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# Automotive fleet repair facility wastewater treatment using air/ZVI and air/ZVI/H$_2$O$_2$ processes

Jan Paweł Bogacki*, Hussein Al-Hazmi

Warsaw University of Technology, Poland
Faculty of Building Services, Hydro and Environmental Engineering

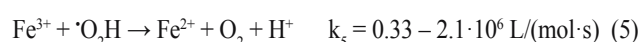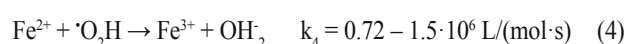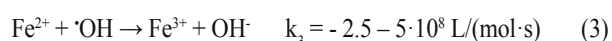*Corresponding author's e-mail: jan.bogacki@is.pw.edu.pl

**Keywords:** Wastewater treatment, zero-valent iron, Advanced Oxidation Processes, AOP, ZVI.

**Abstract:** Advanced automotive fleet repair facility wastewater treatment was investigated with Zero-Valent Iron/Hydrogen Peroxide (Air/ZVI/H$_2$O$_2$) process for different process parameters: ZVI and H$_2$O$_2$ doses, time, pH. The highest Chemical Oxygen Demand (COD) removal efficiency, 76%, was achieved for ZVI/H$_2$O$_2$ doses 4000/1900 mg/L, 120 min process time, pH 3.0. COD decreased from 933 to 227 mg/L. In optimal process conditions odor and color were also completely removed. COD removal efficiency was increasing with ZVI dose. Change pH value below and over 3.0 causes a rapid decrease in the treatment effectiveness. The Air/ZVI/H$_2$O$_2$ process kinetics can be described as d[COD]/dt = -a [COD]t$^m$, where 't' corresponds with time and 'a' and 'm' are constants that depend on the initial reagent concentrations. H$_2$O$_2$ influence on process effect was assessed. COD removal could be up to 40% (560 mg/L) for Air/ZVI process. The FeCl$_3$ coagulation effect was also evaluated. The best coagulation results were obtained for 700 mg/L Fe$^{3+}$ dose, that was slightly higher than dissolved Fe used in ZVI/H$_2$O$_2$ process. COD was decreased to 509 mg/L.

## Introduction

Automotive fleet repair facility wastewater contains many persistent and toxic petroleum organic compounds:wasteoils, petrol components and heavy metals (Makowska and Mazurkiewicz 2016, Piecuch et al. 2015, US EPA 1991). They are refractory to biodegradation. Thus, conventional biological treatment may no longer be considered as satisfactory treatment process.
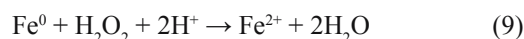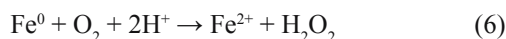
Advanced oxidation processes (AOP), such as Fenton process, are promising treatment methods for wastewater containing hardly biodegradable and potentially toxic organic compounds. They consist in the effective production of free radicals which oxidize organic pollutants. Equation 1 is recognized as Fenton reaction and implies the oxidation of Fe$^{2+}$ to Fe$^{3+}$ ions to decompose H$_2$O$_2$ into ˙OH. It is usually considered as the core of the Fenton chemistry. Furthermore, other reactions must be considered to understand the whole process(Babuponnusami and Muthukumar 2014).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + ˙OH \quad k_1 = -40 - 80 \text{ L/(mol·s)} \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + ˙O_2H + H^+ \quad k_2 = -9.1 - 10^{-7} \text{ L/(mol·s)} \quad (2)$$

$$Fe^{2+} + ˙OH \rightarrow Fe^{3+} + OH^- \quad k_3 = -2.5 - 5·10^8 \text{ L/(mol·s)} \quad (3)$$

$$Fe^{2+} + ˙O_2H \rightarrow Fe^{3+} + OH^-_2 \quad k_4 = 0.72 - 1.5·10^6 \text{ L/(mol·s)} \quad (4)$$

$$Fe^{3+} + ˙O_2H \rightarrow Fe^{2+} + O_2 + H^+ \quad k_5 = 0.33 - 2.1·10^6 \text{ L/(mol·s)} \quad (5)$$

As shown in (Eq. 2), the generated Fe$^{3+}$ ions can be reduced by reaction with excess of H$_2$O$_2$ to form again Fe$^{2+}$ ion. This reaction is called Fenton-like reaction,it is slower than Fenton reaction, and allows for Fe$^{2+}$ regeneration in an effective cyclic mechanism. Equations (2–5), represent the limiting steps in the Fenton chemistry since H$_2$O$_2$ is consumed and Fe$^{2+}$ ionsare regenerated from Fe$^{3+}$ ion through these reactions.

The application of homogeneous Fenton process to treat large quantity of water may produce large amount of sludge in the final neutralization/coagulation step. Usually Fe$^{2+}$ ions are introduced to wastewater as FeSO$_4$ solution, which increases salinity usually above the standard 1000ml/L and 500 mg/L of chlorides and sulfates (VI) respectively (Directive of the Minister of the Environment, Journal of Laws of 18 November 2014, Item 1800). In order to avoid these disadvantages, zero valent iron (ZVI) has appeared as an effective heterogeneous catalyst for wastewater treatment. ZVI and other iron based catalysts were used *inter alia* for the treatment of dye (Chang et al. 2006, Devi et al. 2009, Grcic et al. 2012, Moon et al. 2011, Weng et al. 2013, Zhang et al. 2014, Yang et al. 2015a, Yang et al. 2015b), nitrobenzene (Dong et al. 2010), 2,4-dinitroanisole (Shen et al. 2013), pharmaceutical compounds (Bautitz et al. 2012, Segura et al. 2013), TNT wastewater (Barreto-Rodrigues et al. 2009), phenols and chlorophenols (Kim et al. 2011, Shimizu et al. 2012), pesticides (Fjordboge et al. 2013), BPA (Xi et al. 2014) or coking wastewater (Lai et al. 2007), palm oil mill effluent (Taha and Ibrahim 2014), nitrites reduction (Fatemina et al. 2013, Suzuki et al. 2012), oil sands reclamation (Pourrezaei et al. 2014), and surfactants removal (Martins et al. 2014).

Ferrous and ferric saltsare low cost material widely used in wastewater treatment as coagulant or as a component of Fenton reagent. Adding ZVI in aqueous phase has proved to be a fairly fast process to reduce various organic compounds according to the dissolution of $Fe^{2+}$ ions and electrons transfer to react with the organic molecules on the iron surface (Cao et al. 1999, Chen et al. 2001). In heterogeneous Fenton reaction, oxidation of ZVI provides an alternative means of inducing Fenton oxidation as shown in (Eq. 6–11):

$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \qquad (6)$$

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \qquad (7)$$

$$Fe^{3+} + Fe^0 \rightarrow 3Fe^{2+} \qquad (8)$$

$$Fe^0 + H_2O_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O \qquad (9)$$

$$Fe^0 \rightarrow Fe^{2+} + 2e \qquad (10)$$

$$\text{Organic pollutant} + Fe^0 \rightarrow \text{Reduced organic pollutant} + Fe^{2+} \quad (11)$$

The objective of this study was to provide additional knowledge regarding the treatment of automotive fleet repair facilities wastewater. The studies were especially aimed at the estimation of the efficiency of (i) Air/ZVI,Air/ZVI/H$_2$O$_2$ and coagulation process, (ii) estimation of the stirring method and pH influence on efficiency of Air/ZVI/H$_2$O$_2$ process, and (iii) description of its kinetics.

## Materials and methods

The raw wastewater was collected in April 2014 from automotive fleet repair facility, located in Warsaw, Poland. All types of wastewater produced in facility are collected in equalization tank and thentransferred to emulsion separator. Samples were collected after emulsion separation in the separator. All studies concerning the wastewater treatment were carried out within 72 h after collection of samples. After wastewater collection, the samples were acidified to pH 3.0 and refrigerated at 4°C until analysis to prevent biochemical decomposition processes.

The following parameters were determined according to the EN or ISO standards: COD, COD after 30 min sedimentation (COD$_{sed}$) and COD dissolved (for sample filtered through 0.45 μm filters) COD$_{dis}$(ISO 6060), total suspended solids (TSS) (EN 872), pH (EN ISO 10523), turbidity (EN ISO 7027) and specific conductivity (EN 27888).

Wastewater after 30 min of sedimentation, for easily settleable solids (ESS) removal, were treated by Air/ZVI, Air/ZVI/H$_2$O$_2$ or coagulation process.

Air/ZVI and Air/ZVI/H$_2$O$_2$experiments were carried out in 0.7L cylindrical reactor filled with 0.5L of sample. Four doses of ZVI were used (1000, 2000, 3000, 4000 mg/L). 30% H$_2$O$_2$ solution was added to wastewater in ZVI/H$_2$O$_2$ process. H$_2$O$_2$/COD mass ratio was equal to 0.5, 1, 1.5. Based on density and percentage concentration data, H$_2$O$_2$ volumes added were 1.2, 2.4 and 3.6 mL respectively. All samples were stirred by magnetic or ultrasonic stirrer. Magnetic stirring was very intensive. Stirring speed was set as 1000rpm (Heidolph MR3000). Studies on ultrasonic stirring were performed in ultrasonic bath SONIC 5 630 W (Polsonic). Ultrasound power

used was 2×320W and 40 kHz.The pH was adjusted to 3.0. During studies on pH influence, the pH was adjusted to 2.0, 4.0, 5.0 or 6.0. After preselected times (15, 30, 60, 120 min) the process was stopped by increasing the pH to 9.0 with 1.1 M NaOH. The sample was left overnight for sedimentation of iron precipitate and H$_2$O$_2$ decomposition. Iodometric test on H$_2$O$_2$ removal was performed, and after that COD was determined.

Studies on coagulation were performed in 0.7L reactor with magnetic stirrer (Heidolph MR3000). The reactor was filled with 0.5 L of sample. The wastewater was coagulated with FeCl$_3$ at pH 9.0. The coagulant doses wereinwide range (50 to 700 mg Fe$^{3+}$/L). The samples were stirred for 5 min for fast, followed by 10 min for the slow stirring. The sample was left overnight for sedimentation of iron precipitate. After that COD was determined.

All reagents used in this study were manufactured by POCH and were of puriss p.a. grade.

For ZVI/H$_2$O$_2$process, the efficiency of H$_2$O$_2$ was evaluated according to the Kang and Hwang equation (Eq. 12) (Kang and Hwang 2000):

$$\eta\ (\%) = \{\Delta COD/(0.4706 \cdot [H_2O_2])\} \cdot 100\% \qquad (12)$$

where ΔCOD is the decrease of the COD value (mg/L), 0.4706 is a constant factor for the amount of COD theoretically removed (mg) by 1 mg of H$_2$O$_2$ and [H$_2$O$_2$] is the hydrogen peroxide dose (mg/L).

## Results and disscusion

### Raw wastewater

It must be pointed out that all experiments in this work were carried out with real wastewater, without any dilution or other pre-treatment. The parameters of wastewater are shown in Table 1. All parameters except COD were determined after sedimentation. 30 min sedimentation for ESS removal allows to remove 9.9% of initial COD. Suspended solids left after sedimentation contributed to a 185 mg/L COD value. All treatment processes were performed on wastewater after initial sedimentation and Easily Settleable Solids (ESS) removal.

Raw wastewater wascharacterized by a moderate COD value (in comparison with other industrial wastewater sources, that could generate wastewater with COD even over 100 000 mg/L), but unacceptable color and odor. Based on a known source of wastewater and the smell, it could be suspected that the compounds contained in wastewater are, among others, components of fuels. Crucial for this type of wastewater treatment is to ensurethe color and odorremoval to an acceptable level.

**Table 1.** Raw wastewater parameters

| Parameter | Unit | Value |
|---|---|---|
| COD | mg/L | 1035 |
| COD$_{sed}$ | mg/L | 933 |
| COD$_{dis}$ | mg/L | 748 |
| TSS | mg/L | 640 |
| pH | – | 7.8 |
| Conductivity | mS/cm | 1.241 |
| Colour | – | Dark green |
| Odor | – | Oily, strong |

*Air/ZVI and Air/ZVI/H$_2$O$_2$process*
Results of Air/ZVI and Air/ZVI/H$_2$O$_2$processesare shown in Figures 1–4.

The COD removal was increasing with iron dose in a two-stage pattern. At first sharp decline, followed by a further small decrease in time, was observed. COD during ZVI process rapidly decreasedin 15 min from 933 mg/L to 733–600 mg/L. The decrease was significant in the case of 4000 mg/Lcompared with 1000 mg/L ZVI dose. The COD value increased slowly at time 15 to 60 min for different amount of ZVI. Finally, the second decrease at time 60 min to 120 min was observed. After 15 min COD minimally decreased to 773 mg/L (17%), while after 120 reached the maximal value of 560 mg/L (40% decreasing) for the highest dose.It might be due to some compounds transformation. On the one hand, radical oxidation leads to organic compounds rearrangements and partial decomposition but, on the other hand, coagulation persistent, more polar, compounds could be created. As a result of those two opposite processes, no significant COD removal effect was observed.For longer process times coagulation persistent compounds were decomposed and new ones were not created. Process effect increasedwith increasing ZVI dose, which was consistent with the studies of Lai et al. (Lai et al. 2007). The oxidation-reduction ability of Air/ZVI could transform the structures and characteristics of some compounds. Air/ZVI is more efficient in eliminating low molecular weight compounds, but there were still some residual contaminants which could not be removed by this process (Lai et al. 2007, Cao et al. 1999, Chen et al. 2001).

ZVI addition declined the color and odor significantly. It was observed that color and odor removal increased after the addition of H$_2$O$_2$ The color and odor removal efficiencies incremented promptly to the first 15 min then increasing more with the passage of time to 120 min. In this study, the optimal deodorization and decolorizationwere consistent with some other studies (Cao et al. 1999, Chen et al. 2001). The Air/ZVI process could be used for the decolorization of wastewater, but the COD efficiency was too low to justify its use. To overcome this, Air/ZVI/H$_2$O$_2$ process, that was similar to a Fenton process, was examined.

Air/ZVI/H$_2$O$_2$ system was more effective than Air/ZVI one. There must be a balance between the concentration of H$_2$O$_2$ and ZVI. It was found that the result for Air/ZVI/H$_2$O$_2$ COD/ZVI ratio 1:1 were better than 1:0.5 and 1:2 (Figures 1–4) regardless or ZVI dose. Figures 1–4 show COD rapid decrease at time 0 min to 30 min. The amount of decrease was significant in the case of 4000 mg/L compared with 1000 mg/L ZVI dose. For longer times COD was still decreasing, but the rate was lower. After 120 min COD reached the value of 227 mg/L (76% decreasing) for the highest ZVI dose.

In comparison with other studies (Deng and Engelhardt 2006, Gogate and Pandit 2004, Lau et al. 2001, Zhang et al. 2005) sludge settling characteristic was excellent at the COD/H$_2$O$_2$ ratio 1:1, but became poor for 1:2 ratio. It seemed
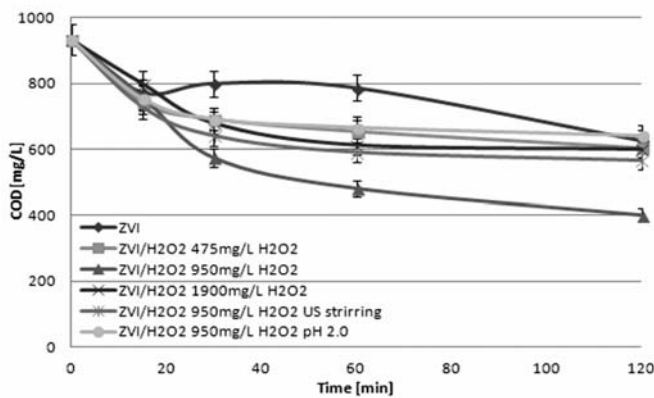


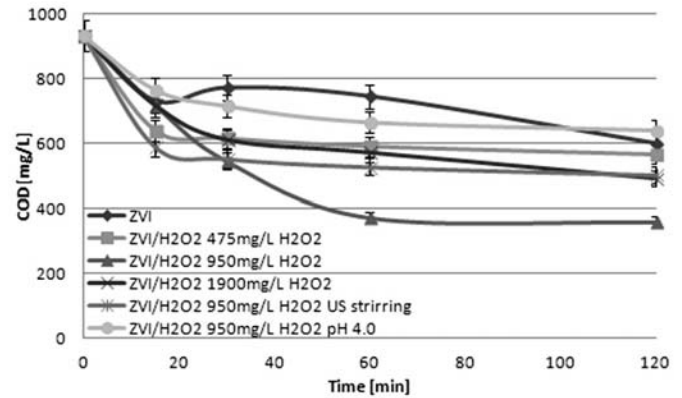**Fig. 1.** COD changes forAir/ZVI and Air/ZVI/H$_2$O$_2$ processes for 1000 mg/LZVI dose



**Fig. 2.** COD changes forAir/ZVI and Air/ZVI/H$_2$O$_2$ processes for 2000 mg/LZVI dose
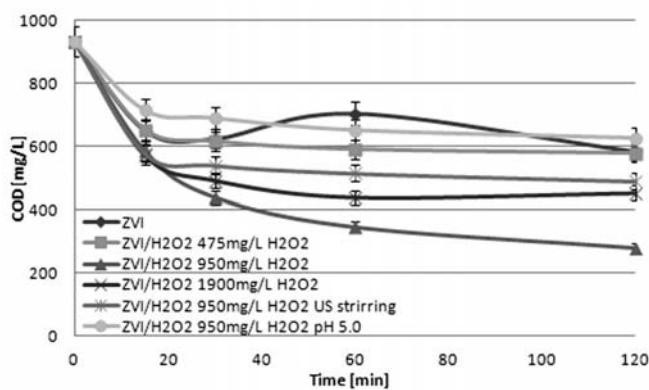


**Fig. 3.** COD changes forAir/ZVI and Air/ZVI/H$_2$O$_2$ processes for 3000 mg/LZVI dose
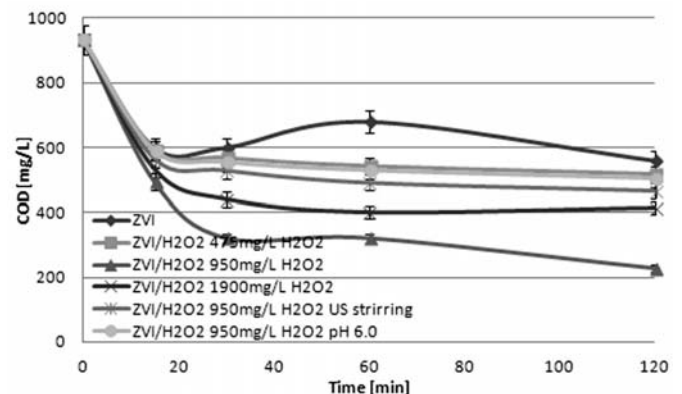


**Fig. 4.** COD changes forAir/ZVI and Air/ZVI/H$_2$O$_2$ processes for 4000 mg/LZVI dose

that excessive H$_2$O$_2$, when decomposed, would produce oxygen bubbles that made sludge settling difficult (Lau et al. 2001, Zhang et al. 2005). In addition, residual H$_2$O$_2$ might inhibit downstream chemical treatment. When COD/H$_2$O$_2$ ratio was 1:0.5 residual ferrous iron was observed, with the bluish green effluent (probably originated by Fe$^{2+}$ compounds such as Fe(OH)$_2$). Iron sludge required further treatment (Deng and Engelhardt 2006, Gogate and Pandit 2004). Therefore COD/H$_2$O$_2$ ratio 1:1 was chosen for further experiments.

### Comparison between dissolving of oxygen by ultrasound and magnetic stirring in Air/ZVI/H$_2$O$_2$ processes

Ultrasonic treatment involves the generation of ˙OH by acoustic cavitation. This phenomenon is produced through compression and expansion cycles of US waves )))), which result in the growth and collapse of the gas bubbles and the production of local areas of high energy and pressure. These conditions are so extreme that they are capable of breaking up the entrapped molecules within the bubbles, such as vaporized water or dissolved gases (e.g.), to produce radicals, mainly ˙OH and ˙OH$_2$ (Eq. 13–17).

$$H_2O + ))) \rightarrow \text{˙H} + \text{˙OH} \tag{13}$$

$$O_2 + ))) \rightarrow 2O \tag{14}$$

$$H_2O + O \rightarrow 2\text{ ˙OH} \tag{15}$$

$$\text{˙H} + O_2 \rightarrow O + \text{˙OH} \tag{16}$$

$$2\text{ ˙H} + O_2 \rightarrow O + \text{˙OH}_2 \tag{17}$$

These radicals are capable of initiating or promoting many fast oxidation reactions, leading to the degradation of more hydrophobic compounds at the bubble–bulk solution interface and to a lesser extent, of more hydrophilic species via ˙OH diffused or ejected into the bulk solution(Rubio-Clemente et al. 2014).

However, the magnetic stirring is more efficient in wastewater treatment than ultrasonic, as shown inthe Figures 1–4. Oxygen is paramagnetic and can be effectively introduced to wastewater by a magnetic field(Kim et al. 2011, Zhang et al. 2005). Reactions of oxygen with dissolving Fe, creation of H$_2$O$_2$ are the most important comparing differences in COD. Where the consumption of dissolved oxygen by ZVI reaction (Eq. 6) was also enhanced in the presence of magnetic field, the competing reaction of H$_2$ production (Eq. 7) from proton reduction was retarded. Since the ZVI induced oxidation is mainly driven by the in situ generated ˙OH (Kim et al. 2011), ZVI constantly consumes dissolved oxygen (Eq. 6). Under condition of weak reaeration (ultrasonic stirring) ZVI reduces protons according to (Eq. 7).

Shimizu et al. (2012) confirmed that in oxygen saturated wastewater ˙OH generation is the same with and without aeration. Afterward the ˙OH generation without aeration was significantly suppressed due to the shortage of dissolved oxygen. It may be concluded that ˙OH generation was significantly related tothe dissolved oxygen concentration. Because of that oxygen introduction mechanism is crucial for the purification effect. Ultrasonic stirring is less effective than magnetic stirring, so even though the reactions (13–17)

take place, they have less effect on the process then dissolved oxygen (Eq. 6).

Moreover Taha and Ibrahim (2014) found that for palm oil mill effluent treated withZVI,sonification intensity and duration time have a weak correlation with Fe$^{2+}$ production and COD decrease. They found by referring to shell – core concept, that at pH 3.0 and 4.0 only a small amount of Fe$^{2+}$ was in aqueous solution resulting from partially dissolved shell.

### Effect of pH

Experiments were also performed to assess the generation of ˙OH for previously foundedoptimal ZVI/H$_2$O$_2$ doses. The slower rate of degradation at lower pH is also due to the excess H$^+$ ions present in the solution acting as ˙OH scavenger according to reaction (Eq. 18) (Devi et al. 2009).

$$H^+ + \text{˙OH} + e^- \rightarrow H_2O \tag{18}$$

While the fresh surfaces were kept, the adsorption ability and reactivity of the ZVI might be high. At the initial stage, pollutant molecules could easily transport and be oxidized by ˙OH formed near Fe$^0$ surface and/or adsorb to Fe$^0$ surface.

At lower pH, Fe$^0$ oxidizes to Fe$^{2+}$ in aqueous acidic conditions due to the dissolution. present in the solution decomposes formed by the follow reaction (Eq. 6, 1) to generate ˙OH.

Therefore, at lower pH the Fenton reaction generating ˙OH may occur near the ZVI powder surface and dominate the overall removal of color and odor (Shimizu et al. 2012).

In this study, it was found that the optimal value for COD was reached at pH 3.0. It means the increasing value of pH effect slightly for decreasing COD, which was consistent with other studies (Devi et al. 2009, Fan et al. 2009). They discovered that although the cumulative ˙OH production at pH 2.0 wasabout a half of that at pH 3.0, the contribution of the Fenton degradation at pH 2.0 was only 0.1%. The excess acidity retarded the degradation rate as excess H$^+$ ions act as ˙OH scavenger shown in reaction (20) (Devi et al. 2009, Fan et al. 2009).

The pH influence is a very important operating parameter which affects color and odor removal efficiency in Air/ZVI/H$_2$O$_2$ and Air/ZVI oxidation process. The decrease of ZVIdecolorization rate by raising pH to the alkaline region is mentioned by Chen et al. (Chen et al. 2001). Fe$^{2+}$ ions, from the iron surface and hydroxyl ions in the alkaline solution precipitate ferrous hydroxide on the surface of iron occupying the reactive sites thus hindering the reaction (Chang et al. 2006).

### Coagulation

Figure 5 shows that COD decreased even for low Fe$^{3+}$ doses. The decrease was significant in the case of concentration of Fe$^{3+}$ 50 mg/L up to 737 mg/L (21%). For increasing Fe$^{3+}$ dose, COD was still decreasing, but the rate was lower for 700 mg/L, it reached the value of 509 mg/L (45% decrease).

The main mechanisms for COD decreasing in coagulation could be pollutants adsorption-followed precipitation. For the removal of organic pollutants in sample, however, the oxidation – reduction mechanism must be considered in addition to the coagulation and precipitation mechanism. On the other hand, Air/ZVI and Air/ZVI/H$_2$O$_2$ could be improved coagulation process, since the contaminants removal was enhanced by oxidation – reduction reactions in the system (Lai et al. 2007).

*Kinetics*

The rate of the ZVI process is difficult to describe. The following equations were used to describe the investigated processes:

– pseudo-first-order reaction with respect to the COD value

$$d[COD] / dt = - k_{1st\ order}[COD]; \qquad (19)$$

– pseudo-second-order reaction with respect to the COD value

$$d[COD] / dt = - k_{2nd\ order} [COD]^2; \qquad (20)$$

– empirical equation that accounts for changes in the process rate due to other factors that influence changes with process time (the Balcerzak's equation, Eq. 21) (Naumczyk et al., 2012):

$$d[COD]/dt = -a [COD]t^m. \qquad (21)$$

Where 't' corresponds with time and 'a' and 'm' are constants that depend on the initial reagent concentrations.

After integration and application of the double logarithm, the following formula was obtained (Eq. 22):

$$\ln \ln[COD]_0/[COD] = (m+1) \ln t + \ln a – \ln (m+1) \qquad (22)$$

where $[COD]_0$ is the initial COD.

Calculations made using the pseudo-first- and pseudo second order reaction equation resulted in too low correlation coefficients for all three investigated processes. Much better correlation coefficients were obtained for (Eq. 21). Usually ZVI processes kinetics isdescribed as first – order one [6]. This simple approach has not worked in the case of automotive fleet repair facility wastewater.

The abovementioned equation has been used to describe the kinetics of the Fenton and photo-Fenton reactions in landfill leachate and cosmetic wastewater treatment(Naumczyk et al. 2012, Marcinowski et al. 2014).

The result of kinetic calculations and $H_2O_2$ efficiency are presented in Tables 2–5.

It was found that in the case of Air/ZVI/$H_2O_2$ process, the Balcerzak's equation (Eq. 21) is characterized by a high compatibility ($R^2$ is usually over 0.9, especially for larger ZVI doses). But for ZVI it failed to satisfactorily describe the kinetics (very low $R^2$ values, decreasing with ZVI dose). In the case of this wastewater ZVI process seems to be too complex for simple approach, but models built on this approach are very complicated (Grcic et al. 2012).

*$H_2O_2$ efficiency*

The oxidant ($H_2O_2$) efficiency is shown in Tables 2–5.The highest oxidant efficiency, up to 157.9% was observed in Air/ ZVI/$H_2O_2$ process, for ZVI/$H_2O_2$ doses 4000/950 mg/L, under magnetic stirring at pH 3. Oxidant efficiency over 100% could be a proof for a chain radical reaction presence. More radicals than just hydroxyl one are used in oxidation process. These conditions are also optimal in the case of COD removal. The most important factor indicating $H_2O_2$ efficiency is pH. If
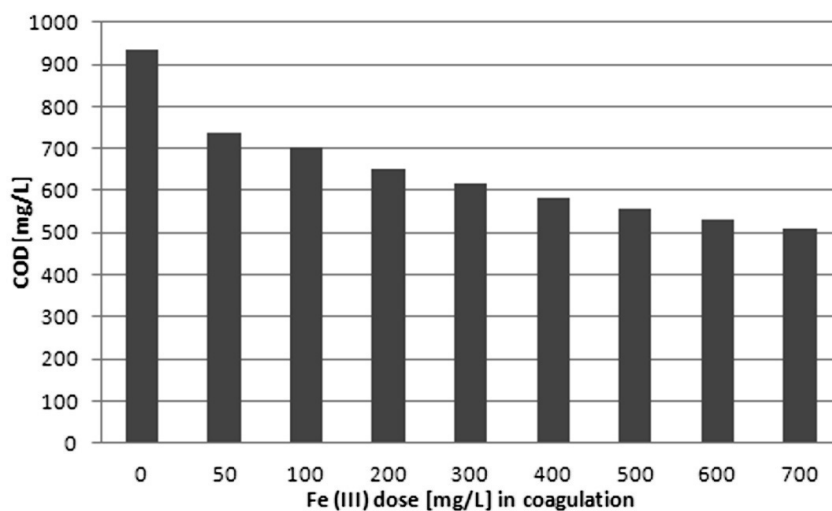


**Fig. 5.** Effect of coagulation

**Table 2.** Kinetics ofAir/ZVI the process

| Doses [mg/L] | Air/ZVI (1000 mg/L) | Air/ZVI (2000 mg/L) | Air/ZVI (3000 mg/L) | Air/ZVI (4000 mg/L) |
|---|---|---|---|---|
| a | 0.0200 | 0.0253 | 0.0181 | 0.0058 |
| m | -0.6603 | -0.7133 | -0.9377 | -0.9853 |
| n | 0.3397 | 0.2867 | 0.0623 | 0.0147 |
| k | 0.0590 | 0.0883 | 0.2914 | 0.3989 |
| $R^2$ | 0.4954 | 0.4759 | 0.0669 | 0.0042 |

**Table 3a.** Kinetics of Air/ZVI/H$_2$O$_2$ process

| Doses [mg/L] | Air/ZVI/H$_2$O$_2$ (1000/450) | Air/ZVI/H$_2$O$_2$ (2000/450) | Air/ZVI/H$_2$O$_2$ (3000/450) | Air/ZVI/H$_2$O$_2$ (4000/450) |
|---|---|---|---|---|
| a | 0.0312 | 0.0357 | 0.0353 | 0.0409 |
| m | -0.6973 | -0.8615 | -0.8579 | -0.8742 |
| n | 0.3027 | 0.1385 | 0.1421 | 0.1258 |
| k | 0.1031 | 0.2582 | 0.2486 | 0.3252 |
| R$^2$ | 0.9917 | 0.9994 | 0.9426 | 0.9997 |
| η | 73.5 | 82.0 | 79.1 | 93.2 |

**Table 3b.** Kinetics of Air/ZVI/H$_2$O$_2$ process

| Doses [mg/L] | Air/ZVI/H$_2$O$_2$ (1000/950mg) | Air/ZVI/H$_2$O$_2$ (2000/950mg) | Air/ZVI/H$_2$O$_2$ (3000/950mg) | Air/ZVI/H$_2$O$_2$ (4000/950mg) |
|---|---|---|---|---|
| a | 0.0272 | 0.0343 | 0.0667 | 0.0954 |
| m | -0.3420 | -0.3596 | -0.5479 | -0.6549 |
| n | 0.6580 | 0.6404 | 0.4521 | 0.3451 |
| k | 0.0413 | 0.0535 | 0.1475 | 0.2766 |
| R$^2$ | 0.9058 | 0.8898 | 0.9583 | 0.8613 |
| η | 119.2 | 128.1 | 146.0 | 157.9 |

**Table 3c.** Kinetics of Air/ZVI/H$_2$O$_2$ process

| Doses [mg/L] | Air/ZVI/H$_2$O$_2$ (1000/1900) | Air/ZVI/H$_2$O$_2$ (2000/1900) | Air/ZVI/H$_2$O$_2$ (3000/1900) | Air/ZVI/H$_2$O$_2$ (4000/1900) |
|---|---|---|---|---|
| a | 0.0238 | 0.0378 | 0.0600 | 0.1343 |
| m | -0.5036 | -0.5895 | -0.806 | -0.6412 |
| n | 0.4964 | 0.4105 | 0.194 | 0.3588 |
| k | 0.0480 | 0.0921 | 0.3097 | 0.3744 |
| R$^2$ | 0.8386 | 0.9496 | 0.7873 | 0.7343 |
| η | 74.4 | 98.4 | 107.3 | 116.3 |

**Table 4.** Kinetics of Air/ZVI/H$_2$O$_2$/US process

| Doses [mg/L] | Air/ZVI/H$_2$O$_2$/US (1000/950) | Air/ZVI/H$_2$O$_2$/US (2000/950) | Air/ZVI/H$_2$O$_2$/US (3000/950) | Air/ZVI/H$_2$O$_2$/US (4000/950) |
|---|---|---|---|---|
| a | 0.0363 | 0.0450 | 0.0466 | 0.0409 |
| m | -0.6649 | -0.8568 | -0.8595 | -0.8742 |
| n | 0.3351 | 0.1432 | 0.1405 | 0.1258 |
| k | 0.1085 | 0.3145 | 0.3316 | 0.3252 |
| R$^2$ | 0.9066 | 0.9840 | 0.9843 | 0.9998 |
| η | 82.0 | 96.1 | 98.8 | 104.6 |

**Table 5.** Kinetics of Air/ZVI/H$_2$O$_2$ process, pH influence

| Doses [mg/L] | pH 2.0, Air/ZVI/ H$_2$O$_2$ (1000/950) | pH 4.0, Air/ZVI/ H$_2$O$_2$ (2000/950) | pH 5.0, Air/ZVI/ H$_2$O$_2$ (3000/950) | pH 6.0, Air/ZVI/ H$_2$O$_2$ (4000/950) |
|---|---|---|---|---|
| a | 0.0293 | 0.0274 | 0.0306 | 0.0469 |
| m | -0.7371 | -0.6837 | -0.8006 | -0.8568 |
| n | 0.2629 | 0.3163 | 0.1994 | 0.1432 |
| k | 0.1116 | 0.0867 | 0.1535 | 0.3276 |
| R$^2$ | 0.9110 | 0.9628 | 0.9922 | 0.9840 |
| η | 65.3 | 65.3 | 68.0 | 96.1 |

system operates in not optimal pH conditions, $H_2O_2$ efficiency rapid decrease is observed even up to 65.3%. Another factor affecting the efficiency is a stirring method (the amount of dissolved oxygen available) but the influence is much smaller-oxidant efficiency decrease only to 82–104.6%, comparing to 65.3–96.1% in case of pH. It is possible that the difference in efficiency, compared with optimum efficiency 157.9%, is related to the $H_2O_2$ produced by the reaction (Eq. 6).

## Conclusion

All processes (Air/ZVI, Air/ZVI/$H_2O_2$, coagulation) are suitable for automotive fleet repair facility wastewater treatment. Effectiveness of the processes was Air/ZVI/$H_2O_2$>Air/ZVI > coagulation.In Air/ZVI/$H_2O_2$ process, the amount of $H_2O_2$ is crucial for the efficiency of the process and must be close to COD value.In Air/ZVI and Air/ZVI/$H_2O_2$ processes higher ZVI dose causes better effectiveness.For the same amount of dissolved Fe, Air/ZVI is better than coagulation through the production of $H_2O_2$ and oxidation of organic compounds. The optimal pH for Air/ZVI/$H_2O_2$ process is 3.0. Change of pH value causes a rapid decrease in the effectiveness. Magnetic stirring is better than ultrasonic, because more oxygen is introduced to wastewater.Economically Air/ZVI and Air/ZVI/$H_2O_2$ are better than coagulation because the ZVI powder is very cheap (steel shavings). The highest COD removal efficiency, 76%, was achieved for Air/ZVI/$H_2O_2$ process and ZVI/$H_2O_2$doses 4000/1900 mg/L, 120 min process time. COD decreased from 933 to 227 mg/L at pH 3.0. Odor and color were also completely removed.

## References

Babuponnusami, A. & Muthukumar, K. (2014). A review on Fenton and improvements to the Fenton process for wastewater treatment, *Journal of Environmental Chemical Engineering*, 2, pp. 557–572.

Barreto-Rodriguesa, M., Silva, F.T. & Paiva, T.C.B. (2009). Optimization of Brazilian TNT industry wastewater treatment using combined zero-valent iron and Fenton processes, *Journal of Hazardous Materials*, 168, pp. 1065–1069.

Bautitz, I.R., Velosa, A.C. & Nogueira, R.F.P. (2012). Zero valent iron mediated degradation of the pharmaceutical diazepam, *Chemosphere*, 88, pp. 688–692.

Chang, M.C., Shu, H.Y., Yu, H.H. & Sung, Y.C. (2006). Reductive decolorization and total organic carbon reduction of the diazo dye CI Acid Black 24 by zero-valent iron powder, *Journal of Chemical Technology and Biotechnology*, 81, pp. 1259–1266.

Cao, J., Wei, L., Hunag, Q., Wang, L. & Han, S. (1999). Reductive degradation of azo dye by zero valent iron in aqueous solution, *Chemosphere*, 38, pp. 565–571.

Chen, J.L., Al-Abed, S.R., Ryan, J.A. & Li, Z. (2001). Effects of pH on dechlorination of trichloroethylene by zero-valent iron, *Journal of Hazardous Materials*, 83, pp. 243–254.

Deng, Y. & Englehardt, J.D. (2006). Treatment of landfill leachate by the Fenton process, *Water Research*, 40, pp. 3683–3694.

Devi, L.G., Kumar, S.G., Reddy, K.M. & Munikrishnappa, C. (2009). Photo degradation of Methyl Orange an azo dye by advanced Fenton process using zero valent metallic iron: influence of various reaction parameters and its degradation mechanism, *Journal of Hazardous Materials*, 164, pp. 459–467.

Dong, J., Zhao, Y., Zhao, R. & Zhou, R. (2010). Effects of pH and particle size on kinetics of nitrobenzene reduction by zero-valent iron, *Journal of Environmental Sciences*, 22, pp. 1741–1747.

Fan, J., Guo, Y., Wang, J. & Fan, M. (2009). Rapid decolorization of azo dye methyl orange in aqueous solution by nanoscale zerovalent iron particles, *Journal of Hazardous Materials*, 166, pp. 904–910.

Fateminia, F.S. & Falamaki, C. (2013). Zero valent nano-sized iron/clinoptilolite modified with zero valent copper for reductive nitrate removal, *Process Safety and Environmental Protection*, 91, pp. 304–310.

Fjordbøge, A.S., Baun, A., Vastrup, T. & Kjeldsen, P. (2013). Zero valent iron reduces toxicity and concentrations of organophosphate pesticides in contaminated groundwater, *Chemosphere*, 90, pp. 627–633.

Gogate, P.R. & Pandit, A.B. (2004). A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions, *Advances in Environmental Research*, 8, pp. 501–551.

Grcic, I., Papic, S., Zizek, K. & Koprivanac, N. (2012). Zero-valent iron (ZVI) Fenton oxidation of reactive dye wastewater under UV-C and solar irradiation, *Chemical Engineering Journal*, 195–196, pp. 77–90.

Guides to Pollution Prevention. The Automotive Repair Industry. United States Environmental Protection Agency (1991). EPA/625/7-91/013.

Kang, Y.W. & Hwang, K-Y. (2000). Effect of re action conditions on the oxidation efficiency in the Fenton process, *Water Research*, 34, pp. 2786–2790.

Kim, D., Kim, J. & Choi, W. (2011). Effect of magnetic field on the zero valent iron induced oxidation reaction, *Journal of Hazardous Materials*, 192, pp. 928–931.

Lai, P., Zhao, H., Wang, C. & Ni, J. (2007). Advanced treatment of coking wastewater by coagulation and zero-valent iron processes, *Journal of Hazardous Materials*, 147, pp. 232–239.

Lau, I.W.C., Wang, P. & Fang, H.H.P. (2001). Organic removal of anaerobically treated leachate by Fenton coagulation, *Journal of Environmental Engineering*, 27, pp. 666–669.

Makowska, M. & Mazurkiewicz, J. (2016). Treatment of wastewater from service areas at motorways, *Archives of Environmental Protection*, 42, (4), pp. 80–89.

Marcinowski, P., Bogacki, J. & Naumczyk, J. (2014). Cosmetic wastewater treatment using the Fenton, Photo-Fenton and $H_2O_2$/UV processes, *Journal of Environmental Science and Health*, Part A, 49, pp. 1531–1541.

Martins, R.C., Nunesa, M., Gando-Ferreira, L.M. & Quinta-Ferreira, R.M. (2014). Nanofiltration and Fenton's process over iron shavings for surfactants removal, *Environmental Technology*, 35, pp. 2380–2388.

Moon, B.-H., Park, Y.-B. & Park, K.-H. (2011). Fenton oxidation of Orange II by pre-reduction using nanoscale zero-valent iron, *Desalination*, 268, pp. 249–252.

Naumczyk, J., Prokurat, I. & Marcinowski, P. (2012). Landfill leachates treatment by $H_2O_2$/UV,$O_3$/$H_2O_2$, modified Fenton and modified Photo-Fenton methods, *International Journal of Photoenergy*, DOI: 10.1155/2012/909157.

Piecuch, T., Andriyevska, L., Dąbrowski, J., Dąbrowski, T., Juraszka, B. & Kowalczyk, A. (2015). Oczyszczanie ścieków ze stacji naprawy samochodów, *Annual Set The Environment Protection*, 17, pp. 814–832.

Pourrezaei, P., Alpatova, A., Khosravi, K., Drzewicz, P., Chen, Y., Chelme-Ayala, P. & El-Din, M.G. (2014). Removal of organic compounds and trace metals from oil sands process-affected water using zero valent iron enhanced by petroleum coke, *Journal of Environmental Management*, 139, pp. 50–58.

Rozporządzenie Ministra Środowiska, Dziennik Ustaw z dnia 18 listopada 2014 r. Poz. 1800, w sprawie warunków, jakie należy spełnić przy wprowadzaniu ścieków do wód lub do ziemi, oraz w sprawie substancji szczególnie szkodliwych dla środowiska wodnego.

Rubio-Clemente, A., Torres-Palma, R.A. & Peñuela, G.A. (2014). Removal of polycyclic aromatic hydrocarbons in aqueous environment by chemical treatments: A review, *Science of the Total Environment*, 478, pp. 201–225.

Segura, Y., Martínez, F. & Melero, J.A. (2013). Effective pharmaceutical wastewater degradation by Fenton oxidation with zero-valent iron, *Applied Catalysis B-Environmental*, 136– 137, pp. 64– 69.

Shen, J., Ou, C., Zhou, Z., Chen, J., Fang, K., Sun, X., Li, J., Zhou, L. & Wang, L. (2013). Pretreatment of 2,4-dinitroanisole (DNAN) producing wastewater using a combined zero-valent iron (ZVI) reduction and Fenton oxidation process, *Journal of Hazardous Materials*, 260, pp. 993–1000.

Shimizu, A., Tokumura, M., Nakajima, K. & Kawase, Y. (2012). Phenol removal using zero-valent iron powder in the presence of dissolved oxygen: Roles of decomposition by the Fenton reaction and adsorption/precipitation, *Journal of Hazardous Materials*, 201–202, pp. 60–67.

Suzuki, T., Moribe, M., Oyama, Y. & Niinae, M. (2012). Mechanism of nitrate reduction by zero-valent iron: Equilibrium and kinetics studies, *Chemical Engineering Journal*, 183, pp. 271–277.

Taha, M.R. & Ibrahim, A.H. (2014). Characterization of nano zero-valent iron (nZVI) and its application in sono-Fenton process to remove COD in palm oil mill effluent, *Journal of Environmental Chemical Engineering*, 2, pp. 1–8.

Weng, C.-H., Lin, Y.-T., Chang, C.-K. & Liu, N. (2013). Decolourization of direct blue 15 by Fenton/ultrasonic process using a zero-valent iron aggregate catalyst, *Ultrasonics Sonochemistry*, 20, pp. 970–977.

Xi, Y., Sun, Z., Hreid, T., Ayoko, G.A. & Frost, R.L. (2014). Bisphenol A degradation enhanced by air bubbles via advanced oxidation using in situ generated ferrous ions from nano zero-valent iron/palygorskite composite materials, *Chemical Engineering Journal*, 247, pp. 66–74.

Yang, S.-T., Zhang, W., Xie, J., Liao, R., Zhang, X., Yu, B., Wu, R., Liu, X., Li, H. & Guo, Z. (2015). Fe3O4@SiO₂ nanoparticles as a high-performance Fenton-like catalyst in a neutral environment, *RSC Advances*, 5, pp. 5458–5463.

Yang, S.T., Yang, L.J., Liu, X.Y., Xie, J.R., Zhang, X.L., Yu, B.W., Wu, R.H., Li, H.L., Chen, L.Y. & Liu, J.H. (2015). TiO₂-doped Fe3O4 nanoparticles as high-performance Fenton-like catalyst for dye decoloration, *Science China Technological Sciences*, 58, pp. 858–863.

Zhang, H., Choi, H.J. & Huang, C.-P. (2005) Optimization of Fenton process for the treatment of landfill leachate, *Journal of Hazardous Materials B*, 125, pp. 166–174.

Zhang, X., He, M., Liu, J.-H., Liao, R., Zhao, L., Xie, J., Wang, R., Yang, S.-T., Wang, H. & Liu, Y. (2014). Fe₃O₄@C nanoparticles as high-performance Fenton-like catalyst for dye decoloration, *Chinese Science Bulletin*, 59, pp. 3406–3412.

# Oczyszczanie ścieków z zakładów naprawczych floty samochodowej z wykorzystaniem procesów powietrze/ZVI i powietrze/ZVI/H₂O₂

**Streszczenie:** Ścieki z zakładu naprawczego floty samochodowej poddano oczyszczaniu z wykorzystaniem żelaza metalicznego i nadtlenku wodoru (Air/ZVI/H₂O₂). Badano wpływ dawki żelaza i nadtlenku wodoru, czasu i pH na efektywność procesu. Największy stopień usunięcia ChZT, 76%, uzyskano dla dawek ZVI/H₂O₂ 4000/1900 mg/L, czasu 120 min i pH 3.0. ChZT zmniejszono z 933 do 227 mg/L. Dodatkowo uzyskano całkowite usunięcie barwy i zapachu. Skuteczność usunięcia ChZT rosła wraz ze wzrostem zastosowanej dawki ZVI. Zmiana pH na inne niż 3, powoduje gwałtowne zmniejszenie efektywności procesu.

Kinetyka procesu może zostać opisana z wykorzystaniem równania d[COD]/dt = -a [COD]tᵐ, gdzie 't' oznacza czas a 'a' i 'm' są stałymi zależnymi od początkowego stężenia reagentów.

Badano także wpływ H₂O₂ na efektywność procesu. Skuteczność usunięcia ChZT wynosi 40% (560 mg/L) w przypadku zastosowania ZVI bez dodatku H₂O₂. Określono także skuteczność koagulacji z wykorzystaniem FeCl₃. Najlepsze rezultaty uzyskano dla dawki Fe³⁺ 700 mg/L, zmniejszając ChZT do 509 mg/L.