

Contents lists available at ScienceDirect

Chemical Engineering Journal



journal homepage: www.elsevier.com/locate/cej

Heterogeneous nZVI-induced Fenton oxidation process to enhance biodegradability of excavation by-products



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ARTICLE INFO

Keywords: Excavation by-products Heterogeneous-Fenton Surfactants EPB Biodegradation Commercial-additive

ABSTRACT

The treatment of excavation by-products has been studied using Fenton and Heterogeneous Fenton processes, by the addition of zero-valent iron nanoparticles (nZVI) as catalyzer. This study demonstrated that both methods could significantly reduce the organic content of the liquid extract from excavated soils. Operating parameters, such as pH and catalyzer/oxidant (w/w) ratio, were varied to investigate their influence on the Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD) removal efficiency. In addition, Biochemical Oxygen Demand (BOD) was evaluated before and after the treatment. The optimal conditions found for conventional Fenton process were: $H_2O_2/COD = 1 (w/w)$, $Fe(II)/H_2O_2 = 0.1 (w/w)$ and pH = 2.5, whereas for Heterogeneous Fenton were: $H_2O_2/COD = 0.75 (w/w)$, $nZVI/H_2O_2 = 1.5 (w/w)$ and pH = 3. Heterogeneous Fenton resulted more efficient with respect to conventional Fenton, leading to a TOC and COD removal efficiency equal to 75.95 and 85.52%, respectively. The BOD₂₈/COD ratio after Heterogeneous Fenton increased by about 200%, indicating the suitability of this oxidation process to achieve a biodegradability increase.

1. Introduction

The European Chemical Agency (ECHA) defines anionic surfactants (ANS) as Unknown or Variable composition, Complex reaction products or Biological materials (UVCB). ANS are constituted by different lengths and different degrees of unsaturation in the hydrocarbon chains as well as different polar groups, a fact that gives rise to a great variety of surfactant compounds characterized by specific characteristics which can be tailored with respect to the application field [1]. The ANS category includes several compounds and the most common are alkylbenzene sulfonate (ABS) which can be linear (LABS) or branched (BABS), alkyl sulfate (AS) and alkylether sulfate (AES) [2]. In particular the latter one represents one of the most used in the excavation industry as main compound in several soil conditioning agents, employed in the Earth Pressure Balance (EPB) tunneling technology and a study on its toxicity and possible environmental fate has been recently published elsewhere [3].

The lack of information about the environmental impact of the chemicals introduced during the tunneling process, could lead to the production of several tons of hazardous waste, whose landfill disposal might be significantly onerous in terms of cost and time [4]. It is suffice to consider that 1 million cubic meters of debris are created as a result of the excavation of a hypothetical 6 km long and 100 m² cross section

tunnel [5]. This implies the characterization and possible way-of-reuse or treatment evaluation of the excavation product, which is a polyphase system (slurry) whose physicochemical characteristics and environmental impact strongly depend on the additive composition, on soil properties and environmental conditions.

The biodegradability showed by soil conditioning agents usually adopted depends on the chemical structure of the base compounds, on the micro-organisms population present in the soil and on the medium characteristics (temperature, dissolved oxygen, ...) [6]. The main aim of the soil conditioning practice is the physicochemical characteristic modifications of the soil, immediately before and during its excavation by the TBM-EPB. The anionic surfactants in the commercial additive formulations are necessary to reach specific characteristics allowing the tunneling process by means of EPB machines [7], whereas the other compound purposes are various: enhancing foam stability [8], modifying foam viscosity [9], preservatives (which could decrease the product biodegradability) [10], reducing the critical micelle concentration [9,10]. This process produces a slurry that could release recalcitrant compounds in the nearby environment through leaching process. This product could raise remarkable concern about its physicochemical and possible toxic characteristics, because of the major presence of amphiphatic and soluble compounds, which constitute the whole soil additive composition [11]. In this context the development

http://dx.doi.org/10.1016/j.cej.2017.10.152

Received 6 September 2017; Received in revised form 20 October 2017; Accepted 26 October 2017 Available online 28 October 2017 1385-8947/ © 2017 Elsevier B.V. All rights reserved.

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of a possible characterization/treatment protocol for the excavation product management seems to be mandatory.

The present study focused its attention on the characterization and treatment of conditioned soil liquid.

The typical surfactant-polluted wastewater treatments are both biological (activated sludge) and physicochemical, depending on its characteristics (presence of other contaminants, initial pH, T, ...) and on surfactant persistency [12]. Over the past few decades, various studies have been conducted on the advanced oxidation processes (AOPs), demonstrating highly effective in the oxidation of organic pollutants, such as ANS [13,14]. AOPs are generally based on the generation of HO['] radicals in the medium, which are highly reactive species, capable of attacking the majority of persistence organic compounds [15]. Recently Heterogeneous Fenton system have been developed and have demonstrated high removal efficiency towards single anionic surfactants, such as sodium dodecyl benzene sulfonate (SDBS) [16] and LABS [17]. Zero-valent iron nanoparticles (nZVI) have already been used in fenton-like system [18,19] and have demonstrated to be a versatile material, capable to reduce/adsorb anionic inorganic compounds [20], heavy metals [21] and organics [22], because of its large specific surface area, high chemical reactivity and capacity to generate active oxygen species in aqueous media [23].

In this study, a comparison between Conventional Fenton (CF) and Heterogeneous Fenton (HF) efficiency on the additive compounds treatment is reported, focusing on their biodegradability characteristics. In particular, the HF was proposed as pre-treatment for a subsequent biological process. The influence of fundamental operative parameters, such as pH and T, was evaluated. To the best of our knowledge, there are no consolidated experiences regarding treatments of the spoils from tunneling excavation employing real commercial additive and this is the first study that evaluates the feasibility of HF process for these peculiar samples employing nZVI.

2. Experimental

2.1. Materials

All reagents used were of analytical grade and purchased from Sigma-Aldrich (Milan) and all solutions were prepared with deionized water.

The soil sample used was a fine sand sieved at 2 mm. The soil was dried at 105 °C in oven for 24 h and conditioned by a commercial additive (CA) dispersed in aqueous solution through a laboratory foam generation system, reproducing the foam injection plant installed on a TBM. The CA is a commercial additive characterized by the presence of various isomers of linear and ethoxylated anionic surfactants (C12-C18) and other linear carbonaceous compounds such as hydroxylated molecules, as reported in the CA data sheet. Subsequently the foam and the soil were mixed with water adopting selected foam and deionized water dosages in order to reproduce the same slurry that could be obtained in a real tunnel excavation process. The slurry was then divided in various

aliquots that were centr	ifuged (10000 rpm,	10 min) and th	e supernatant
(S) was used in the exp	eriments.		

The same procedure was followed to obtain the blank sample (L) of the unconditioned soil that was mixed with deionized water.

2.2. Methods

Liquid samples were characterized, measuring Total Organic Carbon (TOC, mgL^{-1}) by a TOC analyzer (Shimadzu), Chemical Oxygen Demand (COD, mgL^{-1}) according to Italian Standards [24] by the spectrophotometric method using K₂Cr₂O₇ as oxidant, Biochemical Oxygen Demand (BOD, mgL^{-1}) by the manometric method (OxiTop) following the OECD guidelines (method 301F [25]) employing a bacteria inoculum from a selected wastewater plant characterized by a pH equal to 8.52 and a Specific Oxygen Uptake Rate (SOUR) equal to $1.94 \text{ mg L}^{-1} \text{ h}^{-1} \text{ gVSS}^{-1}$, used as received and without any preliminary acclimation. The inoculum was taken from a selected plant treated wastewaters characterized by remarkable surfactants concentration $(100-300 \text{ mg L}^{-1})$, COD = 800-1400 mg L⁻¹ and BOD₂₈ = 250-650 mg L⁻¹. Moreover, preliminary BOD₅ tests were performed on both S and CA (0.1%) samples, in order to evaluate the lag-phase and the possible necessity of a acclimation step, before accomplished BOD₂₈ tests.

The pH was measured with a Crison 421 pH-meter, whereas Fe and Ca (mg L⁻¹) concentrations were determined using Atomic Absorption Spectroscopy with a Flame detector (FAAS, Agilent) and the anion species concentrations (mg L⁻¹) by means of a ion chromatography (Dionex ICS – 1100). Residual hydrogen peroxide concentration was determined by the colorimetric method, using titanium sulfate, in virtue of its simplicity and accurate measurement. Titanium sulfate reacted with the H₂O₂ present in the solution, forming a yellow complex with a maximum absorbance around 410 nm [26].

In addition, three aqueous CA solutions were prepared at different initial concentrations (in the range 0.1-0.3% w/w), and characterized measuring initial COD, TOC, pH, BOD.

Table 1 shows the CA, S and L characteristics.

The soil was characterized by a low organic carbon content, equal to 0.12 g kg^{-1} because of the very low clay presence (< 2%) [27] and a pH equal to 8.3. L and S samples are characterized by similar pH, Fe and Ca content, thus inducing to exclude their presence in the CA. The different TOC and COD values are due to the presence of the organic compounds present in the CA solution, added in the soil during the conditioning procedure.

The BOD tests were carried out until reaching an asymptotic value. Three control tests were performed in the same conditions (T = 25 °C, same mineral medium) in order to estimate the BOD of the culture suspension. The soil TOC and pH (in H₂O suspension at water/soil ratio equal to 2.5/1 (w/w)) were also measured.nZVI used for the HF treatment were prepared according to the procedure described elsewhere [28], without the addition of any dispersing agent, to prevent carbon content increase. The produced nanoparticles were

Fable 1			
Solutions a	nd commercial	additive (CA)	characteristics

Parameter	L	S	CA	CA		
			0.1%	0.25%	0.3%	
$COD (mg L^{-1})$	21.5 ± 1.46	497.8 ± 9.44	543.7 ± 9.12	1281.0 ± 8.22	1609.0 ± 7.14	
TOC (mgL^{-1})	11.8 ± 0.29	209.3 ± 0.1	197.2 ± 1.12	492.8 ± 1.14	589.4 ± 3.09	
NO_{3}^{-} (mg L ⁻¹)	35.4 ± 0.12	35.4 ± 0.27	-	-	-	
PO_4^{3-} (mg L ⁻¹)	$0.5 \pm 0 \ 0.01$	0.5 ± 0.01	-	-	-	
Ca $(mg L^{-1})$	48.0 ± 0.95	47.4 ± 0.91	-	-	-	
Cl^{-} (mg L^{-1})	11.0 ± 0.24	11.1 ± 0.09	-	-	-	
SO_4^{2-} (mg L ⁻¹)	69.6 ± 0.84	295.6 ± 1.17	-	-	-	
pH	7.9 ± 0.04	7.8 ± 0.04	$6.4~\pm~0.05$	6.4 ± 0.05	6.4 ± 0.04	



characterized by Dynamic Light Scattering (DLS) using the instrument Plus 90 supplied by Brookhaven.

Fig. 1 displays the nZVI particle size distribution (PSD).

The nZVI mean size was about 120 nm and, as reported in Fig. 1, it was characterized by a bimodal distribution. This was due mainly to the aggregation forces that tend to increase the size of the nZVI clusters. The first cluster family presented a mean size of around 100 nm, whereas the second one a larger mean size, about 250 nm. The absence of dispersing agent did not hinder/reduce the attractive forces among the nanoparticles and, as a consequence, a higher mean nZVI size and a bimodal size distribution was obtained, with respect to the mean nZVI size and unimodal distribution reported in previous work, where the carboxymethylcellulose was employed in nanoparticle synthesis [28]. The nZVI cluster can be well observed also in Fig. 2a and b (analysis were performed using a STEM PHILIPS CM20).

2.3. Experimental procedure

S or CA samples were shaken in 150 mL flasks by an orbital shaker (Heidolph Unimax 101) at 150 rpm: selected amounts of H₂O₂ $(105 \text{ mM}, 3.6 \text{g L}^{-1})$ and FeSO₄ * 7H₂O (13.16 mM, 2 g L⁻¹) or nZVI $(17.9 \text{ mM}, \sim 1 \text{ g L}^{-1})$ were added from stock solutions. Temperature (T) was controlled by a thermostatic bath. The following operative parameters were investigated: H₂O₂/COD (w/w) (0.75, 1.00 and 1.25), Fe (II)/H₂O₂ (w/w) (0.1 and 0.2), nZVI/H₂O₂ (w/w) (0.5, 0.75, 1.00, 1.50 and 2.00), pH, by H₂SO₄ 1 M addition (2-4), corresponding to amount ranges equal to $16.1-2011 \text{ mg H}_2\text{O}_2\text{L}^{-1}$, 1.6-92.2 mg Fe(II) and 8.1-988.4 mg nZVI, respectively. In addition, both CF and HF processes were performed at original alkaline S pH and neutral CA pH (indicated in the test with UN). According to previous studies, the effect of temperature on surfactant degradation was also investigated, in the range between 15 and 35 °C [16,29-31]. Basing on preliminary tests performed on both CA and S samples, contact time was set to 3 h for CF and to 2 h for HF.

TOC and COD were measured at the end of each test, after pH adjustment to 7, when the pH value was lower than 7, to let Fe(III) precipitation, and after centrifugation (10000 rpm, 10 min), evaluating the

Fig. 1. Particle size distribution of the nZVI used in the experiments.

overall treatment efficiency, according to the following parameters:

$$\eta_{TOC}(\%) = 100 \frac{TOC_f}{TOC_0} \tag{1}$$

$$\eta_{COD}(\%) = 100 \frac{COD_f}{COD_0} \tag{2}$$

where the subscript *f* indicates the final parameter value measured at the end of the treatment, and *0* indicates the initial parameter value, whereas η_{TOC} represents the TOC Removal Efficiency and η_{COD} the COD Removal Efficiency. The measured solution pH after CF process was always in the range 5.5–6.5, whereas after HF process it was in the range 6.5–8.

The BOD test was repeated on the treated samples after the Fenton process, to establish the suitability of this AOP to increase their biodegradability. The degradation rate was determined by calculating the BOD/COD₀ ratio over the time [20,21]. All tests and measures were conducted in triplicate; the mean values are reported.

Data modeling and non-linear data regression was performed using Python ver.3.6.1 and the fitting procedure was carried out by *scipy.optimize.curve_fit* function. The second-order fitting surface equation used has a general form $aX^2 + bY^2 + cXY + dX + eY + f$, where a, b, c, d, e and f are the term coefficients, X represent the pH whereas Y represents Fe(II)/H₂O₂ ratio in CF data fitting and nZVI/H₂O₂ ratio in HF data fitting. The *scipy.linalg.lstsq* function was used for this purpose [32].

3. Results and discussion

3.1. Biodegradability study results

Fig. 3 shows the biodegradation test results on the characterized samples (blank values have been subtracted to BOD values).

The biodegradation results clearly demonstrate that the S sample results more biodegradable with respect to CA solutions and its asymptotic value was reached after 30 days. A possible explanation could be that some compounds present in the CA formulation are

Fig. 2. HR-TEM images of nZVI produced: the reported scale is 2500 A (a) and 1000 A (b).







Table 2BOD/COD ratio after 5 and 28 days incubation.

Sample	BOD ₅ /COD (%)	BOD ₂₈ /COD (%)
S CA (0.1%) CA (0.25%)	8.9 ± 0.2 9.6 ± 0.7 9.0 ± 0.5	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$
CA (0.3%)	8.6 ± 0.5	$25.1~\pm~1.1$

recalcitrant and bacteria communities are not capable to degrade them; in fact, the CA concentration increasing leads to the BOD values decrease. Table 2 reports the BOD/COD ratio at 5 and 28 days of the tested samples.

To classify a singular compound as *readily biodegradable*, according to OECD, the BOD₂₈/COD ratio should be larger than 0.6 [25], whereas usually in literature a *biodegradable* substance is characterized by a BOD₅/COD ratio value larger than 0.4 [33].

As showed in Table 2 the OECD standard has never been achieved in the tests. More in detail, the differences among the BOD_5/COD values obtained for each samples is negligible, whereas it slightly increases until reaching 28 days of incubation. The former ratio was always below 10% (0.1), that is significantly lower with respect to the required 40% (0.4) for the *biodegradable* label. Regarding the BOD_{28}/COD values, S and CA 0.1% reached a similar value (32.8 and 31.5, respectively) that are quite far from the required 60% (0.6). In particular, the increase of CA concentration determined a reduction of the BOD_{28}/COD ratio, due probably to the high concentration of more recalcitrant compounds and to the more probable presence of micelles, with respect to the lower concentrated CA samples, where the monomeric form of surfactant molecules is probably predominant.

As regards anionic surfactants, several biodegradation studies have already been carried out, mainly on singular substances or on compound couples. Linear alkyl sulphates for instance, are considered readily biodegradable both in aerobic and anaerobic conditions [34,35], though other authors reported that their biodegradation decreased when concentration exceeded 30 mg L⁻¹ [36]. The biochemical degradation mechanism consists of a first enzymatic hydrolysis of the ester bond, producing the corresponding alcohol and inorganic sulfate salt; the alcohol is enzymatically oxidized to aldehyde and carboxylic acid, which is further metabolized by β -oxidation. The other surfactant belonging to ANS category result as well readily biodegradable in aerobic conditions and even the biochemical mechanism of the recalcitrant SDBS, in function of the benzene group position, was partially determined [37,38]. On the contrary, in the commercial product formulations, different classes and various organic compounds are present Fig. 3. Results of biodegradation test performed on conditioned soil supernatant (S) and commercial additive (CA).

and, as a consequence, the biodegradation rate of the main anionic surfactants could be strongly influenced, due to adverse or synergistic effects [39,40] and possible larger toxicity of the intermediate produced by partial compounds oxidation [41,42]. Similar studies and results are reported by other authors in particular on phenols [43], pesticides [43], polycyclic aromatic hydrocarbons and non-ionic surfactants [44].

The biodegradation kinetics was studied through pseudo-first order kinetic, according to the following equation:

$$\frac{O(t)}{O(0)} = \exp(-kt) \tag{3}$$

where $O(t) = BOD_{asy}$ -BOD(t) (mg L⁻¹) represents the oxygen variation during the incubation time, BOD_{asy} (mg L⁻¹) is the asymptotic BOD value, $O(0) = BOD_{asy} - BOD(0)$ (mg L⁻¹) is the initial oxygen concentration and k (day⁻¹) is the pseudo-first order kinetic constant. Table 3 shows the kinetic parameters obtained by non-linear data regression.

The S kinetic constant value obtained is larger than that obtained for CA data modeling and the same trend is followed by half-lives values. The fitting goodness is represented by correlation coefficient values (R^2).

3.2. Conventional Fenton tests results

Figs. 4–9 display the calculated η_{TOC} and η_{COD} from experimental tests.

The oxidation by hydrogen peroxide alone only lead to a negligible mineralization (results reported in Supporting Information, SI). A comparison between η_{COD} and η_{TOC} values reported in Figs. 4 and 5 immediately show the optimal pH value and the influence of Fe(II)/ H_2O_2 ratio. More in detail, from the results analysis it is possible to state that:

• An optimal pH value of 2.5 was found: the treatment efficiency decreases with the pH increase but seems to reach an asymptotic value after pH equal to 4, in fact, increasing pH up to the unvaried pH, the TOC and COD removal efficiencies did not undergo to a

 Table 3
 Biodegradation kinetic parameters obtained in kinetic tests.

Parameter	S	CA
k (day ⁻¹)	0.09	0.06
t _{1/2} (day)	8.15	11.18
R ²	0.987	0.989

Fig. 4. TOC and COD removal efficiency at selected pH $(H_2O_2/COD = 0.75; Fe(II)/H_2O_2 = 0.1)$.





Fig. 5. TOC and COD removal efficiency at selected pH $(H_2O_2/COD = 0.75 \text{ and } Fe(II)/H_2O_2 = 0.2).$

significant reduction;

• The optimal H_2O_2/COD and Fe(II)/ H_2O_2 ratios were 1 and 0.1 w/w, respectively, as shown in Fig. 6. In particular, fixing the H_2O_2/COD ratio to 1 w/w, the treatment efficiency obtained in the UN test on CA samples is very close to that obtained under acidic condition (pH = 3); this result is very important because the optimal pH in Fenton system is acid, near 3 [45]. In fact, the hydrogen peroxide activation and decomposition is mediated by ferrous ions in acidic environment, which leads to the hydroxyl radicals generation (initiation process, see equations below) [46]:

 $Fe(II) + H_2 O_2 \rightarrow Fe(III) + HO + OH^-$ (4)

$$Fe(III) + H_2 O_2 \rightarrow Fe(II) + HOO' + H^+$$
(5)

where Eq. (5) shows the Fenton-like system initiation. The maximum percentage removal values obtained were 65.6% and 57.4% for S η_{COD} and η_{TOC} , respectively. A high Fe(II) and H₂O₂ concentration could lead to the excessive HO⁻ radicals formation, which could behave as scavengers. Thus, increasing the Fe(II)/H₂O₂ ratio could not improve the treatment efficiency. In addition, the residual hydrogen peroxide measured at the end of each test were always higher when a H₂O₂/

COD = 1.25 w/w was adopted. More in detail, a residual H_2O_2 concentration in the range 7.2–12.7%, with respect to the initial amount, was measured, at $H_2O_2/COD = 1.00 \text{ w/w}$, whereas, at $H_2O_2/COD = 1.00 \text{ w/w}$, a reduction in the oxidant consumption was observed, and the residual concentration was in the range 16.4–23.1%, with respect to the initial amount;

• At uncontrolled pH treatment efficiency was dramatically reduced, due to the quick oxidation of pH ferrous ions to Fe(III), thus inducing insoluble hydroxydes precipitation [47].

The above optimized conditions were then adopted in the tests performed to investigate the effect of temperature on the removal efficiency: the results of such test, in term of η_{TOC} and η_{COD} are shown in Fig. 10.

Fig. 10 shows that the treatment efficiency increased at increasing temperature. The TOC efficiency removal increased by about 20%, from 15 °C to 35 °C, whereas the COD efficiency removal underwent to a less remarkable improvement, about 15%. Similar results are reported by Zhang and co-authors [48] which increased the system T until 37 °C with a COD removal efficiency increase on landfill leachate of about 30% (from 42.3 to 56.2%) with respect to that reported at 13 °C; other

Fig. 6. TOC and COD removal efficiency at selected pH $(H_2O_2/COD = 1 \text{ and } Fe(II)/H_2O_2 = 0.1).$







 $(H_2O_2/COD = 1 \text{ and } Fe(II)/H_2O_2 = 0.2).$



Fig. 9. TOC and COD removal efficiency at selected pH $(H_2O_2/COD = 1.25 \text{ and } Fe(II)/H_2O_2 = 0.2).$





Fig. 10. Effect of temperature on TOC and COD removal efficiency.

studies on recalcitrant organic compounds such as methyl *tert*-butyl ether (MTBE) also showed a Fenton oxidation efficiency enhancement with the T increase [49]. A possible explanation to the reported efficiency enhancement with temperature increase has already been discussed by Zazo and co-authors [50]. The authors claimed that increasing medium temperature leads to a more efficient hydrogen peroxide decomposition into hydroxyl radicals, rather than the generally accepted thermal breakdown of H_2O_2 into O_2 and H_2O . This implies an enhanced iron-catalyzed H_2O_2 decomposition, permitting also the initial oxidant concentration and catalyser/oxidant ratio.

3.3. Heterogeneous Fenton test results

Fig. 11(a–d) display the η_{TOC} and η_{COD} obtained in the tests on S and CA 0.1% (the CA 0.25% and CA 0.3% results are very similar to those obtained for CA 0.1% and are not reported), in function of nZVI/H₂O₂ ratio and pH in a 3D graph with the second-order fitting surface.

The test performed using only nZVI (at nZVI/COD = 1.00 w/w) showed always a η_{COD} or a η_{TOC} below 45% at pH equal to 2.5 (results reported in SI). These results are in agreement with the nZVI oxidation by-products analysis reported by several studies [23,51,52], that show the presence of hydrogen peroxide and Fe(II) as nZVI oxidation products, indicating that nZVI alone could lead to the generation of Fenton process. nZVI oxidation by water and dissolved oxygen in acidic environment also produces hydrogen peroxide, which can react with

ferrous ions, generated by nZVI oxidation, thus promoting the well-known Fenton reaction:

$$Fe(0) + O_2 + 2H^+ \to Fe(II) + H_2O_2$$
 (6)

$$Fe(0) + 2H_2O \rightarrow Fe(II) + H_2 + 2OH^-$$
 (7)

$$Fe(II) + H_2 O_2 \rightarrow Fe(III) + HO' + OH^-$$
(8)

In addition, He and co-authors [52] reported a further possible hydrogen peroxide regeneration mechanism, according to the following equations:

$$Fe(II) + O_2 \leftrightarrow Fe(III) + O_2^-$$
 (9)

$$O_2^- + O_2^- + 2H^+ \to O_2 + H_2O_2$$
 (10)

Such reactions are a simplification of a more complex radical mechanism, mainly divided in three steps: initiation (Eqs. (5) and (6), propagation (Eqs. (14)–(16)) and termination (17)–(19) [47].

$$RH + HO' \rightarrow R' + H_2 O \tag{11}$$

$$Fe(II) + R \rightarrow RH + Fe(III)$$
(12)

 $Fe(III) + R^{\cdot} \rightarrow R^{+} + Fe(II)$ (13)

$$\mathbf{R}^{\,\cdot} + \mathbf{R}^{\,\cdot} \rightarrow \mathbf{R} - \mathbf{R} \tag{14}$$

 $Fe(II) + HO \cdot \rightarrow Fe(III) + OH^{-}$ (15)

$$\mathrm{HO}^{\,\cdot} + \mathrm{HO}^{\,\cdot} \rightarrow \mathrm{H}_2 \,\mathrm{O} \,+ \,\mathrm{O}_2 \tag{16}$$

where R represents the generic organic compound.

Experimental data showed in Fig. 11a–d were well-fitted by a quadratic surface equation (R^2 values were in the range 0.94–0.99) and the obtained coefficients are reported in the following equations for the commercial additive solution (CA):

$$\eta_{TOC}(\%) = -3.418pH^2 - 15.788 \left(\frac{nZVI}{H_2O_2}\right)^2 - 0.966pH \frac{nZVI}{H_2O_2} + 26.897pH + 50.105 \frac{nZVI}{H_2O_2} - 5.375$$
(17)

$$\eta_{COD}(\%) = -2.807 p H^2 - 13.077 \left(\frac{nZVI}{H_2O_2}\right)^2 - 0.937 p H \frac{nZVI}{H_2O_2} + 21.778 p H + 41.064 \frac{nZVI}{H_2O_2} - 15.307$$
(18)



Fig. 11. Heterogeneous Fenton oxidation tests results on conditioned soil supernatant (S) with the fitting surface (η_{TOC} , $H_2O_2/COD = 1.00$ w/w (a), η_{COD} , $H_2O_2/COD = 1.00$ w/w (b), η_{TOC} , $H_2O_2/COD = 0.75$ w/w (c), η_{COD} , $H_2O_2/COD = 0.75$ w/w (d)).



Fig. 12. Effect of initial temperature on TOC and COD removal efficiency in Heterogeneous Fenton oxidation tests on conditioned soil supernatant (S).

and the following equations for the supernatant of the conditioned soil (S):

$$\eta_{TOC}(\%) = -1.256pH^2 - 11.668 \left(\frac{nZVI}{H_2O_2}\right)^2 - 0.537pH\frac{nZVI}{H_2O_2} + 11.066pH + 35.183\frac{nZVI}{H_2O_2} - 21.828$$
(19)

$$\eta_{COD}(\%) = -1.459 p H^2 - 12.436 \left(\frac{nZVI}{H_2O_2}\right)^2 - 0.633 p H \frac{nZVI}{H_2O_2} + 12.866 p H + 38.306 \frac{nZVI}{H_2O_2} - 26.383$$
(20)

Focusing on the pH and nZVI/H₂O₂ ratio influences, it is noticeable the larger relevance of the latter term with respect to the former one, demonstrated by the highest coefficient value associated to nZVI/H₂O₂. In particular, the mixed pH nZVI/H₂O₂ term is associated with the lowest coefficient (always < 1) that implies its poor influence on both η_{COD} and η_{TOC} obtained values.

The optimal operating parameters were nZVI/H₂O₂ = 1.5 w/w and pH = 3, leading to a η_{TOC} and η_{COD} values, for the conditioned soil supernatant (S), equal to 75.95 and 85.52%, respectively, whereas for CA 0.1% solution, the same conditions lead to 87.60 and 89.93%. These results are significantly better with respect to those obtained by HF process. Similar results were reported on Tergitol TMN-10, where authors reported remarkable Fenton oxidation improvement through iron nanoparticles addition [29]. As already observed for CF, the higher H₂O₂/COD value, the higher the residual oxidant concentration. A residual H₂O₂ concentration in the range 4.4–7.7%, with respect to the initial amount, was measured, fixing H₂O₂/COD equal to 0.75 w/w, whereas the H₂O₂/COD increase to 1.00 w/ w caused a reduction in the oxidant consumption, whose residual concentration lays in the range 11.2–16.9%, with respect to the initial amount.

The results obtained at unadjusted pH, on both samples, were higher than those reported for CF. This implies that the nZVI use in Fenton system lead to good performance in a wider range of pH. This result has already been observed by Takayanagi and co-authors [16] that reported high SDBS removal efficiency ($\eta_{TOC} = 77.8\%$) using nZVI in Fenton system at pH = 6. Similar results were reported elsewhere

time (days)



Fig. 13. Results of BOD test on the treated soil conditioned supernatant (S) by Heterogenous Fenton (HF) and Conventional Fenton (CF).

Fig. 14. Results of BOD test on the commercial additive solution (CA) at 0.1% by Heterogenous Fenton (HF) and Conventional Fenton (CF).





Fig. 16. Results of BOD test on the commercial additive solution (CA) at 0.3% by Heterogenous Fenton (HF) and Conventional Fenton (CF).

Table 4

BOD/COD ratio values calculated in BOD tests performed after CF and HF oxidation.

Sample	BOD ₅ /COD (%)		BOD ₂₈ /COD (%)	
	Process			
	HF	CF	HF	CF
S CA (0.1%) CA (0.25%) CA (0.3%)	$\begin{array}{rrrrr} 49.67 \ \pm \ 1.5 \\ 48.31 \ \pm \ 1.79 \\ 46.98 \ \pm \ 1.55 \\ 45.68 \ \pm \ 1.49 \end{array}$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{r} 68.08 \ \pm \ 1.4 \\ 62.17 \ \pm \ 1.44 \\ 61.04 \ \pm \ 1.39 \\ 60.36 \ \pm \ 1.47 \end{array}$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$

Table 5

Kinetic parameters for S and CA biodegradation.

Parameter	S	S Process		СА	
	Process				
	HF	CF	HF	CF	
k (day ⁻¹) $t_{1/2}$ (day) R^2	0.157 4.41 0.96	0.146 4.75 0.97	0.215 3.22 0.98	0.250 2.77 0.95	

[53], where the TOC removal by Heterogeneous Fenton treatment of a synthetic greywater (mainly containing anionic surfactants) reached about 70% at neutral pH. The difference observed among treatment efficiency on S and CA could be attributed to the presence of Ca and nitrates in S. nZVI chemical activity can be in fact reduced by Ca ions, as a consequence of colloidal stability decrease and subsequent aggregation [54], leading to a lower available specific surface [55]. Regarding nitrates presence effect on nZVI, the oxidation of nZVI by nitrates has been widely documented in several studies [20,21,28,56,57].

Fig. 12 reports the Heterogeneous Fenton treatment efficiency calculated at different temperatures.

The T increase lead to an overall treatment efficiency, even if in this case the η_{TOC} and η_{COD} rises was lower than those obtained in CF processes. In fact, the TOC efficiency removal increased by about 10%, whereas the rise of COD efficiency removal was about 13%.

3.4. Biodegradability test results after Fenton treatments

BOD tests at the optimal operative conditions were then carried out to investigate biodegradability enhancement caused by Fenton treatment, as shown in Figs. 13–16.

The BOD trend over time for the treated samples was quite different with respect to the corresponding trend observed for the untreated ones: in particular, the lag-phase completely disappeared. Such differences have been already observed by Wang et al. [58] on an anionic surfactant treated with CF. A remarkable enhancement of biodegradability following Fenton treatment was also obtained on well-known toxic non-ionic surfactants [59].

Table 4 shows the BOD/COD ratio values after 5 and 28 days incubation.

The BOD/COD ratio of HF treated samples were always higher (up to 1.5 times) than those obtained on CF treated samples. This result is fundamental for the pre-treatment process selection: HF appeared more selective in oxidizing the more recalcitrant compounds present in the S and CA. In particular, the treated S by HF reached a BOD₂₈/COD value higher than 0.6 and a BOD₅/COD values larger than 0.4. Another important result is the strong biodegradability enhancement of treated CA solutions. A comparison among BOD/COD trends clearly show the significant improvement of sample biodegradability after the Fenton oxidation process. In detail, for CA 0.25% and CA 0.3% the BOD₂₈/COD values increase 10-fold, with respect to biodegradation data observed on untreated solution. The biodegradation results of the three CA solutions were similar and independent on the initial additive concentration. Such behaviour could be addressed to the formation of micelles, which result less biodegradable with respect to the simple surfactant monomer [60].

The above discussed improvements are in accordance with the biodegradation kinetic parameters reported in Table 5.

The kinetic constant values increased from 2- to 3-fold with respect to those obtained on un-treated solution and, consequently, the halflives considerably decreased. This confirmed that HF pre-treatment was successful in enhancing biodegradation of both the conditioned soil supernatant and the additive.

4. Conclusions

This study reports the treatment of excavation by-products and a soil conditioning agent derived from tunneling excavation industry. The liquid phase of conditioned soil (S) by a commercial additive employed in real excavation sites was collected, characterized (BOD, COD, TOC, pH, anionic profile, Fe and Ca contents) and treated by conventional and Heterogeneous Fenton processes. Before the treatment, poor biodegradability was observed, well below the values required to readily biodegradable label (BOD₂₈/COD equal to 0.6). A strong enhancement was then observed as a consequence of Fenton treatment, mainly when Heterogeneous Fenton oxidation was carried out. Optimal operating

parameters for HF were $H_2O_2/COD = 0.75 \text{ w/w}$, pH = 3 and $nZVI/H_2O_2 = 1.5 \text{ w/w}$. Higher COD and TOC removal efficiency, with respect to those obtained by Conventional Fenton were achieved in HF treatment. In fact, a BOD₂₈/COD value higher than 0.6 was observed only on HF treated samples.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2017.10.152.

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