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was titrated with standard NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub>, using ferroin as an indicator. The COD of wastewater after treatment was determined as the following equation:

$$COD = \frac{8000. C. (V_1 - V_2)}{V_0}$$
(2)

Wherein, C is the concentration of  $NH_4Fe(SO_4)_2$  (mol/l), Vo is the volume of wastewater sample before dilution (ml), Vi is the volume of  $NH_4Fe(SO_4)_2$  to titrate

the blank sample (ml), and  $V_2$  is the volume of NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub> to titrate the test sample (ml).

### Results and discussion

### Characterization of the ZVI catalysts

XRD is well-known as a common method to determine the composition of solids. This method is only suitable to characterize crystals, but amorphous phases. In this work, the XRD method was also used to identify the crystalline nature of the synthesized ZVI. Figure 1 presents the typical XRD pattern of the synthesized ZVI sample corresponding to the synthesis conditions: the NaBH<sub>4</sub> concentration of 0.2 M, the reaction temperature of 25 °C and the dropping rate of 3 ml/min. For comparison, the XRD pattern of the commercial ZVI purchased from AMS company was also included. As observed from Figure 1, no typical diffraction peaks of crystalline ZVI phase were detected for both the synthesized and commercial ZVI samples [4]. This indicates the amorphous phase nature of both synthesized and commercial ZVI samples.



Figure 1: XRD patterns of synthesized and commercial ZVI samples

Generally, the small sized particles often have tendency to applomerate, leading to loss of the extraordinary properties of fine particles (nanoparticles and particles). Thus, the distribution of submicron nanomaterials and submicron particles in solvents is crucial to guarantee good heterogeneous catalysis performance. At first, in the present work, the morphology of the synthesized ZVI particles was observed by micro spectroscopy with a magnification of 10,000 times. As seen in Figure 2, the synthesized ZVI sample exhibits better distribution than that of the commercial one at the same magnification. As for the commercial ZVI (Figure 2b), the large clusters are dominant because of agglomeration while the distinct ZVI particles are observable for the synthesized ZVI. This result verifies the superior particle distribution of synthesized ZVI catalyst the commercial product.



Figure 2: Optical images of (a) synthesized and (b) ZVI samples with a magnification of 10000x

In addition, based on the analysis results obtained from Lazer diffraction particle size analyzer in Figure 3, it can be stated that the commercial ZVI had a broader range of size distribution than that of the synthesized ZVI. In specific, the particle size of the commercial ZVI distributes in a large range of  $1.7-262 \ \mu m$  with an average particle size of 11.8  $\mu m$ . Meanwhile, the synthesized ZVI sample showed the particle size distribution in a narrow range of  $0.3-17 \ \mu m$ . The average size of the synthesized ZVI particles was 3.9  $\mu m$ , three times smaller than that of the commercial sample. These results are totally in agreement with the optical microscope results as shown in Figure 2 above. So, the microstructure results suggest the better catalytic activity of the synthesized ZVI compared with the commercial sample.



Figure 3: Particle size distribution plots of the ZVI samples

### Optimization of the synthesis conditions of the ZVI catalyst

Based on the analysis data from XRD patterns and optical microscopy images, it can be concluded that the ZVI catalyst of micro- and submicro-particles was prepared successfully. However, as mentioned above, the small particle size is regarded as the most important factor influencing the treatment performance of the resultant ZVI. The particle size is strongly affected by the synthesis conditions such as reaction temperature, reductant concentration, dropping rate. Therefore, in this work the effect of three mentioned factors was evaluated.

#### Effect of NaBH<sub>4</sub> concentration

The concentration of NaBH4 reductant is the first factor under investigation. Theoretically, the high concentration of NaBH4 leads to rapid reduction process. The large amount of ZVI nuclei is formed simultaneously, followed by the agglomeration phenomenon of the fine particles. As an undesired result, the large ZVI particles are formed. Otherwise, the small concentration of NaBH4 enables the formation of a small amount of ZVI nuclei, which then grow into the large particles. Therefore, the concentration of NaBH4 should be optimized.





Before the redox reaction occurrence, the FeCl3 solution was dark yellow. Once the NaBH4 reductant was added, the change in the color of the FeCl3 solution occurred. At the low reductant concentration of 0.05 M, the black ZVI particles were only recognized after 40 minutes of reaction since the first drop of the reductant was added. When the concentration of NaBH<sub>4</sub> increased, the period of formation of the black ZVI particles became shorter: 20 minutes for the concentration of 0.1 M, 5 minutes for the concentration of 0.2 M and less 1 minute for the concentration of 0.4 M. As seen from the inset in Figure 4, the synthesized sample at the NaBH4 concentration of 0.05 M was reddish brown, suggesting the formation of undesired products, which were not ZVI. Probably, it took long time to form the ZVI particles at the low concentration of the reductant. Thus, the exposure time of these particles in the aqueous environment was prolonged and facilitated the occurrence of the oxidation reactions of ZVI.

Figure 4 shows the dependence of the particle size distribution of the synthesized ZVI samples on the concentration of the NaBH4 reductant. The smallest average particle size of 3.9  $\mu$ m was recorded for the ZVI sample synthesized at the concentration of 0.2 M.

Meanwhile, at the lower or higher concentration, viz. 0.1 M and 0.4 M, the produced ZVI had the bigger average particle sizes of 10.1 µm and 14.2 µm, respectively. It can be explained that, at the high concentration of NaBH<sub>4</sub>, a massive amount of ZVI nuclei was released in the nucleation stage. These nuclei grew gradually into the ZVI nanoparticles. Because of the high surface energy of the nascent ZVI nanoparticles, they tended to applomerate to diminish this energy. As a result, the particle size increased. Otherwise, at the low concentration of the NaBH4 reductant, during particle growth process, only a small amount of the nuclei was formed in the initial nucleation stage. In the next stage, these nuclei had enough time to grow up into larger ZVI particles. This also resulted in the production of large particle size. Hence, the formation of the fine sized ZVI particles was only promoted when the ZVI nuclei were released with a reasonable amount. In this work, the NaBH4 concentration which enabled producing the ZVI particles of the smallest size was found to be 0.2 M. This value was fixed for the further experiments.

### Effect of reaction temperature

Theoretically, the temperature affects the kinetics of reaction process. The high temperature will accelerate kinetics of reaction process to form a large amount of the ZVI nuclei, causing the small particle size. Nevertheless, the high temperature also promotes impact between the ZVI particles, inducing the agglomeration of the primary ZVI particles into larger clusters. Thus, it is necessary to optimize temperature reaction in the present work.

To assess the effect of the reaction temperature on the particle size of ZVI, the ZVI samples were prepared at reaction temperatures of 15 °C, 25 °C, 35 °C, and 45 <sup>•</sup>C. As shown in the inset in Figure 5, at such a high temperature of 45 °C, the nascent ZVI particles were easily oxidized to yield Fe2O3 colloid with color in reddish brown. According to the analysis results of the particle size distribution of ZVI in Figure 5, it is worthy seeing that at the slightly high temperature of 35 °C the particle size of the obtained ZVI particles was bigger than those at lower temperatures, 15 °C and 25 °C, as predicted before. Since the redox reaction to synthesize ZVI is regarded as an exothermic reaction, according to Le Chatelier's principle, lowering the reaction temperature would drive the reaction to occur in direction so that the temperature will increase. It means that at low reaction temperatures more ZVI https://doi.org/10.51316/jca.2022.057 particles with a small size were generated. Both reaction temperatures of 15 °C and 25 °C enabled producing relatively small average particle sizes of 3.5 and 3.9  $\mu$ m, respectively. Two values are similar together. However, regarding required energy consumption cost of the lower reaction temperature, the reaction temperature of 25 °C (room temperature) would be chosen to be the synthesis condition of ZVI for the next experiment.





#### Effect of reductant dropping rate

The reductant dropping rate is among important specifications that influences the initiation and growth of ZVI particles in the solution. In this work, the different dropping rates ranging from 1 to 7 ml/ min were investigated. As observed in the inset (a) in Figure 6, at the slowest rate of 1 ml/min the product obtained upon the occurrence of the redox reaction shows reddish brown. This implies the oxidation of nascent ZVI by oxygen dissolved in the solution to compound s of higher valent iron. Although the nitrogen gas was aerated into the solution of FeCl3 and NaBH4 during the synthesis process, the presence of oxygen trace in the solutions was unavoidable. To hinder the oxidation of nascent ZVI, the higher dropping rate is necessary. On the other hand, as shown in the inset (b) of Figure 6, at the higher dropping rates, the synthesized products show the typical black color of ZVI. In addition, the size of the ZVI particles changed obviously after the dropping rate of NaBH4 increased. The largest average particle size of 19.6 µm was found for the ZVI sample synthesized at the dropping rate of 7 ml/min (Figure 6). Whilst, at the lower dropping rates such as 3 ml/min and 5 ml/min, the average sizes of the ZVI particles measured were 3.9 µm and 4.3 µm, respectively. Likely, at the high dropping rate the large amount of ZVI nuclei was formed, favorable for the occurrence of the agglomeration phenomenon. As a result, the obtained ZVI particles had the large size. So, the dropping rate of 3 ml/min was a reasonable parameter to ensure the appropriate growth of fine sized ZVI particles.





In brief, for the synthesis of the fine sized ZVI particles, the optimum synthesis conditions were found including the concentration of NaBH<sub>4</sub> as 0.2 M, reductant dropping rate as 3 ml/min and the reaction temperature at 25 °C. In the conditions, the ZVI particles had the average size of 3.9  $\mu$ m.

### Optimization of the secondary treatment of the used cutting fluid by the ZVI catalyst

As mentioned above, the waste cutting fluid from Samsung Electronics Vietnam Thai Nguyen company was pre-treated by flocculation. The treatment efficiency was considerably high, 97.2%, corresponding to the decrease in the COD of the cutting fluid from 147200 mg/l to about 4023 mg/l [4]. However, this output COD value is still 20 times higher than Vietnam standard of treated wastewater. Thus, a secondary treatment stage is indispensable before discharging in the environment. In the present work, the waste cutting fluid was continuously treated secondarily by using the ZVI catalyst with the average particle size of 3.9  $\mu$ m. It means that, the input wastewater of the secondary treatment process was pretreated using flocculationsedimentation only as reported in the literature [4] (Scheme 1). To find out the suitable conditions for the secondary wastewater treatment stage, the effects of some key factors such as pH, the used content of ZVI (solid-to-liquid ratio), treatment time on the treatment efficiency were investigated systematically.

### Effect of pH

The first factor investigated is the pH of the wastewater because of its strong effect on the formation of radicals which determined the catalysis capacity. In this part, the content of ZVI and the treatment time were fixed to be 20 mg/l and 30 min respectively meanwhile the pH was controlled from 3 to 8. After treatment, the COD of the wastewater was determined, and the obtained results are present in Figure 7. It is recognized that, the COD of the wastewater reached the lowest value of 2340 mg/l at pH 5. At that time, at the higher and lower pH values, viz. pH 3, pH4, pH 6, pH 7 and pH 8, the COD of the wastewater after secondary treatment are higher. It means that the highest treatment efficiency achieved at pH 5. According to the previous report [19], at the acidic pH values, ZVI donates two electrons to O2 on catalyst surface to yield hydrogen peroxide (H2O2) in the initial stage (reaction (3)). Subsequently, H<sub>2</sub>O<sub>2</sub> may be reduced by ZVI to water (reaction (4)) or react with ferrous ion - Fe(II) which was previously formed in the reaction (3) to make hydroxyl radical (HO<sup>•</sup>) (reaction (5)).



Figure 7: Effect of pH on the COD of the wastewater after treatment with ZVI

$$Fe_s^0 + O_2 + 2H^+ \rightarrow Fe(II) + H_2O_2$$
 (3)

$$Fe_s^0 + H_2O_2 + 2H^+ \to Fe(II) + 2H_2O$$
 (4)

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + HO^{\bullet} + HO^{-}$$
(5)

At higher pH values, the occurrence of the reaction (4) was dominant, and those of the reactions (3) and (5) was negligible. This is ascribed to the low content of oxidants in the reaction of wastewater treatment resulting in low treatment efficiency. So, the ZVI

catalyst exhibit the high catalytic performance at a pH range of 4 - 6.

### Effect of the ZVI content

Because of the complexity in the composition of the waste cutting fluid, the use of the reasonable content of the ZVI catalyst is very important. The use of abundant amount of the ZVI catalyst will cause secondary waste. In contrast, the use of insufficient amount of the ZVI catalyst will result in inefficient treatment of the wastewater. To determine the reasonable amount of the ZVI catalyst for the secondary treatment of the waste cutting fluid, the ZVI content was used for the secondary treatment ranging from 5 to 35 mg/l. pH of the wastewater was fixed to be 5. The treatment efficiency of the ZVI catalyst was evaluated based on the COD index. The COD results of the wastewater after treatment with ZVI are displayed on Figure 8. From Figure 8, it is observable that with the increase in the ZVI content from 5 to 20 mg/l, the COD index of the wastewater attained after treatment decreased from 3931 mg/l to 2340 mg/l, corresponding to the treatment efficiency of 40.5% for the secondary treatment process and 98.4% for the total treatment process. As the ZVI content increased over 20 mg/l, the COD index remained almost unchanged. Thus, according to the obtained results, the reasonable ZVI content for treatment of wastewater after pre-treatment throughout flocculation and separation was 20 mg/l.



Figure 8: Effect of the ZVI content on the COD of the wastewater obtained after treatment

#### Effect of treatment time

The treatment time is hardly concerned in the wastewater treatment on laboratory scale, but it is meaningful in pilot scale or in practical application. Thus, in this study, the effect of the treatment time was examined as well. The period of the treatment time or

the period that the ZVI catalyst was dispersed into the wastewater was varied from 5 to 90 min. The change in the COD of the wastewater after treatment against the treatment time is depicted in Figure 9. Before treatment, the COD of the wastewater was 4023 mg/l. In the presence of 20 mg/l of the ZVI catalyst in the wastewater, the COD of the wastewater diminished gradually with the increase in the treatment time. Especially, after 45 min of treatment, the COD value reached 2059 mg/l, corresponding to the treatment efficiency of 48.8% for the secondary treatment process and 98.6% for the total treatment process. After that, the COD index almost remained unchanged at the value of around 2000 mg/l according to the treatment time. Hence, a period of 45 min was required minimum treatment time so that the ZVI showed the best catalysis performance. Based on the above investigation results, it can be stated that, we succeeded in optimization of the secondary treatment conditions for the used cutting fluid collected from Samsung Electronics Vietnam Thai Nguyen factory by using the ZVI microparticles as catalyst. The optimum conditions of the secondary wastewater treatment were found to be pH 5, the ZVI content of 20 mg/l, the treatment time of 45 min, respectively.



Figure 9: Effect of reaction time on the COD of the wastewater obtained after treatment

Comparison on the catalysis performance between the synthesized and commercial ZVI

It was determined that ZVI is easily oxidized in air, so the ZVI catalytic activity will be gradually reduced with storage time. Therefore, this study synthesized ZVI and preserved it in ethanol and then treated it for wastewater treatment Herein, to demonstrate the difference in the catalytic activity of the ZVI material synthesized in this work against the commercial ZVI product in the wastewater treatment, the commercial ZVI was also used as catalyst for the secondary treatment of the waste cutting fluid of Samsung Thai Nguyen factory in the same treatment conditions. The wastewater obtained after treatment with the commercial ZVI was measured the COD index. The obtained results showed that the COD of the output wastewater after treatment with the commercial ZVI was 2743 mg/l, corresponding to the COD removal treatment efficiency of 31.8%, lower than that of the synthesized ZVI (48.8%). Because of the commercial catalysis, the ferric iron particles have been oxidized to form a larger particle size than the synthetic catalysis.

### Conclusion

In this work, the ZVI micromaterials have been synthesized successfully via a simple chemical redox reaction between ferric chloride and sodium borohydride. The obtained ZVI particles showed the average size of 3.9 µm, corresponding to the optimized synthesis conditions: the reductant content of 0.2 M, the reaction temperature at 25°C and the dropping rate at 3 ml/min. The obtained ZVI particles were used as catalyst for the secondary treatment of the waste cutting fluid from Samsung Thai Nguyen factory. The synthesized ZVI material showed the best wastewater treatment performance at pH 5 with the ZVI content of 20 mg/l and the treatment time of 45 min. After secondary treatment with ZVI, the COD of the input wastewater reduced by half, to 2059 mg/l. Although the COD value of the output wastewater obtained from the waste cutting fluid of Samsung Thai Nguyen factory after primary and secondary treatments was still higher than the national standard of treated wastewater, the present work already offered helpful information about the prospective in the utilization of the synthesized and commercial ZVI catalyst. Because of its environmental benignity and low cost of the ZVI material, the catalytic activity of the ZVI is likely enhanced further by coupling with other elements like sulfur, copper, or nickel.

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### References

 Sánchez-Oneto, J.R. Portela, E. Nebot, E. Martín e z de la Ossa. J. Hazard. Mater, 2007, 144, 639-644. https://10.1016/j.jhazmat.2007.01.088

- 2. P. Rajasulochana, V. Preethy. Resource-Efficient Technologies, 2016, 2, 175-184. https://doi.org/10.1016/j.reffit.2016.09.004
- S. Ma, K. Kim, J. Huh, D.E. Kim, S. Lee, Y. Hong. Sep. Purif. Technol., 2018, 199, 289-297. https://10.1016/J.SEPPUR.2018.02.005
- C.T. Hai Nam, N.T. Thu Hien, N.T. Thu Huyen, H.H. Hiep, N.T. Thuong. Journal of Chemistry, 2021, 2021, 7248402.

https://doi.org/10.1155/2021/7248402

- QCVN 40:2011/BTNMT National Technical Regulation on Industrial Wastewater. Minister of Natural Resources and Environment, 2011.
- T.A. Aragaw, F.M. Bogale, B.A. Aragaw. J. Saudi Chem. Soc., 2021, 25, 101280. https://doi.org/10.1016/j.jscs.2021.101280
- H. Wu, W. Wei, C. Xu, Y. Meng, W. Bai, W. Yang, A. Lin. Ecotoxicol. Environ. Saf, 2020, 188, 109902. https://10.1016/j.ecoenv.2019.109902
- Y. Hu, X. Peng, Z. Ai, F. Jia, L. Zhang. Environ. Sci. Technol., 2019, 53, 8333-8341. https://10.1021/acs.est.9b01999
- X. He, X. Min, T. Peng, F. Zhao, Y. Ke, Y. Wang, G. Jiang, Q. Xu, J. Wang. J. Chem. Eng. Data, 2020, 65, 1936-1945. https://pubs.acs.org/doi/10.1021/acs.jced.9b01110?g oto=supporting-info
- M. Liu, Y. Wang, L. Chen, Y. Zhang, Z. Lin. ACS Appl. Mater. Interfaces, 2015, 7, 7961-7969. https://doi.org/10.1021/am509184e

- L. Liang, X. Guan, Z. Shi, J. Li, Y. Wu, P.G. Tratnyek. Environ. Sci. Technol., 2014, 48, 6326-6334. https://doi.org/10.1021/es500958b
- H. Yu, T. Zhang, Z. Jing, J. Xu, F. Qiu, D. Yang, L. Yu. Chem. Eng. Sci., 2019, 205, 278-286. https://10.1016/j.ces.2019.05.012
- J.C. Koenig, H.K. Boparai, M.J. Lee, D.M. O'Carroll, R.J. Barnes, M.J. Manefield. J. Hazard. Mater., 2016, 308, 106-112. https://doi.org/10.1016/j.envint.2019.01.030
- F. He, Z. Li, S. Shi, W. Xu, H. Sheng, Y. Gu, Y. Jiang,
   B. Xi, Environ. Sci. Technol., 2018, 52, 8627-8637. https://doi.org/10.1021/acs.est.8b01735
- 15. C. Tan, Y. Dong, D. Fu, N. Gao, J. Ma, X. Liu. Chem. Eng. J., 2018, 334,1006-1015. https://doi.org/10.1016/j.cej.2017.10.020
- S. Rodriguez, L. Vasquez, A. Romero, A. Santos. Ind. Eng. Chem. Res., 2014, 53,12288-12294. https://doi.org/10.1021/ie501632e
- 17. O. Eljamal, R. Mokete, N. Matsunaga, Y. Sugihara. Chem. Eng., 2018, 6, 6207-6220. https://doi.org/10.1016/j.jece.2018.09.012
- Y.-Y. Zhang, H. Jiang, Y. Zhang, J.-F. Xie. Chem.
   Eng. J., 2013, 229, 412-419. https://doi.org/10.1016/j.cej.2013.06.031
- 19.
   C.K. Remucal, C. Lee, D.L. Sedlak. Environ. Sci.

   Technol.,
   2011,
   45,
   3177-3178.

   https://10.1021/es102401d
   3177-3178.
   3177-3178.