



Assessment of Fenton systems based on metabisulphite as a low-cost alternative to hydrogen peroxide

Francesco Savia^a, Adeniyi Olufemi Adesina^{a,b}, Luca Carena^a, Davide Vione^{a,*}

^a Dipartimento di Chimica, Università di Torino, Via Pietro Giuria 5, 10125 Torino, Italy

^b Department of Chemistry, Federal University of Technology, Akure, Nigeria

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ABSTRACT

Here we show that a Fenton-like system based on zero-valent iron and metabisulphite (ZVI-MBS) is able to effectively degrade both ibuprofen (a non-steroidal anti-inflammatory drug) and its toxic product 4-isobutylacetophenone in 30 min at pH 3. Based on scavenging experiments, the main reactive species involved in the degradation process would be $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$, with $\text{SO}_4^{\bullet-}$ likely acting as $\bullet\text{OH}$ source. Compared to well-known ZVI- H_2O_2 , ZVI-MBS loses performance considerably at $\text{pH} > 3$. Furthermore, differently from ZVI- H_2O_2 where the ZVI surface plays major role, dissolved Fe species are important in ZVI-MBS. In presence of MBS, it would thus be more convenient to add Fe^{2+} directly in the form of ferrous salts than to use ZVI as source of dissolved iron. Fe^{2+} -MBS, similarly to ZVI-MBS, experiences considerable drop in performance above pH 3. MBS is much cheaper, more stable, and safer to operate than H_2O_2 . However, the need to treat water at pH 3 has the important drawback that conductivity/salinity is increased by water acidification for treatment and neutralisation after treatment. That would be appropriate in most cases for water discharge, but could limit reuse of treated water in some fields such as irrigation.

1. Introduction

The occurrence of contaminants of emerging concern (CECs) in surface waters is a growing environmental problem, because of harmful effects on aquatic organisms and, potentially, on human health [1,2]. CECs mainly reach surface waters from treated wastewater, because the traditional techniques for wastewater treatment are unable to efficiently remove biorecalcitrant and polar compounds, which are hardly degraded by activated sludge and undergo poor removal upon partitioning on biosolids [3]. Many important CECs belong to the class of pharmaceuticals and personal care products (PPCPs), of which the non-steroidal anti-inflammatory drugs are among the most used medicines. Some examples are paracetamol, ibuprofen, acetylsalicylic acid, and diclofenac [4].

Several techniques are being proposed to technologically upgrade wastewater treatment plants to improve their ability to eliminate CECs [5], including advanced oxidation processes (AOPs) that generate powerful oxidants such as the hydroxyl radical ($\bullet\text{OH}$) [6–8]. Current drawbacks of many AOPs include elevated cost and the possible production of harmful transformation products from parent CECs [9].

Fenton and Fenton-like techniques are interesting AOPs and are

relatively cheap when used to eliminate CECs from partially treated wastewater (tertiary wastewater treatment) [10]. The traditional Fenton reaction involves Fe^{2+} and H_2O_2 that produce $\bullet\text{OH}$ (reaction (1)) and/or less powerful oxidants, such as ferryl (FeO^{2+}) [11].



Unfortunately, this process is most active at pH 3 [12] and requires wastewater acidification plus pH correction after treatment, which increases both process costs and water salinity [13]. For this reason, Fenton-like processes have been proposed in alternative to traditional Fenton. An interesting possibility is to replace Fe(II) salts with magnetic materials containing Fe, which can be easily removed after treatment [14,15]. In this framework, metallic Fe (zero-valent iron, ZVI) combines low cost, efficiency, and low drop in performance when its surface is oxidised upon contact with air (Fe(II) species are produced in this case, which are still Fenton-active) [16–18]. Another interesting issue of ZVI- H_2O_2 is that there is evidence it is a genuine heterogeneous process that involves reaction between H_2O_2 and the ZVI surface. In fact, when achieving effective ZVI- H_2O_2 degradation of contaminants at pH 5–6, dissolved Fe species were undetectable and thus extremely unlikely to

* Corresponding author.

E-mail address: davide.vione@unito.it (D. Vione).

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account for contaminant removal [16–19]. Therefore, ZVI in the presence of H_2O_2 should be regarded as a solid that operates through its exposed surface rather than a mere source of dissolved Fe for a homogeneous Fenton process.

The use of H_2O_2 in the Fenton reaction has advantages such as environmental compatibility (it forms H_2O and O_2 as main by-products), but also some drawbacks. H_2O_2 is in fact relatively unstable, it poses safety issues when used in concentrated solutions [20], and its cost gives a significant contribution to the total expenditure in reagents of Fenton treatments [18,19]. Among possible alternatives to H_2O_2 , some of us have recently shown that metabisulphite ($S_2O_5^{2-}$, hereinafter MBS) is potentially interesting [21]. In the mentioned work, MBS has been tested as substitute for H_2O_2 in a Fenton-like process that uses the Fe-TAML complex as catalyst (TAML = tetra-amido macrocyclic ligand). Compared to H_2O_2 , MBS is slightly less reactive but has considerable advantages including lower cost, much safer handling, higher stability, and easier storage [21]. However, Fe-TAML differs from typical Fenton catalysts because it is most active under basic conditions [22,23]. Furthermore, its current cost is still too high to allow for practical applications [21].

For the above reasons, the goal of the present work was to test the performance of MBS in Fenton conditions that do not involve Fe-TAML, starting from ZVI-MBS because of the potential of ZVI in Fenton-like systems. We chose the pharmaceutical ibuprofen as substrate because it is conveniently degraded by the Fenton reaction, and because it yields 4-isobutylacetophenone (IBAP) as main toxic intermediate [19]. Monitoring the time trends of ibuprofen and IBAP gives insight into the overall treatment performance, where the aim is to achieve degradation of both ibuprofen and the IBAP that may have been produced by the reaction.

2. Materials and methods

2.1. Chemicals

Metallic iron (product number 44890, purity >99.5 %, particle diameter < 10 μm), NaOH (>90 %), HCl (37 %), ibuprofen sodium salt (98 %), 4-isobutylacetophenone (98 %), ascorbic acid (99 %), o-phenanthroline (99 %), $FeSO_4 \cdot 7H_2O$ (>99 %), Na_2HPO_4 (>98 %), NaH_2PO_4 (>98 %), H_3PO_4 (85 %), H_2SO_4 (96 %), tert-butanol (>99.5 %), 2-propanol (>99.5 %), and methanol (gradient grade) were purchased from Sigma-Aldrich and used as received, without further purification. Water used was produced by a Milli-Q apparatus (resistivity 18.2 $M\Omega\text{ cm}$, TOC < 2 ppb).

2.2. Degradation experiments

The degradation of ibuprofen was carried out in 200 mL beakers under magnetic stirring, on 100 mL aqueous suspensions containing ibuprofen, ZVI (10 mg L^{-1}), and MBS (multiple additions, *vide infra*). The solution pH was continuously monitored by means of a HI98103 Checker pH meter by Hanna Instruments, and adjusted when needed with H_2SO_4 or NaOH. The initial concentration of ibuprofen in the experiments was 10 μM , which is comparable to the highest levels of this compound detected in wastewater [24]. Ten μM is also appropriate because the relevant degradation time trend can be reliably monitored by liquid chromatography, without any need of sample pre-concentration.

To monitor the degradation process, 1.5 mL aliquots of the suspensions were withdrawn at predetermined time intervals and introduced into 4 mL vials, which already contained 0.5 mL methanol to stop the Fenton reaction. The resulting suspensions were immediately filtered on 0.2 μm Pall Acrodisc 13 mm GHP MS syringe filters, and the solution thus obtained was introduced into HPLC vials for subsequent analysis. Similar procedure was followed for the monitoring of Fe species, except that in that case initial aliquots of 3 mL were withdrawn from the

reaction beaker.

For runs to be carried out in the absence of oxygen, the beaker was covered with aluminium foil and the suspension containing ZVI + H_2SO_4 was bubbled for 15 min with high-purity N_2 (99.998 %, SIAD, Bergamo, Italy). The N_2 -delivering needle was then placed above the water level to limit air entrance by saturating the headspace of the suspension with N_2 , but without purging the solution to avoid stripping of ibuprofen after the latter's addition. About 200 μL aliquots of freshly prepared IBP and MBS stock solutions were subsequently added to the N_2 -purged suspension in order to achieve required concentrations of IBP and MBS, and the entire degradation process was monitored in the same manner as experiments conducted under air atmosphere. The N_2 flow was maintained above the water level throughout the reaction time.

2.3. Quantification of ibuprofen, 4-isobutylacetophenone, Fe species, and total organic carbon (TOC)

The time trends of ibuprofen and 4-isobutylacetophenone were monitored by high-performance liquid chromatography interfaced with diode-array detection (HPLC-DAD), using a VWR-Hitachi LaChrom Elite system equipped with L-2200 autosampler, L-2300 column oven, L-2130 quaternary pump for low-pressure gradients, and L-2455 DAD detector. Samples were isocratically eluted with a 75:25 mixture of methanol and water acidified with H_3PO_4 (pH 3), on a column RP-C18 LiChroCART (Merck, 125 $\text{mm} \times 4\text{ mm} \times 5\text{ }\mu\text{m}$). The eluent flow rate was 1 mL min^{-1} and the retention times/detection wavelengths were 3.9 min/220 nm (ibuprofen) and 4.3 min/258 nm (4-isobutylacetophenone).

Dissolved iron was determined by spectrophotometry with o-phenanthroline. For the quantification of Fe(II), the sample solution (1 mL) was added with 50 μL of 0.1 M H_3PO_4 and 60 μL of 0.011 M o-phenanthroline, and introduced into a cuvette with 1 cm optical path length. Absorbance was measured against water, 3 min after addition of the last reagent, with a Varian Cary 100 Scan double-beam UV-Vis spectrophotometer. For the quantification of total iron (Fe_{TOT}), the procedure was the same except for the addition of 100 μL of 0.01 M ascorbic acid to reduce Fe(III) to Fe(II). The concentration of Fe(III) was then determined as $Fe(III) = Fe_{\text{TOT}} - Fe(II)$.

The TOC was quantified by using a Shimadzu TOC-VCSH analyser, based on catalytic combustion and non-dispersive infra-red detection of the generated CO_2 .

3. Results and discussion

Preliminary experiments were carried out at pH 3, where Fenton and Fenton-like processes usually show maximum efficiency [25]. In the case of the ZVI- H_2O_2 Fenton-like systems, the ZVI: H_2O_2 ratio plays a very important role because an excess of either reactant causes scavenging of $\cdot\text{OH}/FeO^{2+}$ and inhibits degradation. Therefore, optimisation of the ZVI: H_2O_2 ratio and of the respective concentrations is essential in ZVI- H_2O_2 [16]. The same might apply to ZVI-MBS and, for this reason, a preliminary optimisation study was carried out in this case as well.

The ZVI:MBS ratio was thus varied in the range from 22 to 100 $\text{g}_{\text{ZVI}}:\text{mol}_{\text{MBS}}$, and the best degradation of ibuprofen (~50 % in 1 h) was obtained with 10 mg L^{-1} ZVI and 0.2 mM MBS (ZVI:MBS = 50 $\text{g}_{\text{ZVI}}:\text{mol}_{\text{MBS}}$). With this optimal ratio kept constant, the ZVI loading was then varied in the range of 5–30 mg L^{-1} (MBS was adjusted accordingly, as 0.1–0.6 mM). The best degradation was again observed with 10 mg L^{-1} ZVI and 0.2 mM MBS. Optimal ZVI:MBS ratio and reagent dose are likely observed because ZVI and MBS take part in a Fenton-like process, but they both behave as reductants when taken individually [19,21]. An excess or a high (still) unreacted concentration of either ZVI or MBS would likely inhibit ibuprofen degradation by scavenging reactive species.

Note that optimal ZVI loading and MBS concentration only induced ~50 % degradation of ibuprofen. Formation of IBAP from 10 μM ibuprofen was also detected, with IBAP concentration reaching ~5 μM

after 5 min and decreasing to 4 μM in one hour. The optimised conditions were thus unable to ensure complete degradation of either ibuprofen or IBAP, which suggests that higher reagent doses might be required. However, the optimisation study has already shown that an increase in either/both ZVI loading and/or MBS concentration would actually worsen the degradation efficiency.

A possible way out of the problem is to split reagent addition into multiple aliquots, exploiting the gradual disappearance of Fenton reagents as the reaction proceeds. An overall high reagent dose can thus be added in small aliquots and avoid excessively high concentrations at any time [13,18,19]. In the case of MBS, it was possible to obtain complete ibuprofen degradation in around 30 min with 10 mg L^{-1} ZVI. To achieve this goal, the concentration of MBS was 0.2 mM at the beginning of the reaction, after which it was gradually increased by 0.1 mM every 3.5 min (last MBS addition at 14 min). The time trends of both ibuprofen and IBAP are reported in Fig. 1a, showing practically complete degradation of both compounds at 30 min reaction time. By comparison, no degradation of ibuprofen (and no IBAP formation) was observed in the presence of ZVI alone or MBS alone (data not shown).

3.1. Effect of pH

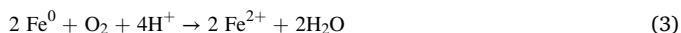
Ibuprofen degradation decreased progressively when raising pH from 3 (100 % degradation in 30 min) to 4 (~50 % degradation) and 5 (<40 % degradation) (Fig. 1). Such a finding is quite common in the case of Fenton and Fenton-like processes. The time evolution of pH is shown in Fig. S1 of the Supplementary Material (hereinafter SM), which also reports the timing of pH corrections. The suspension pH was or could be kept reasonably stable around the target values.

Unfortunately, in the case of ZVI-MBS it was not possible to offset the loss in system reactivity by increasing ZVI loading and/or MBS concentration, differently from ZVI- H_2O_2 where an increase in reagent concentration has been shown to induce effective degradation at $\text{pH} > 3$ [18,19]. Therefore, pH 3 is the only condition where complete IBP degradation could be achieved with ZVI-MBS.

The time trend of dissolved Fe species was also studied at pH 3–5. The results are reported in Fig. 2 in the case of Fe(II), showing that up to 150 μM Fe^{2+} was released in aqueous solution. By comparison, Fe(III) was always below 10 μM . Interestingly, 150 μM Fe^{2+} means that approximately 85 % of the initial ZVI would be released into the homogeneous aqueous phase, which is to be expected when operating with ZVI at pH 3 [26]. The implications of this finding will be discussed in a later section.

3.2. IBP degradation pathways

MBS is a source of sulphite (reaction (2)) [27], which is known to yield reactive species such as $\text{SO}_3^{\bullet-}$ and $\bullet\text{OH}$ under Fenton-like conditions [28,29]. Compared to $\text{HSO}_3^-/\text{SO}_3^{2-}$, MBS is more stable, less prone to auto-oxidation, and more effective [21]. Based on literature reports [27–29], a series of reactions can be hypothesised to take place within ZVI-MBS after reaction (2):



Among the radical species that would be generated in the system, reactivity should follow the order $\bullet\text{OH} \sim \text{SO}_4^{\bullet-} > \text{SO}_5^{\bullet-} > \text{SO}_3^{\bullet-} \gg \text{HO}_2^{\bullet}$

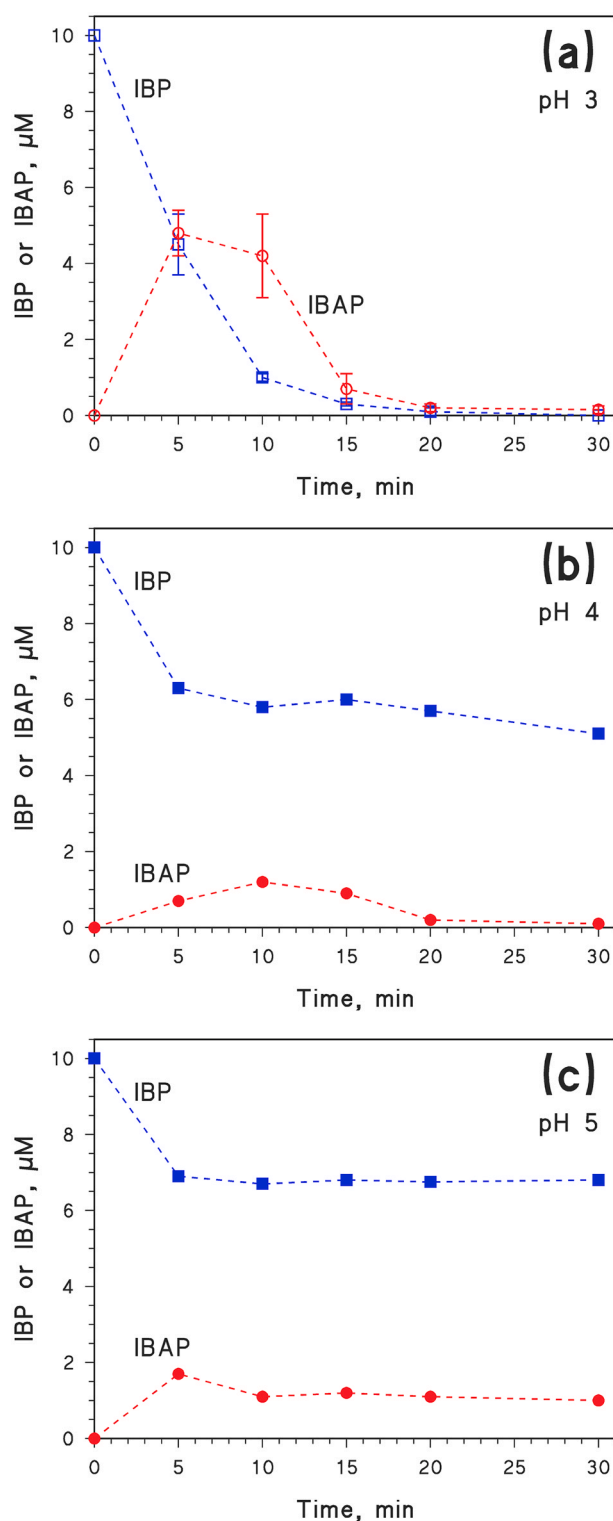


Fig. 1. Time trends of ibuprofen (IBP, initial concentration 10 μM) and IBAP, in the presence of 10 mg L^{-1} ZVI and MBS (initial MBS concentration 200 μM , then increased by 100 μM every 3.5 min to finally reach 600 μM at 14 min), at (a) pH 3 (the error bars represent the standard error of experiments run in duplicate); (b) pH 4, and (c) pH 5.

[30,31]. Reaction (6) between $\text{SO}_3^{\bullet-}$ and O_2 is a key process for the generation of $\text{SO}_5^{\bullet-}$, $\text{SO}_4^{\bullet-}$, and $\bullet\text{OH}$. Coherently, the degradation of ibuprofen was slower in the experiment carried out under N_2 (Fig. S2, SM), although degradation under such conditions (N_2) might still be due to O_2 traces still occurring in the system, or to O_2 formation in reaction

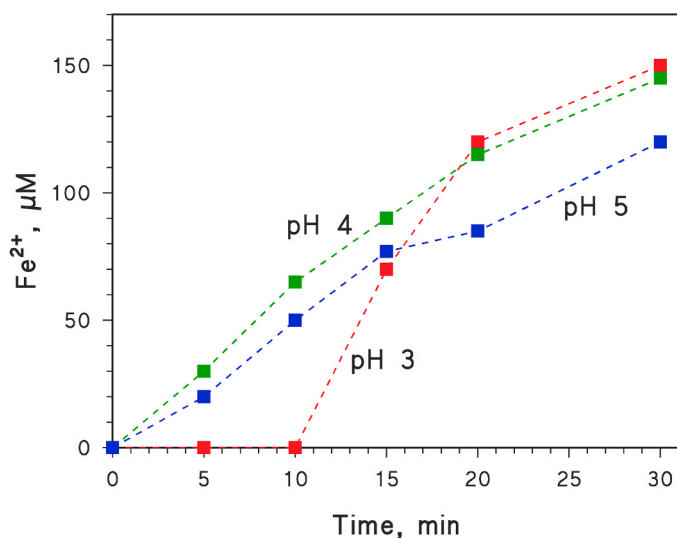


Fig. 2. Time trend of dissolved Fe(II), released in solution in the presence of 10 mg L⁻¹ ZVI and MBS (initial MBS concentration 200 μM, then increased by 100 μM every 3.5 min up to 600 μM at 14 min), at different pH values.

(7).

The alcohols 2-propanol (2-Prop) and t-butanol (t-But) are a good couple of quenchers for SO₄^{•-} and •OH, with second-order reaction rate constants $k_{2\text{-Prop},\bullet\text{OH}} = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $k_{2\text{-Prop},\text{SO}_4^{\bullet-}} = 4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{t-But},\bullet\text{OH}} = 4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, and $k_{\text{t-But},\text{SO}_4^{\bullet-}} = 3.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [30,31]. In particular, while 2-Prop scavenges •OH to a higher degree than it scavenges SO₄^{•-}, t-But scavenges the two radicals to a similar extent. As shown in Fig. 3, addition of both 2-Prop and t-But was able to quench ibuprofen degradation considerably.

The effect of 2-Prop suggests that •OH is involved in degradation. Furthermore, because •OH is a by-product of SO₄^{•-} reactions in Fenton-sulphite systems [28,29], it can be concluded that both SO₄^{•-} and •OH take part in the process.

Therefore, MBS acts as source of HSO₃⁻ and ZVI as source of Fe²⁺ (*vide infra*), which take part in the formation of SO₄^{•-} and, as a consequence, SO₄^{•-} and •OH.

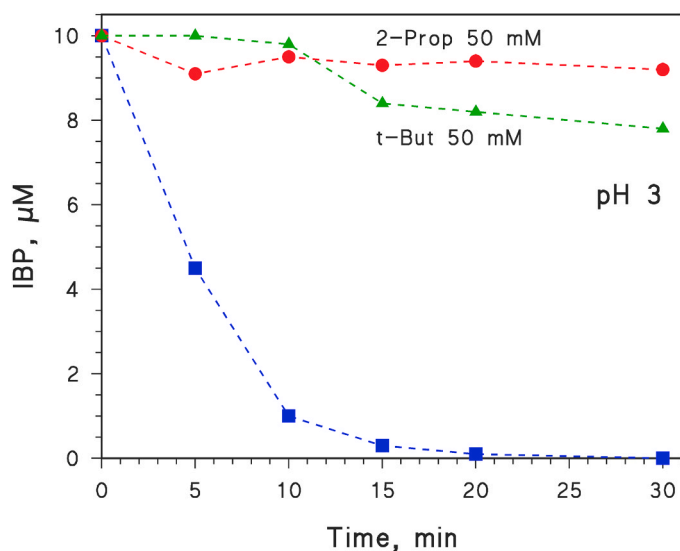


Fig. 3. Time trends of ibuprofen (IBP, initial concentration 10 μM) in the presence of 10 mg L⁻¹ ZVI and MBS (initial MBS concentration 200 μM, then increased by 100 μM every 3.5 min up to 600 μM at 14 min) at pH 3, and effects of the addition of 50 mM 2-propanol (2-Prop) or t-butanol (t-But).

3.3. Homogeneous vs. heterogeneous-phase degradation

As shown in Fig. 2, dissolved Fe(II) would account for a considerable fraction of the initially occurring ZVI. ZVI could thus play a role of its own (as in ZVI-H₂O₂), or only act as source of dissolved Fe(II). Indeed, reactions (4,5) might involve Fe(II) species occurring at the ZVI surface, or dissolved iron. The insert in Fig. 4a shows ibuprofen degradation in the presence of 10 mg L⁻¹ ZVI in suspension (which generates up to 150 μM Fe²⁺), and in the presence of 40 μM FeSO₄ (homogeneous solution). Ibuprofen degradation was practically the same with ZVI or in homogeneous Fe²⁺ solution (FeSO₄), which suggests that homogeneous reactions might play significant role in the presence of ZVI.

Similarly to the ZVI-MBS system (Fig. 1), loss in reactivity with increasing pH was observed with the homogeneous solution as well (40 μM Fe²⁺, Fig. 4). Such a pH trend is similar to that observed with Fe²⁺ + H₂O₂ and it is more marked compared to systems containing ZVI + H₂O₂, where the main process occurs on the ZVI surface [18,19]. In the latter case, recycling of surface Fe(III) by Fe⁰ (Fe⁰ + 2 Fe(III) → 3 Fe(II)) possibly explains why the process was still operational at pH 5 [17], while the same cannot occur in the presence of soluble Fe(II) salts.

These results suggest that, when using either ZVI-MBS or Fe²⁺-MBS, effective degradation can only be expected at pH 3. Actually, the loss in performance with increasing pH is too important to provide for an effective treatment at pH > 3, despite the potential saving of acidification/basification reagents.

Similarities in ibuprofen degradation with ZVI-MBS and Fe²⁺-MBS (see insert in Fig. 4a) suggest that it might be more convenient to add Fe²⁺ directly, rather than use ZVI as source of Fe²⁺. Indeed, when considering that ZVI costs 800 USD ton⁻¹ and FeSO₄ costs 60 USD ton⁻¹ [32], 40 μM Fe²⁺ would cost around 1/10 compared to 10 mg L⁻¹ ZVI. The economic comparison would change if ZVI could be recycled in different treatments, although the dissolution of around 85 % of the initial ZVI at pH 3 (*vide supra*) places a *caveat* to such an approach. Reasonable recovery of a residual (15 % non-dissolved) fraction of the initial 10 mg L⁻¹ ZVI used here is not feasible on a laboratory scale, thus we used a different approach that consisted in spiking again IBP to the ZVI-MBS system after complete disappearance of the substrate. The degradation results in three repeated cycles (Fig. S3, SM) show a gradual loss in performance that is most likely accounted for by ZVI dissolution. This finding suggests that ZVI in ZVI-MBS is a reagent that should be added each time rather than a recyclable catalyst.

On the one side, 10 mg L⁻¹ ZVI as a reagent would increase water treatment costs by a mere 0.008 USD m⁻³ [18] that is quite little, when compared with the cost of traditional wastewater treatment (around 0.38 USD m⁻³ for primary sedimentation, activated sludge, secondary sedimentation, and disinfection [13], which do not effectively eliminate emerging contaminants). On the other hand FeSO₄ is also a reagent, and it is considerably cheaper than ZVI.

Finally, performance towards ibuprofen mineralisation (measured as TOC loss) was compared for ZVI-MBS, Fe²⁺-MBS, and ZVI-H₂O₂. In the former two cases, the conditions leading to ibuprofen degradation at pH 3 were used (see Figs. 1a and 4a). In the case of ZVI-H₂O₂, used conditions were those already shown to induce ibuprofen degradation at pH 3 (10 mg L⁻¹ ZVI, 50 μM H₂O₂, single H₂O₂ addition [19]). Total reaction time for these TOC monitoring experiments was 1 h. The results (TOC time trends, Fig. S4, SM) suggest that ZVI-H₂O₂ induced ~50 % mineralisation after 1 h, while the mineralisation degree was low to negligible for both ZVI-MBS and Fe²⁺-MBS. However, in actual applications to wastewater, the TOC monitoring would be less significant because of the natural occurrence of organic matter in the wastewater matrix, the mineralisation of which would hardly be the treatment target. In such a case, lack of formation of toxic by-products such as IBAP would be a more important figure of merit.

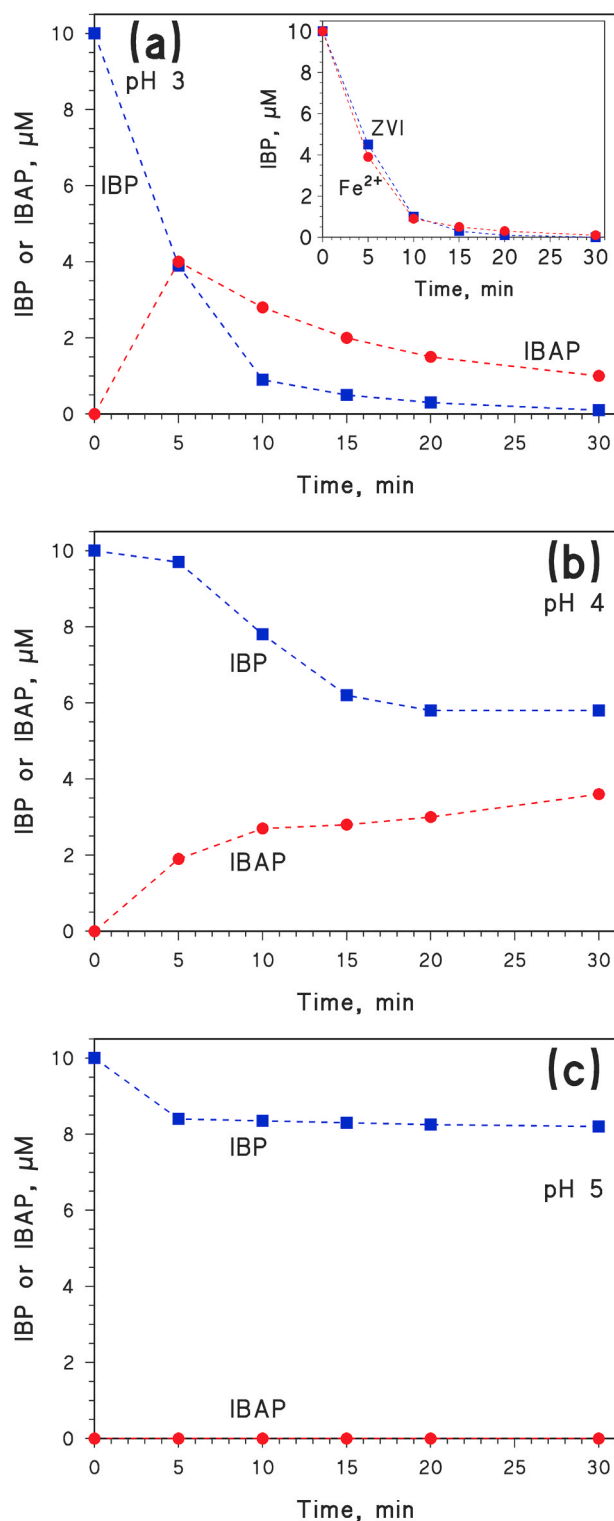


Fig. 4. Time trends of ibuprofen (IBP, initial concentration 10 μM) and IBAP, in the presence of 40 μM FeSO_4 and MBS (initial MBS concentration 200 μM , then increased by 100 μM every 3.5 min up to 600 μM at 14 min), at (a) pH 3; (b) pH 4, and (c) pH 5. The insert in Fig. 4a compares the time trends of IBP in the presence of 10 mg L^{-1} ZVI and of 40 μM FeSO_4 , with otherwise identical conditions.

4. Conclusions

Metabisulphite (MBS) is a cheap way to add sulphite ions to aqueous solutions [21]. Combination of low cost and ease of use could make MBS suitable as water-treatment reagent in resource-poor environments, but MBS is significantly less reactive than H_2O_2 in the presence of Fe^{2+} or ZVI. Here we show that ZVI + MBS can induce complete degradation of both ibuprofen and toxic 4-isobutylacetophenone at pH 3, but the same is not achieved at higher pH values.

The degradation of ibuprofen would involve both $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ radicals, as shown by experiments where the process was effectively quenched by addition of alcohols. The reaction is likely to involve dissolved Fe(II) to some extent, and the combination of FeSO_4 + MBS was about as effective as ZVI + MBS towards ibuprofen degradation. Moreover, FeSO_4 at the required dose would be much cheaper than ZVI.

As shown in recent work, water treatment at pH 3 entails costs for system acidification and pH correction after treatment [26], but such costs would not be particularly high when compared to other techniques such as ozonation [33]. A potentially important drawback concerns the possible use of treated wastewater, because acidification at pH 3 followed by neutralisation increases water conductivity, by around 1 mS cm^{-1} above the conductivity value before treatment [26]. In most cases such an increase would not prevent discharge of treated wastewater into rivers or streams, but it could make treated wastewater less suitable for, e.g., reuse in agriculture [34].

CRedit authorship contribution statement

Francesco Savia: Investigation, Methodology, Data curation, Writing – original draft. **Adeniyi Olufemi Adesina:** Investigation, Methodology, Data curation, Writing – review & editing. **Luca Carena:** Supervision, Validation, Formal analysis, Writing – review & editing. **Davide Vione:** Conceptualization, Investigation, Supervision, Validation, Data curation, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jece.2023.110707](https://doi.org/10.1016/j.jece.2023.110707).

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