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Hydraulic fracturing flow-back fluid treatment by ZVI/H_2O_2 process

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ABSTRACT

Hydraulic fracturing flow-back fluid (HFFBF) was treated by a zero-valent iron (ZVI)/H_2O_2 process. The initial HFFBF chemical oxygen demand (COD) was 3,440 mg/L and the 5-d biochemical oxygen demand (BOD_5)/COD ratio was 0.259. Under the optimal 500/6,884 mg/L of ZVI/H_2O_2 reagent doses, and a 120-min process time, COD was decreased to 680 mg/L (80.2% removal). Additionally, as a result of pollutants' chemical oxidation, the wastewater's susceptibility for biodegradation was essentially increased to BOD_5/COD 0.971. To assess the maximum share of coagulation in the total ZVI/H_2O_2 process treatment effect, a coagulation process was additionally employed. The coagulation for an optimal 1.5mL/L of iron-based PIX 111 coagulant dose obtained 1,200 mg/L of COD, 65.1% removal. The use of coagulation only allowed an increase in BOD_5/COD to 0.625. As a result of the oxidation step during ZVI/H_2O_2 process, the persistent compounds were transformed to more vulnerable ones.

Keywords: Hydraulic fracturing flow-back fluid; Wastewater treatment; ZVI; ZVI/H_2O_2 process; Zero-valent iron

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1. Introduction

1.1. Shale gas

Shale gas is new, unconventional natural gas source. Large deposits of this resource are located in the USA, China, and Poland [1]. Poland is one of the pioneers in the development of shale gas extraction technology [2]. In Poland, the estimated available gas resources are from 346 to 865 bln m^3 [3]. Industrial shale gas production process began about 30 years ago [4,5]. In order to increase shale gas extraction, it is necessary to increase the permeability of the shale. This is achieved by using a hydraulic fracturing technology. The main components (98.0%–99.5%) of fracturing fluid are water and proppant. The amount of water used in this process could be even 20,000 m^3/well [6]. The proppant is used to prevent the closure of fractures [7]. In addition, some chemical additives (0.5%–2.0%) are added to the fracturing fluid. Many of the additives are characterized by a considerable toxicity [8–12]. The compositions of the fracturing fluids differ depending on the manufacturer, the country of use, and the borehole depth. The proper selection of the proppant and fracturing fluid composition may be crucial for the economic viability of the fracturing process [13]. Hydraulic fracturing is a controversial process. The most important issues are risk of soil and water pollution, and huge water consumption [14,15]. Shale gas exploitation transforms the natural environment into a heavy industrial zone, with significant antropopresion [16–18]. For both technological and ecological reasons, shale gas extraction in Poland has not been developed. On the other hand, because shale gas is a rich potential source of energy, research on alternative methods for hydraulic fracturing has been developed [19–21].

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1.2. Flow-back fluid treatment

The fracturing fluid is pumped from the well in the fracturing process. Hydraulic fracturing flow-back fluid (HFFBF) has a slightly different chemical composition and lower volume compared with the fracturing fluid [14]. The chemical composition change is due to the partial consumption of additives in fracturing process, leaving the proppant in shale and draining salty underground water from the well. The salinity can possibly be over 100 g/L. HFFBF can also contain significant amounts of petrochemical hydrocarbons.

HFFBF may be treated with membrane processes [22–28], adsorption [29], coagulation [26,29,30], electrocoagulation [31,32], electrodialysis [30,33], oxidation, and advanced oxidation processes [34–37], and photocatalysis [38]. An alternative for physicochemical treatment could be biological treatment such as rhizoremediation or algal bioreactors [14], biologically active filtration [39], or microbial capacitive desalination cell [40]. HFFBF, oil and gas production water treatment options are also summarized in some review articles [41–44].

Most of the cited articles and review ones deal with oily wastewater or synthetic wastewater, not with HFFBF ones. The authors believe that this article fill that lack of knowledge. HFFBF treatment is difficult because of high salinity and organic compounds content. There are some technologies dealing with salinity removal, for example, variety of membrane processes, but they are hard to apply because of high membrane costs and energy consumption destruction of membranes by salts from HFFBF. In Polish conditions, wells were situated next to the Baltic Sea Coast and according to legal regulation HFFBF after treatment could be discharged into the sea. Because of that, even high salinity is not considered as significant problem. Main problem, that we were focused on, was to remove organic pollutants. Because of the low efficiency of biological treatment for highly saline wastewater and the unacceptably high cost of membrane treatment, there is a need for alternative treatment options.

1.3. ZVI process

Zero-valent iron (ZVI) has appeared to be an effective heterogeneous catalyst for wastewater treatment. ZVI and other iron-based solid catalysts were used inter alia for the treatment of the dyes [45–52], nitrobenzene [53], 2,4-dinitroanisole [54], pharmaceutical [55,56], trinitrotoluene (TNT) wastewater [57], phenols and chlorophenols [58,59], pesticides [60], bisphenol A (BPA) [61], landfill leachates [62] or coking wastewater [63], palm oil mill effluent [64], nitrites reduction [65,66], oil sands reclamation [67], or surfactants removal [68].

Iron and its salts, as low-cost materials, are widely used in wastewater treatment. Adding ZVI into the aqueous phase starts two catalytic mechanisms. The first one is heterogenic catalysis, related with the presence of dispersed ZVI phase. On the solids' surface, numerous processes take place, including oxidation and reduction of pollutants and catalysts, precipitation and co-precipitation of metal oxides and hydroxides, adsorption, and coagulation [69]. As a result, Fe^{2+} and Fe^{3+} ions are transferred in the aqueous phase according to reactions (1)–(4):

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \quad (1)$$

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

$$Fe^0 \rightarrow Fe^{2+} + 2e \quad (3)$$

$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \quad (4)$$

As shown in Reaction (4), H_2O_2 could be produced by this process. Adding H_2O_2 could possibly increase treatment efficiency (Reaction (5)).

$$Fe^0 + H_2O_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O \quad (5)$$

The second treatment mechanism is homogenous catalysis, related with the presence of dissolved Fe^{2+} and Fe^{3+} ions in the aqueous solution, which starts Fenton/pseudo-Fenton process [70] according to reactions (6) and (7):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^\bullet OH \quad (6)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^\bullet O_2H + H^+ \quad (7)$$

1.4. Aim

The aim of this study is to assess the efficiency of the ZVI/H_2O_2 process used in HFFBF treatment. Based on a review of available literature [44], Fenton process and any of its modification were not used for organic compounds removal from HFFBF. This is also the first paper concerning organic pollutants removal from HFFBF with ZVI.

2. Materials and methods

The HFFBF was collected in July 2016 from a wellbore located in Poland. After collection, flow-back fluid sample was acidified to pH 3.0 and refrigerated at 4°C until analysis.

The following parameters were determined according to the EN or ISO standards: chemical oxygen demand (COD), COD after 30 min sedimentation (COD_{sed}) and COD dissolved (COD_{dis}, for sample filtered through 0.45 μm filters) (DIN 38409-41:1980-12), (5-d biochemical oxygen demand (BOD_5) and BOD_5 dissolved (BOD_{5dis}, for sample filtered through 0.45 μm filters) (PN-EN 1899-1), total suspended solids (TSS) (EN 872), organic and inorganic suspended solids (OSS and IOSS), pH (EN ISO 10523), turbidity (EN ISO 7027), and conductivity (EN 27888). The amount of dissolved iron was determined with 1,10-phenanthroline method after H_2O_2 removal, under alkaline condition. All reagents used were of analytical grade (pure per analysis).

Wastewater after 30 min of sedimentation for easy suspended solids removal was treated with the ZVI/H_2O_2 process. The experiments were carried out in a 1.5-L cylindrical reactor filled with 1 L of sample. Ferox Target (325 mesh), the ZVI used in the experiments, was supplied by Hepure (Hillsborough, NJ, USA). Three doses of ZVI (500, 1,000, and 1,500 mg/L) and 30% H_2O_2 (POCH, Gliwice, Poland) solution was used. The H_2O_2/COD mass ratio was equal to 1, 2, 4, and 8.

The settings of the experimental system, regarding operation and design, strictly followed their standard guidelines and related publications [71,72]. Doses were selected based on our previous research related with ZVI/H_2O_2 process [73–75]. In order to estimate whether the doses of reagents used are correct, few random preliminary tests were used, in a wider range of doses, to narrow down the area of the experiment. Preliminary test results are not shown in the article.

All samples were stirred by a magnetic stirrer (Heidolph MR3000, Schwabach, Germany). The pH was adjusted to 3.0. After intervals of 5, 15, 30, 60, and 120 min, the process was stopped by increasing the pH to 9.0 with 3 M of NaOH. The sample was left overnight for the sedimentation of iron to precipitate and H_2O_2 decomposition. After that, COD was determined.

Studies on coagulation were performed in a 1.5-L reactor with a magnetic stirrer (Heidolph MR3000). The reactor was filled with 1 L of the sample. The wastewater was coagulated with Fe-based PIX coagulants: 110, 111, 112, 113, and 122 (Kemipol, Police, Poland). Optimal pH was set at 9.0, according to preliminary studies. The coagulant doses were in the range of 0.5–2.5 mL/L. The samples were subjected to 5 min of fast stirring, followed by10 min of slow stirring. The sample was left overnight for sedimentation of iron precipitate. After that, the COD value was determined.

3. Results

3.1. Raw flow-back fluid

The raw HFFBF parameters are presented in Table 1. Crucial for HFFBF treatment there was very high salinity, expressed as conductivity 96.1 mS/cm and a chlorides concentration 60,100 mg/L. Because of that, it was impossible to use the ISO 6060 standard COD determination method. The DIN 38409-41:1980-12 method, dedicated to solutions with high salinity, was used to assess the COD value of 3,440 mg/L. BOD_5, determined with manometric method, was also found under the influence of high salinity. Due to that condition, microorganism activity could not be considered optimal and BOD_5 would be underestimated.

As the microorganisms are responsible for organic compounds biodegradation, most of them, used in WWTP and biodegradability tests could not survive in such a saline wastewater. We assume that organic compounds present in HFFBF after treatment could be decomposed biologically in higher rate, if the salinity of matrix would be lower.

Table 1
Raw HFFBF parameters

Parameter	Value
COD (mg/L)	3,440
COD_{dis} (mg/L)	2,880
BOD_5 (mg/L)	890
BOD_{5dis} (mg/L)	735
BOD/COD	0.259
BOD_{dis}/COD_{dis}	0.255
TSS (mg/L)	285.6
OSS (mg/L)	66
IOSS (mg/L)	219.6
pH	6.23
Conductivity (mS/cm)	96.1
Cl^- (mg/L)	60,100

The salinity of all treated samples should be very high and constant (Table 1). During treatment, no process or mechanism allowing effective salt removal was employed. Amounts of acid/base added for pH adjustment were same for all samples, as we operate constantly with the same pH values—one for the process, one for process termination. What is more if "natural" salinity of the sample would be compared with salinity added as a result of pH adjustment, the influence should be very small. The eventual underestimation should be similar in all BOD_5-determined samples, making it possible to compare the sample results.

The BOD_5/COD and BOD_{5dis}/COD_{dis} ratios are similar, 0.259 vs. 0.255, in relationship to the fact that most of suspended solids, 219.6 out of 285.6mg/L, are inorganic. HFFBF parameters are similar to others reported in the literature [23,26,28,29,34,43,44].

3.2. ZVI/H_2O_2 process

The results of the HFFBF treatment with the ZVI/H_2O_2 process are shown in Figs. 1–3. The application of ZVI or H_2O_2 alone did not result in a significant change in the COD value. The COD removal was always below 5%. During the

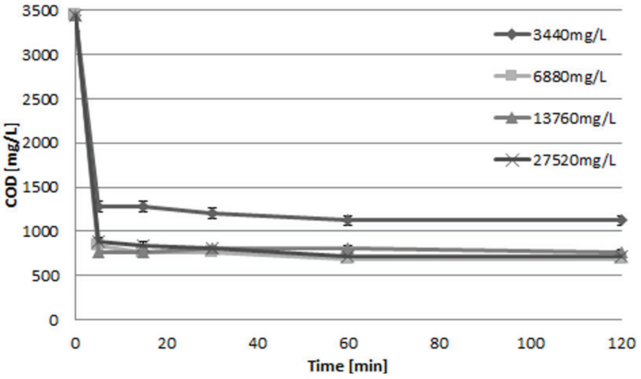

Fig. 1. COD removal during ZVI/H_2O_2 process for 500 mg of ZVI dose and at different H_2O_2 dosages.

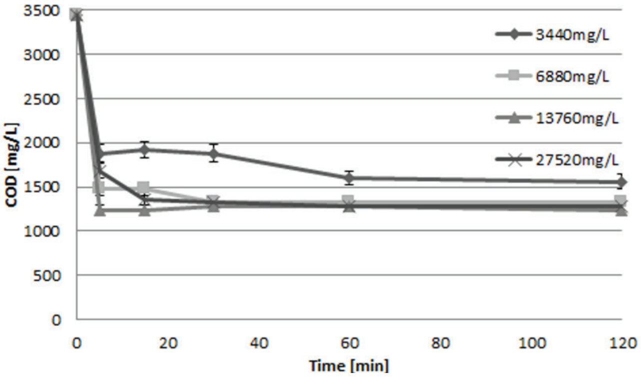

Fig. 2. COD removal during ZVI/H_2O_2 process for 1,000 mg of ZVI dose and at different H_2O_2 dosages.

ZVI/H_2O_2 process, regardless of the ZVI and H_2O_2 dose used, the initial rapid COD value decreased for a short 5–15-min process time. The largest decrease was observed in the smallest ZVI dose. For longer process times, further decreases after 120 min was observed, but it was small in comparison with initial value. The best treatment results were achieved using 500/6,880 mg/L of ZVI/H_2O_2 doses. COD/H_2O_2 1:2 mass ratio provides the best effectiveness of ZVI dissolution (Reaction (5)) and radical production (Reaction (6)). For larger H_2O_2 doses, reagent excess did not provide an increase in process efficiency and may even have decreased the efficiency because of the possible scavenging of radicals. Additionally, final coagulation was hindered in high H_2O_2 doses because of H_2O_2 decomposition. The newly created oxygen bubbles broke the flocs and precluded sedimentation. As a result, the COD removal time deteriorated. The importance of this process is the disruption mechanism decreasing over time, because of continuous H_2O_2 consumption during process.

The ZVI/H_2O_2 process should be complete after the shortest 5-min time or even replaced with coagulation (see Section 3.3.), if the only aim of the process is to remove COD. COD after 5 and 120 min for optimal dose 500/6,880 mg/L is 840 and 680 mg/L, respectively. But, if the aim of the process is to prepare HFFBF for biological treatment, the BOD_5 should be as high as possible. Because of that, a longer process is needed.

The BOD_5 levels after the 120-min ZVI/H_2O_2 process is shown in Table 2. The most important benefit of the ZVI/H_2O_2 process, except COD removal, is the chemical transformation of pollutants leading to increasing biodegradability. This is expressed as a BOD_5/COD ratio. Regardless of reagent doses, all treated samples can be considered as susceptible for biodegradation. The best results achieved for optimal COD removal was the 500/6,880 mg/L of ZVI/H_2O_2 doses. The BOD_5/COD was increased to 0.971. For all ZVI doses, the worst results were obtained in the highest ZVI doses and lowest ZVI/H_2O_2 ratio.

The amount of dissolved iron after the oxidation step was linearly increased with time, up to 400 mg/L, for the highest ZVI dose of 1,500 mg/L. Although the optimal ZVI/H_2O_2 reagent doses were found in one of the smallest doses used, 500/6,880 mg/L, additional ZVI dose decreasing is not recommended. Lower amounts of ZVI probably would not provide the required amount of Fe^{2+} ions (reactions (1)–(5)) for a Fenton reaction (Reaction (6)). The results obtained for HFFBF are consistent with other studies on the ZVI/H_2O_2 process for automotive fleet repair facility [74] and cosmetic wastewater [75].

3.3. Coagulation

Coagulation was conducted to estimate the maximum share of the secondary coagulation that occurs in the ZVI/H_2O_2 process, at the alkalization step. The characteristics of coagulants used are shown in Table 3. The results of HFFBF treatment by coagulations with different Fe-based coagulants are shown in Table 4. The effectiveness of chlorides containing coagulants was better than that of chlorides containing sulfates. This is in agreement with the Hardy-Schulze rule. Optimal doses for chlorides containing coagulants were higher than chlorides containing sulfates, but regardless of dose, chlorides containing coagulants always provide better results. On the other hand, low pH in the coagulants resulted

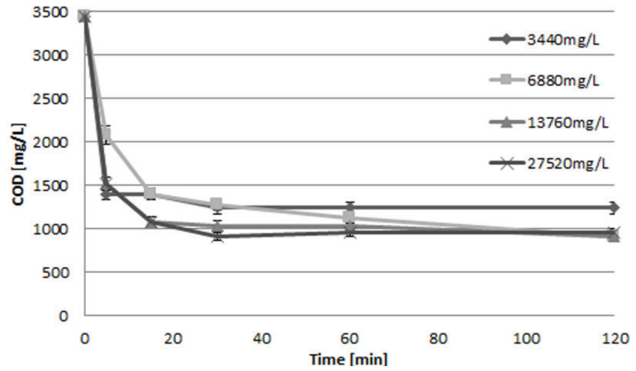

Fig. 3. COD removal during ZVI/H_2O_2 process for 1,500 mg of ZVI dose and at different H_2O_2 dosages.

Table 2
BOD_5 after ZVI/H_2O_2 process

ZVI/H_2O_2 doses (mg/L)	BOD_5	BOD_5/COD
500/3,440	850	0.697
500/6,880	660	0.971
500/13,760	670	0.882
1,000/3,440	650	0.417
1,000/6,880	700	0.530
1,000/13,760	705	0.569
1,500/3,440	550	0.444
1,500/6,880	635	0.690
1,500/13,760	660	0.717

Table 3
Coagulants characteristics

Coagulant PIX no.	111	112	113	110	122
Active substance	$FeCl_3$	$Fe_2(SO_4)_3$	$Fe_2(SO_4)_3$	$FeClSO_4$	$Fe_2(SO_4)_3$
Total Fe (%)	13.4 ± 0.6	12.0 ± 0.4	11.8 ± 0.4	12.5 ± 0.5	12.6 ± 0.3
Fe^{2+} max. (%)	0.3	0.06	0.4 ± 0.3	0.5	0.06
Free acid max (%)	3.0	4	5	3–4	3–4
Cl^- (%)	27.0 ± 1.0	–	–	16.0	–
Density kg/m^3 (20°C)	1,380–1,500	1,500–1,560	1,500–1,570	1,390–1,540	1,550–1,570
pH	<1	<1	<1	<1	<1

in a significant amount of alkali used for final pH adjustment which was negligible in context of initial wastewater salinity.

COD removal during coagulation was significantly less effective than during ZVI/H_2O_2 process, regardless of the coagulant used. Because of that, it can be concluded that, in comparison with the ZVI/H_2O_2 process, coagulation is not recommended. The share of coagulation in the total effect of ZVI/H_2O_2 process is not significant, especially in context of the low amount of dissolved iron (up to 400 mg/L for ZVI/H_2O_2 process). Additionally, due to the fact that in coagulation pollutants are just transferred from the water phase into a sludge phase, the BOD_5/COD ratio, 0.625, after coagulation was lower than that after the ZVI/H_2O_2 process.

3.4. UV-Vis spectra

Absorbance of light for raw filtered wastewater and after the 120 min of ZVI/H_2O_2 process is shown in Fig. 4. The highest, 10 times higher than the others, absorbance was observed for wavelengths shorter than 250 nm, in both raw and treated wastewater. High absorption of this region confirms the concentration of high organics. Absorbance removal increases with an increasing H_2O_2 dose and decreases with an increasing ZVI dose, especially for a wavelength lower than 250 nm. The reagent dose providing the best absorbance removal was 500/27,520 mg/L of ZVI/H_2O_2. The highest differences in absorbance removal between reagent doses were observed for wavelengths in the range of 215–240 nm. For other wavelengths, the differences were not significant.

The absorbance was in the range of 0.078–3.693 and 0.018–3.582 for raw and treated wastewater, respectively. For optimal COD removal in 500/6,880 mg/L of ZVI/H_2O_2 doses, the percentage absorbance removal was increased with the wavelength from 2.35% for 200 nm to 76.92% for 350 nm. On the other hand, the maximum value of absorbance decreased in the range of 0.832–0.941, which was observed for the range of 230–235 nm (25.5%–35.4% relative removal). Similar trends and values were observed for all other reagent doses.

Table 4
Coagulation effectiveness

Coagulant PIX	111	113	110	112	122
Optimal dose (mL/L)	1.5	1.0	2.0	1.0	1.0
COD (mg/L)	1,200	1,720	1,459	1,637	2,064
COD removal (%)	65.1	50.0	57.6	52.4	40.0

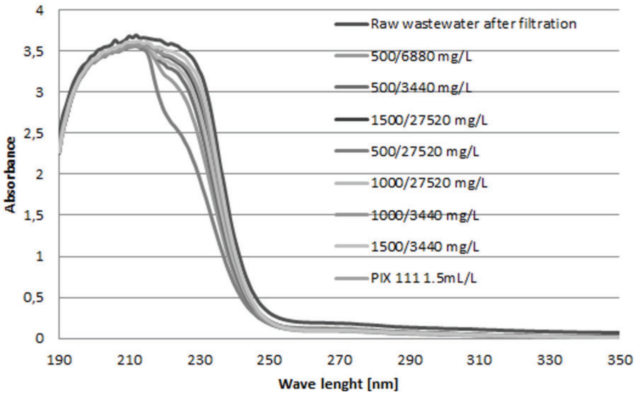

Fig. 4. Absorbance of light for raw filtered wastewater and treated with coagulation ZVI/H_2O_2 in 2-h process time.

The lower absorption decreased in the 500/6,880 mg/L of ZVI/H_2O_2 doses, in comparison with 500/27,520 mg/L dose, could be related to the fact that transformation products created during radical oxidation could still possibly absorb UV radiation [76].

Coagulation efficiency in absorbance removal was far worse than that for the ZVI/H_2O_2 process.

3.5. Kinetics

Usually ZVI processes kinetics is described as first-order one. This simple approach is not effective in the case of HFFBF. The rate of the ZVI/H_2O_2 process is difficult to describe. Several independent processes influence the overall treatment effect: ZVI dissolution, chemical oxidation, co-precipitation, or coagulation. Because of that, the following equations were used to describe the investigated processes:

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

$$d\left[\mathrm{COD}\right]/\,dt=-k_1\left[\mathrm{COD}\right] \tag{8}$$

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

$$d\left[\mathrm{COD}\right]/\,dt=-k_2\left[\mathrm{COD}\right]^2 \tag{9}$$

- 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. (10)) [70]:

$$d\left[\mathrm{COD}\right]/\,dt\;=\;-a\left[\mathrm{COD}\right]t^m \tag{10}$$

where t corresponds with time, and a and m are constants that depend on the initial reagent concentrations.

Calculations made using the pseudo-first-order and pseudo-second-order reaction equations resulted in low-correlation coefficients. Much better, but still in many cases not good enough, correlation coefficients were obtained for Balcerzak's model (Eq. (10)). The result of the kinetic calculations is shown in Table 5.

3.6. Possibility of practical application and costs consideration

ZVI/H_2O_2 process is not a typical process used for wastewater treatment; there are just a few process applications, in much smaller scale, that it is required for HFFBF treatment. Because of that it is hard to predict costs. Second challenge that has to be faced is changing scale from laboratory to industrial one. In general, to perform the process space (reactor), reagent and time are required. As fracturing is periodical process, time should not be a problem. As a reactor, tanks used for preparation of fracturing fluid could be used.

Table 5
Kinetics of ZVI/H_2O_2 process

ZVI (mg/L)	500	500	500	500	1,000	1,000	1,000	1,000	1,500	1,500	1,500	1,500
H_2O_2 (mg/L)	3,440	6,880	13,760	27,520	3,440	6,880	13,760	27,520	3,440	6,880	13,760	27,520
a	0.042273	0.059244	−0.00605	0.060051	0.207083	0.037196	−0.00409	0.063329	0.039654	0.101798	0.096336	0.099749
m	−0.953	−0.955	−1.004	−0.952	−0.901	−0.952	−1.004	−0.904	−0.952	−0.714	−0.866	−0.864
n	0.047	0.045	−0.004	0.048	0.099	0.048	−0.004	0.096	0.048	0.286	0.134	0.136
k	0.899425	1.316531	1.512857	1.251071	2.091748	0.774916	1.022244	0.65968	0.826133	0.355938	0.718924	0.733447
R^2	0.859	0.92	0.1	0.932	0.694	0.741	0.1	0.769	0.741	0.921	0.806	0.713

The amount of HFFBF is much lower than hydraulic fracturing one. Some costs will be generated by the reagents, but the ones used for pH adjustment are cheap and used for hydraulic fluid preparation. In case of ZVI, metallurgical wastes or steel shot could be used to decrease costs. What is more, as a replacement for ZVI, iron-based minerals could be used (e.g., magnetite or hematite). There are some literature reports about proppant modifications with iron or magnetic materials [2,77,78]. Residual proppant present in HFFBF could be used as a source of iron [79]. If metallic iron would be used, residual solid catalyst could be reused. The material can be separated from treated HFFBF in two ways: electromagnetically or through sedimentation.

4. Conclusion

The ZVI/H_2O_2 process was successfully applied for HFFBF treatment. Initial HFFBF COD was 3,440 mg/L and the BOD_5/COD ratio, described as susceptibility for biodegradation, was 0.259. Under optimal conditions, described as 500/6,884 mg/L of ZVI/H_2O_2 reagent doses and 120-min process time, COD was decreased to 680 mg/L (80.2% removal). The maximum share of coagulation in the total ZVI/H_2O_2 process treatment effect was also assessed. Coagulation for optimal 1.5 mL/L of PIX 111 coagulant dose allows the decrease of COD from initial 3,440 to 1,200 mg/L (65.1% removal). The most important achievement of this work, as a result of pollutants' chemical oxidation in ZVI/H_2O_2 process, was that the ratio of BOD_5/COD in wastewater was essentially increased to 0.971. The use of coagulation allows for increase of BOD_5/COD ratio to only 0.625. As a result of the oxidation step during the ZVI/H_2O_2 process, persistent compounds are transformed to more vulnerable ones.

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