Assessing the treatment efficiency of heterogeneous UVA-photo-Fenton processess using different iron oxides and zero valent iron catalysts

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Advanced oxidation processes (AOPs) are water treatment technologies that have been reported to successfully address the efficient removal of several bio-recalcitrant substances, including pharmaceuticals. In particular, the Fenton process has adressed very high and fast removal rates; but the generation of iron sludges and the acid pH environment requirement limit its applicability to a wider extent. Heterogeneous photo-Fenton systems can over-come these drawbacks. In particular, the use of zero-valent iron and iron oxides as catalysts for these processes is herein partially assessed. These iron-based catalysts are often combined with other materials to improve its catalytic activity; thus, fundamental research on its application without being included in a composite material is still limited. In this experimental piece of research, 3 commercial iron-based catalysts (ZVI microspheres, magnetite, and hematite), and 1 synthetized in our laboratory (maghemite), have been applied to the degradation of acetaminophen by an heterogeneous UVA-photo Fenton system aiming to assess the comparative degradation efficiency addressed by photo-oxidation processes using these catalysts.

Introduction

The overall comsuption of pharmaceuticals has increased over the last decades as they become more affordable for the general population; part-icularly, after the COVID-19 pandemic the levels of some of these substances in acuatic ecosystems have turned to be even higher than before [1]. Because they are not usually degraded by convent-ional processes implemented in Wastewater Treat-ment Plants (WWTPs), its presence may represent a significant hazard to human health and the environ-ment [2], and its removal is a challenge for the de-velopment of new water treatment tecnologies [3].

In this sense, the Fenton process efficiency in the treat-ment of bio-recalcitrant compounds has pre-viously been verified, and is considered a low cost and environmentally friendly process [4,5]; but its large-scale application is limited by the drawback of iron sludge generation, which may be overcome by heterogeneous photo-Fenton processes consisting in the use of a solid state catalyst as the source of iron, and in assisting the treatment with radiation to further enhance ferric to ferrous iron recycling minimising catalyst addition; and it is also very convenient that the catalyst is recoverable.

Different iron-based materials have already been used to catalyze these processes, whether in pure state, or as a composite in combinations of themselves or with other materials [6-7]. Degradation efficiency of these processes with iron oxides (hematite, maghemite, and magnetite) and ZVI has not completely been verified yet, and further research effort would be necessary to totally unravel their performance in heterogeneous photo-Fenton processes. The main objective of this contribution is to set a reference comparison on the performance of 3 iron oxides (magnetite, maghemite & hematite) and ZVI as the catalysts in the hetero-geneous photo-Fenton treatment of 4-Acetamido-phenol (ACE) as a reference recalcitrant pharmaceut-ical, including the monitorization of ACE's degradation and mineralization and catalyst stability.

Materials and Methods

ACE (98%) and other reagents were purchased from MERCK KGA; commercial iron oxide powders of magnetite (MGN, Fe_3O_4) & hematite (HEM, α-Fe_2O_3) were supplied by Sigma-Aldrich; ZVI microspheres were provided by BASF; & maghemite (MGH, γ-Fe_2O_3) was synthesized [8]. XRD analysis was applied to verify iron oxide nature.

100 mL of ACE solution (10 mg·L^{-1}) was poured into a glass reactor on an orbital agitator, and the catalyst dose (0.5 g.L^{-1}) was then incorporated before the stoichio-metric H_2O_2 dosage was added to the reactor as the the UVA LED-lamp (365 nm; I=250 mA) was turned on to start the photo-Fenton reaction (t=300 min). The initial natural pH value of the solution was 6.5. Complementary trials were performed pH= 3.5 adding 0.1M HCl. The contribution of adsorption to the treatment pocess was assessed in blank trials

without the addition of H_2O_2 and the application of UVA radiation.

H_2O_2 and total Fe contents were monitored along the process measuring their content by the titanium tiosulfate and the 1,10-phenantrolline methods, respectively [9-10]. ACE degradation was monitored by HPLC and TOC measurements. The discrimination of the oxidizing agents ($HO\cdot$, $O_2\cdot^-$, h^+) along treatment was assessed by trapping experiments with the addition of methanol (MeOH, 100 mM), p-benzoquinone (p-BQ, 1 mM) and potassium iodide (KI, 1 mM) as scavengers, respectively.

Results and Discussion

Adsorption was negligible (<5%) even though ZVI increased adsorption efficiency up to ≈10% under acid conditions because of degradation effects on the surface of ZVI microspheres.

H_2O_2 consumptions were of the 54%, 65%, 64%, and 80%; and ACE removals were of the 86%, 61%, 24%, 34% for the photo-Fenton essays performed at natural initial pH conditions and ZVI, MGN, MGH, and HEM, as the catalyst, respectively (figure 1).

Iron leaching was very low (<0.1 mg.L^{-1}) in any case, veryfing the advantages of using the heterogeneous system. All the catalysts but hematite are magnetically rcoverable. Limited mineralization was addressed and further research must unravel ACE degradation mechanisms under these conditions.

ZVI efficiency was inhibited by MeOH and KI; therefore, the predominant oxidizing agents for the degradation of ACE were $HO\cdot$ and holes (h^+). In the case of HEM, inhibition was detected in p-BQ and KI tirals; thus, $HO\cdot$ radicals did not seem to contribute to ACE degradation when HEM was used. Finally, all the added scavengers reduced the efficiency of both MGN and MGH; thus, all the three oxidizing agents ($HO\cdot$, $O_2\cdot^-$, and h^+) would have contributed to the degradation process.
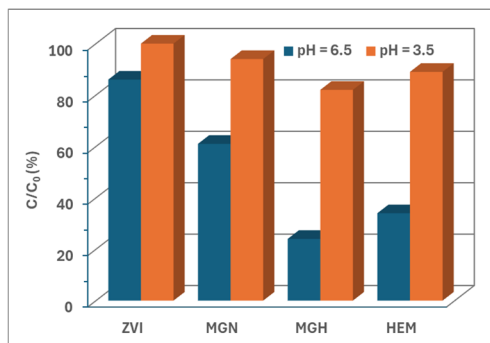
Figure 1. Degradation of 4-Acetamidophenol by heterogeneous photo-Fenton treatment with iron-based catalysts (zero-valent iron, ZVI; magnetite, MGN; maghemite, MGH; and hematite, HEM).

Photo-Fenton trials under acid conditions showed a relevant increase in the degradation efficiency for iron oxides, addressing a 94%, 82%, and 89% ACE degradation with MGN, MGH, & HEM, respectively (figure 1). A total ACE removal was achieved within 30 min of treatment with ZVI as the catalyst; but iron leaching was considerable addressing a high homogeneous catalytic contribution. Iron leaching was very low for all the tested iron oxides under acid conditions (<1 mg·L^{-1}), indicating their high stability of these catalysts.

Conclusions

Different reaction mechanisms may participate in the degradation process of ACE by heterogeneous photo-Fenton processes using iron oxides or ZVI as the catalysts. Adsorption did not significantly contributed to the removal of ACE in the solution. ZVI proved to be more efficient than iron oxides although a more or less limited mineralization was addressed for the applied iron catalyst under natural pH conditions. A significant improvement was addressed for the degradation of ACE when the pH was initially adjusted to optimal acid values for Fenton processes, and the stability of iron oxide catalysts was further verified. However, no improvement is reported regarding the mineralization rate.

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