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Iron-based catalysts under solar and visible radiation for contaminants of emerging concern removal

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Abstract

The ubiquitous presence of CBZ, SMX and LRZ in water is a subject of increasing concern. This study represents a new approach in terms of these contaminants' removal through Fenton process in three different ways, employing a solid catalyst, RM, which, alone, is a source of Fe^{3+} just as much is a source of environmental problems. Alongside RM, 100 mg/L of H_2O_2 were utilized as the initial solution's pH remained unaltered. It was observed that, at these operating conditions, an appreciable degradation rate of contaminants was achieved. Solar photo-Fenton under visible light radiation led the way by attaining more than 50% removal for all three contaminants, reaching its peak when degrading around 62% of LRZ initially present. Therefore, RM, a residue from the alumina industry, seems to be a promising choice in terms of CECs degradation through Fenton process. Nevertheless, some parameters still need optimization, in order to achieve a better understanding and certainty of this oxidation process' skilfulness for detoxifying CECs from the world's water resources.

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Keywords: Decontamination; Fenton process; Pharmaceuticals; Red mud; Sunlight radiation; Waste management

1. Introduction

In addition to the presence of conventional pollutants – organic matter, fat, suspended solids, etc. – that can be found in an effluent coming from a WWTP and the problems linked to their removal before discharge in a watercourse, for the past few years, researchers and scientists have encountered a new threat, CECs [1]. Here, artificial sweeteners, flame retardants, pharmaceuticals, pesticides, antibiotics, personal care products, among others [2] are included. These products, soon turning into pollutants, are the result of a changing society. More people are affected by work-related stress and anxiety, ending up consuming higher amounts of medication, as are the

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Nomenclature

AOPs	Advanced oxidation processes
CBZ	Carbamazepine
CECs	Contaminants of emerging concern
CPC	Compound parabolic collector
LRZ	Lorazepam
RM	Red mud
SMX	Sulfamethoxazole
WWTP	Wastewater treatment plant

cases of CBZ, LRZ and others [3]. CBZ, an anti-epileptic and anti-convulsant drug, is one of the most common pharmaceuticals detected in WWTPs and watercourses [4,5]. LRZ is an anxiolytic drug, inhibiting anxiety, has experienced an increase in sales, especially in Portugal, according to Portuguese National Authority of Medicines and Health Products (INFARMED, IP). Moreover, this compound has also been detected at nano gram scale in WWTP and water courses [6,7].

Besides those two pharmaceuticals mentioned above, antibiotics are another kind of medication used very often by people across the world, and, among them, one can easily find SMX. Although having different applications, SMX shares the same ability not to be 100% metabolized, so it is plausible that a fraction of the compound exits the body through either urine or feces unscathed into the WWTPs [8]. Here, the CECs are not subject to any kind of effective treatment due to their bio refractory character, so they manage to be dumped into watercourses almost equally unchanged. So, further treatment is almost compulsory in order to keep CECs away from aquatic environments, promote water reutilization and avert deepening water scarcity.

AOPs such as Fenton's process, have been considered as a promising choice for degradation of these compounds and achieve both human and eco-friendly results [9–11]. The parting of CECs in a Fenton oxidation process is through electron interactions taking place between the reactants, H_2O_2 , employed as the oxidant, and Fe^{2+} , as the catalyst, that, ultimately, will lead to $\bullet\text{OH}$ radical's generation, as described by Eq. (1). Li et al. [9], through Fenton oxidation process, employing 20 mg/L of Fe^{2+} , a $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio of 2.5 and in an acidic environment (pH 3) achieved a CBZ removal of 100% in 30 min. As for Lorazepam, Sousa et al. [12] managed to successfully remove it in 20 min of reaction, through photocatalytic treatment with UVA lamps radiation (main emission line at 366 nm) as 200 mg/L of TiO_2 and 200 $\mu\text{g/L}$ of LRZ's initial concentration were both employed.



Typically, in this kind of processes the iron source provided from chemical resource (such as iron sulfate solution), which compromises the sustainability of natural resources. Besides, iron recovery and reuse are compromised when homogeneous Fenton is applied. In fact, at the end of the reaction stage, iron precipitation as $\text{Fe}(\text{OH})_3$ sludge is promoted leading to a second source of pollution. Therefore, RM it will be considered a good source of iron for Fenton oxidation processes, and, on top of that, it is a way of keeping RM away from threatening the environment, promoting a circular economy within the aluminum industry through a process of valorization in the market [13]. In fact, RM is a residue easily found in aluminum industry as a result of alumina production. Its generation is followed by discharge in stockpiles poisoning the soil encircling the RM containers through leaching. RM is rich in a wide variety of metals, mostly iron and aluminum. For instance, and although information in the literature about the role played by this process in degradation of CECs using RM as source of iron in Fenton's process is rather scarce, this waste was used for propylparaben degradation through persulfate activation and further oxidation of this emerging contaminant, employing $\text{SO}_4^{\cdot-}$, as the oxidant [14]. The use of a solid catalyst may be an important option to overcome the iron sludge production drawback associated to classical Fenton's process. The choice of testing the catalytic activity of a waste is a way to reduce the operating costs related with catalysts production.

That being said, the purpose of the present work is to study a new approach towards CBZ, SMX and LRZ degradation through heterogeneous Fenton-like processes, under dark, Visible artificial and solar light. This approach will also be subject to comparison with photocatalytic oxidation process under the same amount of red mud sharing the same radiation sources.

2. Materials and methods

2.1. Red mud and reagents

RM was provided from a Greek aluminum producer. The RM was washed and dried at 105 °C for 24 h, after that was grinded until a powder was obtained. The red mud load used in the experiments was 70 mg/L. RM was previously characterized in the work, Domingues et al. [15]. Hydrogen peroxide (33% w/V) was purchased from Panreac. The hydrogen peroxide load used was 100 mg/L. The CECs (Carbamazepine; Lorazepam and Sulfamethoxazole) used in the experiments were purchased from Sigma-Aldrich. The initial concentration was 1 mg/L of each contaminant. The experiments were performed for the mixture of three compounds.

2.2. Experimental procedure

The photocatalytic and Fenton's experiments were carried out in a cylindrical borosilicate photo-reactor with a working volume of 0.5 L. This reactor is equipped with CPC to absorb the maximum of radiation. The reactor was equipped with a porous stone axially placed to disperse air during the reaction which also promotes the mixture. For the dark condition's aluminum foil was used to cover the reactor during the reaction time. The required amount of dried RM is added 10 min before to start the experiments to test the adsorption and, in the Fenton's experiments the reaction started when H₂O₂ was introduced. For photo-Fenton's experiments a high-pressure sodium grow lamp (LUMATEK 600 W) and natural sunlight were both used. Under sunlight experiments the photon flux was followed through the radiometer Oceans Optics USB 4000 fiber optic spectrometer. As for the visible light experiments, the typical wavelength of the lamp applied is within the range 480–700 nm and the its medium photon flux is about 70 W/m² (±10 W/m²). Samples taken periodically were filtered using 1 μm glass fiber membranes to remove the catalyst particles and then a few drops of Na₂S₂O₃ (0.1 N) were added to remove the remaining H₂O₂, stopping the reaction.

2.3. Analytical procedure

SMX, CBZ and LRZ were quantified by high-performance liquid chromatography, equipped with a diode array detector (HPLC-DAD, UFLC, Shimadzu) at the wavelength of 255 nm. The method used consists in a 40/60 ratio of acetonitrile and NaH₂PO₄ in MQ water with a flow rate of 1 mL/min. The volume of injection was 100 μL through a Silia Chrom C-18 column under isocratic conditions.

H₂O₂ concentration, at the end of the reaction, was followed spectrophotometrically (PG Instruments T60 spectrophotometer) using the potassium titanium (IV) method [16].

3. Results and discussion

3.1. Heterogeneous fenton process

The original solution containing the three contaminants, CBZ, SMX and LRZ, was submitted to three different sorts of Fenton oxidation, without correcting the initial pH, which was around 6.5. Firstly, the reaction mixture was submitted to dark Fenton-like process in which all the three contaminants were poorly degraded — by the end of the reaction time, CBZ, SMX and LRZ presented removal percentages of approximately 15.7, 16.5 and 24.1, respectively. These results can be seen in Fig. 1a. When the reaction went through photo-assisted Fenton oxidation through visible light, the outcome was slightly better. As LRZ achieved better degradation than the other two, almost 40%, CBZ managed to attain around 35% and SMX only 26%, approximately (Fig. 1b). Lastly, photo-Fenton process under sunlight, the obtained results improved substantially comparing it to the previous two. Here, all three components managed to be parted more than 50% (Fig. 1c). Once again LRZ, of all three, presented the best results with a removal percentage around 62%. As for SMX and CBZ, their results worsened a little as the former and the latter presented 51% and 58% removal, respectively (Fig. 1c).

According to Fig. 1., the effect of radiation, either visible or UV, is well perceivable, since the degradation performances of all three contaminants are thus enhanced, contrasting with dark Fenton's results. The three contaminants exhibit similar degradation behaviors throughout the entire reaction time in the three experiments.

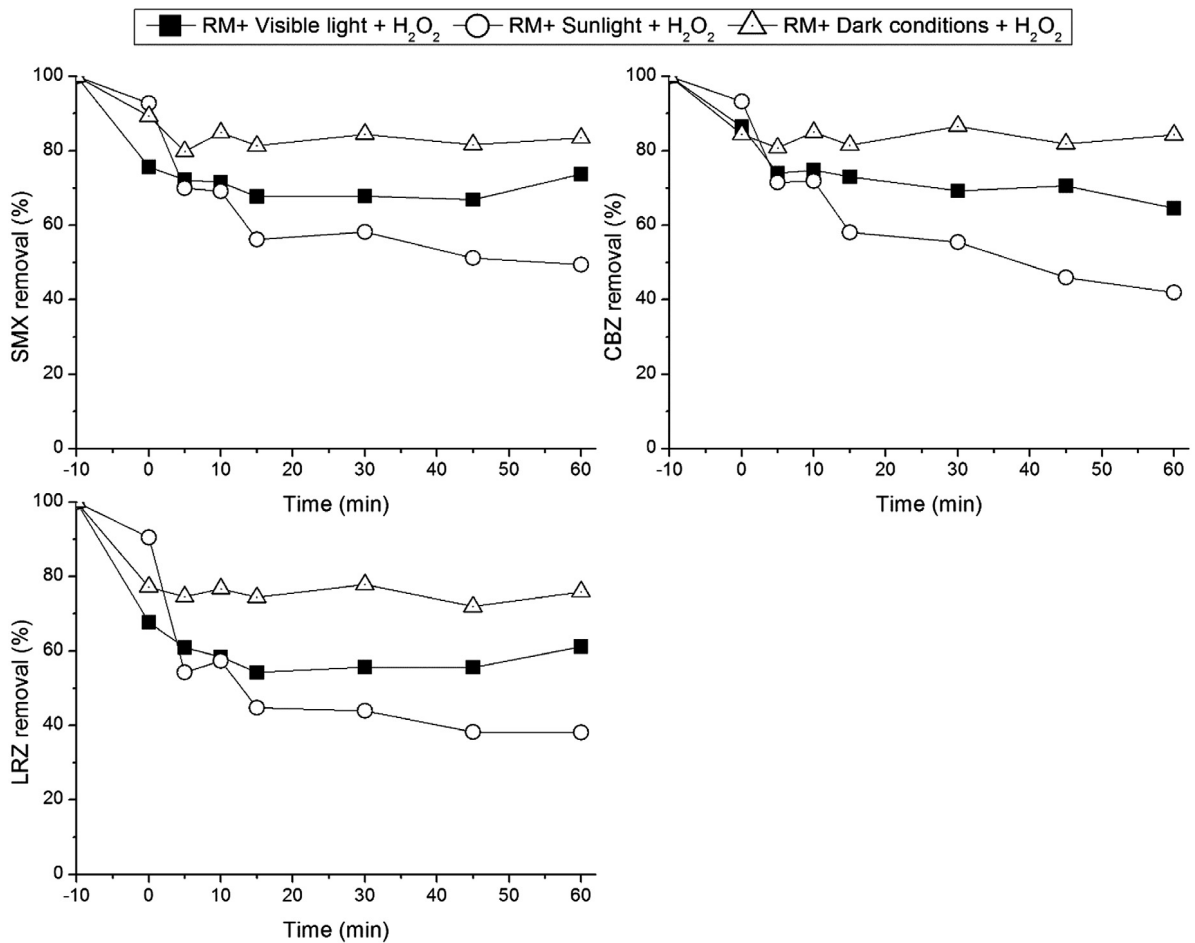


Fig. 1. Application of Fenton under dark, visible and sunlight radiation over SMX (a), CBZ (b) and LRZ (c) removal.

Under sunlight, a rapid decrease in concentration in the first 5 min of reaction, due to H_2O_2 addition to the mixture, takes place, especially for LRZ. Such behavior is also noticeable when the mixture is subject to visible light, however to a less extent. This could be explained by easing the $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycle under radiation – as shown by reactions (2) and (3) [10] – promoting a much faster formation of OH^\bullet radicals, thus enhancing the contaminants' degradation.



As a result, there will be only small traces of H_2O_2 in the mixture, then hampering CECs degradation for the remaining reaction time. In the aftermath of both experiments, the concentrations of H_2O_2 were 8.7 mg/L under sunlight, and 19.4 mg/L under visible light. On the other hand, in dark Fenton process the addition of H_2O_2 does not seem to have the same sort of impact as before. Here, 25.5 mg/L of residual H_2O_2 were measured. So, one might say that there is a correlation between the amount of residual H_2O_2 present in the mixture and the CECs degradation performance. This means that there was still H_2O_2 present in the end that could be transformed into OH^\bullet radicals, which did not happen. The catalyst load and, therefore, the concentration of iron, could not be enough for a total H_2O_2 consumption, limiting OH^\bullet formation, through Eq. (1). Moreover, if H_2O_2 is in excess in solution, hydroxyl radicals scavenging effect may occur which reduces the process efficiency.

On top of that, the initial solution's pH was not corrected to 3, as is supposed when applying Fenton's process, which resulted in a final pH of 6.5, approximately, favoring H_2O_2 decomposition into water and molecular oxygen [17,18]. This could explain why the results obtained were not that good.

Klammerth et al. [19], used solar photo-Fenton over a solution having 15 CECs with a concentration 0.1 mg/L apiece. By initially adding 50 mg/L of H₂O₂ and 5 mg/L of soluble Fe²⁺, in an acidic environment to remove the carbonates, 50% of CBZ and SMX was obtained, in 60 min of reaction. In spite of the homogeneous source for iron, these results indicate that the heterogeneous application can be a suitable solution. Therefore, it can be concluded that solid RM usage in Fenton's process can degrade CECs. Moreover, further tests to optimize the ratio of iron and hydrogen peroxide should be analyzed in terms of CEC degradation.

4. Conclusions

The contaminants of emerging concern are recalcitrant compounds which need advanced oxidation technologies for their abatement. On this way Fenton's process was used considering a waste provided by the alumina industry as a source of iron commonly called red mud. CBZ, LRZ and SMX were partially removed in Fenton-like processes at natural pH.

In a general sense, solar photo-Fenton attained the best results, achieving about 58%, 62% and 51% removal for CBZ, LRZ and SMX, respectively, after 1h of reaction. Also, of all three kinds of experiments, (dark, visible and solar light) the solar photo-Fenton presented less amount of residual H₂O₂, hence the higher levels of degradation when comparing them with those obtained from the other two.

RM performances under such conditions used in this study are a clear indicator that this source of Fe is a good alternative in CECs removal. However, more experimentation should be put to test improving the operating conditions — lowering the pH to a minimum of 3 and optimizing the ratio between the reactants. Thus, giving this alumina industry solid waste a new purpose, sparing the surrounding environment to its menaces, and submitting it to a circular economy.

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