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Olivier Monfort, Guillaume Voyard, Marcello Brigante, Gilles Mailhot. Innovative depollution treatment using multi-valent iron species: from fundamental study to application in municipal wastewater. *Environmental Science and Pollution Research*, 2020, 27 (16), pp.19736-19745. 10.1007/s11356-020-08502-z . hal-02932226

HAL Id: hal-02932226

<https://hal.science/hal-02932226v1>

Submitted on 7 Sep 2020

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Innovative depollution treatment using multi-valent iron species: From fundamental study to application in municipal wastewater

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Abstract

In this work, a new combination of oxidation treatments for the degradation of bisphenol A (BPA) is investigated. This innovative wastewater (WW) treatment includes the use of ferrate (FeO_4^{2-}) and its decomposition byproducts under dark and UVA irradiation. The oxidation by ferrate leads to a fast but incomplete degradation of BPA with a degradation extent of 45% after 60 minutes under adopted experimental conditions. However, the ferrate decomposition byproducts which are constituted by solid iron species can be used to further improve the pollutant degradation efficiency. Indeed, ferrate-mediated heterogeneous photo-Fenton process is employed for the first time to enhance the degradation of BPA. With respect to the application for wastewater treatment, UVA irradiation (which is part of solar light), non-toxic and natural origin compounds such as ascorbic acid (AA) and ethylenediamine-N,N'-disuccinic acid (EDDS) are used to design a sustainable process. Under optimized conditions, the degradation extent of BPA using this newly designed treatment reaches almost 100% with AA and 70% with EDDS. In order to assess the feasibility of this treatment, the ferrate-mediated photo-Fenton process is applied to treat municipal wastewater. The obtained results in WW are highly encouraging since a maximum BPA degradation extent of 63% and 60% is observed after 300 min by using AA and EDDS, respectively.

Keywords

Advanced oxidation process; Wastewater treatment; Environmental chemistry; Photo-Fenton; Ferrate; Hydroxyl radical

1. Introduction

For several decades, different chemical oxidation processes are investigated in order to degrade the organic recalcitrant pollutant in water. Ferrate (FeO_4^{2-}) is considered as a promising oxidant for the removal of contaminants in the environment (Dong et al. 2019; Jiang et al. 2018; Luo et al. 2019; Monfort et al. 2019; Peings et al. 2017; Sharma et al. 2015, 2016; Xie and Cheng 2019). Although the chemistry of ferrate is sophisticated and not yet fully understood (Han et al. 2018; Lee et al. 2014; Machalova Siskova et al. 2016; Sharma 2010; Sharma et al. 2011, 2015, Yu et al. 2017), one of its undoubtedly advantages is its oxidation properties (2.2 V vs. SHE in acidic medium) (Jiang and Lloyd 2002) and its high reactivity (Chen et al. 2018; Rush and Bielski 1994; Sharma 2002, 2013). Compared to “classic” oxidants such as permanganate (MnO_4^-), hydrogen peroxide (H_2O_2) and ozone (O_3), ferrate can degrade more efficiently a wider range of organic pollutants such as pesticides, pharmaceuticals or emerging pollutants (Feng and Baum 2019; Han et al. 2015; Peings et al. 2017; Sharma et al. 2016). However, the mineralization of target contaminants in water using reasonable ferrate concentrations is never completely achieved. For this reason, several strategies have been proposed to improve the oxidation by ferrate. One of them is the use of sulfate-based radical precursors to produce reactive sulfate species which increase the mineralization extent (Feng et al. 2019, 2018; Feng and Sharma 2018; Shao et al. 2019; Sun et al. 2018; Zhang et al. 2017). Thus, the combination of sulfite and ferrate leads to the formation sulfate and/or hydroxyl radicals ($\text{SO}_4^{\cdot-}$, HO^{\cdot}) which enhance the degradation efficiency of the target molecule (Feng and Sharma 2018; Shao et al. 2019; Sun et al. 2018). Another strategy is the use of the coagulation properties of ferrate since their decomposition byproducts are Fe(III) species (Jiang 2007; Zheng and Deng 2016) or the use of ferrate as pre-oxidation step in conventional chemical treatments (TiO_2 photocatalysis or H_2O_2 photolysis) (Ma et al. 2015; Matin et al. 2018; Sharma et al. 2001, 2010; Wang et al. 2010). However, these processes imply the addition of hazardous chemicals or the displacement of the pollution (in the case of coagulation) which is not economically and environmentally viable.

It is admitted that ferrate decomposes into Fe(III) oxides/hydroxides. Recently, Goodwill et al. have demonstrated that the reduction of ferrate reduction yields to crystallized ferric species such as Fe_2O_3 (Goodwill et al. 2015; Jiang et al. 2015; Lv et al. 2018). Therefore, heterogeneous Fenton and photo-Fenton processes can be potentially applied to improve the oxidation process of ferrate, and this is for the first time demonstrated here

in the so-called ferrate-mediated photo-Fenton oxidation process. Although heterogeneous photo-Fenton processes have several drawbacks compared to homogeneous systems (availability of iron, lower efficiency, etc.), their strongest advantage is the efficiency at environmentally relevant pH (from 5.5 to 8.0), which is an important condition for the engineering of water and wastewater treatments (Miklos et al. 2018; Wang et al. 2016).

In this work, the improvement of oxidation by ferrate is operated through the valorization of its decomposition byproducts using advanced oxidation processes (AOPs) including photo-Fenton process. In the literature, few works are focused on comparative studies between these two types of oxidation treatments (Batarseh et al. 2007; Vela-Gala et al. 2014; Zboril et al. 2012) but none of them has ever tested the combination of ferrate and Fenton-based oxidation processes in a single treatment. In addition, UVA irradiation and natural/non-toxic compounds are used in this work to valorize the ferrate decomposition byproducts (Hou et al. 2016; Huang W et al. 2013, 2017; Wang et al. 2019) and to design a sustainable treatment. Published works devoted to the application of ferrate-based processes in real wastewater are scarce (Jiang et al. 2018); therefore, to assess the feasibility of such an innovative treatment, it is tested in the depollution of water from municipal wastewater plant. Bisphenol A (BPA) is chosen as model pollutant since it is a persistent endocrine disruptor widely spread in the environment (Crain et al. 2007; Suzuki et al. 2004) and thus, a good probe to investigate the efficiency of this ferrate-mediated heterogeneous photo-Fenton processes. BPA is a contaminant from plastic products (including packaging materials) which easily leaches out into the environment and food (Nomiri et al. 2019). BPA exposure is associated to many human diseases including diabetes, cancer, hepatotoxicity or hormonal deregulation (Nomiri et al. 2019).

2. Materials and methods

2.1. Chemicals

Potassium ferrate (K_2FeO_4), pure (98%) and in the form of mixture (20%), were purchased from Santa Cruz Biotechnology and NanoIron (Czech Republic), respectively. Hydrogen peroxide (H_2O_2 , 30% in water), L-ascorbic acid (AA, reagent grade), Ethylenediamine-N,N'-disuccinic acid trisodium salt solution (EDDS, 35% in water), bisphenol A (BPA, 99%), 3-(2pyridyl)-5,6-diphenyl-1,2,4-triazine-4',4''-disulfonic acid sodium salt (ferrozine, 97%), 4-hydroxyphenylacetic acid (HPAA, 98%), Ethylenediaminetetraacetic disodium salt (EDTA, 99%), peroxidase from horseradish (POD) and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate) (ABTS) were supplied by Sigma-Aldrich. The chemicals were used without further purification and the solutions were

prepared with ultra-pure water (milli-Q system from Millipore; 18.2 M Ω cm) except when it is specified. The pH of the solution was adjusted with perchloric acid (HClO₄) when necessary. Ferric oxide/hydroxide powder including hematite (Fe₂O₃) and goethite (FeOOH) were obtained also from Sigma-Aldrich.

2.2. Characterization methods

The potassium ferrate salt in the form of mixture was characterized by SEM/EDX in order to investigate the chemical composition. Results were compared to those from pure ferrate. These semi-quantitative chemical analyses were performed by SEM using a Cameca SX100 device equipped with EDX (SDD brüker). In addition, the concentration of ferrate in solutions from the pure and mixture forms is investigated by a colorimetric method using ABTS (see Text 1 in ESM). The decomposition byproducts of the ferrate mixture were analyzed by XRD using PANalytical X'Pert Pro X-ray diffractometer (Bragg Brentano geometry; Cu-K α radiation) equipped with an X-Celerator Scientific detector to determine the crystalline phase composition. In solution, the stability of the ferrate mixture at different concentrations was investigated both in the dark and under UVA irradiation using UV-visible spectroscopy (Varian Cary 3 UV-visible spectrophotometer) with a 5 cm and 1 cm path length quartz cells for 0.04 g L⁻¹ and 0.4 g L⁻¹ ferrate solution, respectively.

2.3. Degradation experiments and analysis of BPA

All experiments in the dark and under UVA irradiation were performed in batch mode. Typically, the degradation of 50 μ M of BPA was investigated using different concentrations of ferrate ranging from 0.01 to 0.4 g L⁻¹ in the dark and under UVA. Other experimental conditions were also tested to improve the degradation efficiency. To this end, after 1h of oxidation by ferrate in the dark, different concentrations of AA or EDDS were added to the solution. Then, after 30 min kept, H₂O₂ was spiked into the solution to trigger the (photo)Fenton reaction either in the dark or under irradiation. For irradiation experiments, the solution was placed in a thermostated (293 \pm 2 K) Pyrex reactor in which 4 UVA lamps (Sylvania Black light F15W/350BL-T8) were located on the top. The emission spectrum reaching the solution was quantified to be 1.89 mW cm⁻² between 290 and 400 nm with a maximum at 350 nm (Fig S1).

To assess the degradation extent, 500 μ L samples were withdrawn at fixed time intervals, filtered using 0.45 μ m PTFE filter and quenched into 500 μ L of methanol (MeOH) to stop the reaction. The BPA concentration in the sample was determined using High Performance Liquid Chromatography (HPLC, Nexera LC-20AD XR) equipped with C18 column (Agilent) and diode array detector (prominence SPD-M20A) set at 225 nm. The

mobile phase was composed of a mixture of milli-Q water and MeOH in gradient mode (H₂O/MeOH from 55:45 to 30:70 reached in 8 min). The flow rate was 1.0 mL min⁻¹ and injection volume was 25 µL.

2.4. Assessment of Fe(II) and H₂O₂ concentrations in solution

Fe(II) formation in solution was determined using a ferrozine complexation method (Stookey 1970). Briefly, 500 µL of sample was mixed with 50 µL of 20 mM ferrozine solution in 100 µL of phosphate buffer solution (pH = 6.5). Then, using the Beer-Lambert law with the maximum absorbance of Fe(II)-ferrozine complex at 562 nm and an extinction coefficient ($\epsilon = 27900 \text{ M}^{-1} \text{ cm}^{-1}$), the concentration of Fe(II) can be determined.

H₂O₂ concentration in solution was determined using fluorescence detection. Briefly, 500 µL of the sample was added to a mixture of 2 mL of 1 mM HPAA and 1 mL of a phosphate buffer solution (pH 6.5) containing 10 mM EDTA and few mg of POD. In presence of H₂O₂, the POD catalyzed the formation of highly fluorescent HPAA dimer which was detected using fluorescence spectrophotometer (Varian Cary Eclipse) at 410 nm for an excitation wavelength of 320 nm.

2.5 Application to municipal wastewater

Wastewater (WW), after a primary treatment stage, was collected the 24th September 2019 in a municipal wastewater treatment plant of the metropole of Clermont-Ferrand. In order to remove the solid particles, filtration using 0.45 µm PTFE filter was performed. Analyses using total organic carbon (Shimadzu, TOC-L) and ionic chromatography (Thermo Scientific, ICS5000) exhibited that, among the 60 mgC L⁻¹ contained in the WW, around 35 mgC L⁻¹ is from organic compounds while ions concentrations are reported in Table S1. The pH of WW was 8.0. The same experimental conditions as those described in section 2.3 were used to investigate the feasibility of the ferrate-mediated heterogeneous photo-Fenton process in the treatment of municipal wastewater.

3. Results and discussion

3.1. Characterization of ferrate and its decomposition byproducts

3.1.1. SEM/EDX and XRD

Since the solid ferrate mixture dissolves in water, the main purpose of SEM/EDX analysis is to investigate the chemical element composition and repartition within the solid salt (Fig. 1). The ferrate mixture is essentially composed of K, Fe, and O chemical elements with trace amount of Cl (Table 1). The elements distribution is heterogeneous (Fig. 1) and according to the semi-quantitative EDX analysis recorded in the marked zones in Fig.

1A, the solid compound contains a mixture of ferrates with different stoichiometries (*i.e.* different iron oxidation states). In addition, the ferrate is embedded in a matrix which is rich in potassium (especially KOH and to a smaller extent KCl). This is probably due to byproducts from ferrate synthesis (Jiang and Lloyd 2002; Sharma et al. 2016). For comparison, the pure ferrate is also investigated by SEM/EDX (Fig. S2). Although only ferrate(VI) is identified in the pure form, the solid compound contains a large amount of impurities which is not consistent with the information from the supplier. These impurities are composed of KOH and KCl (Fig. S2). In addition, the concentration of ferrate in both the pure form and the mixture is calculated to be similar according to titration by the ABTS method (see Text S1 in ESM). Therefore, for economic and scientific reasons, ferrate mixture is used in this work to investigate the ferrate-mediated oxidation processes for WW treatment.

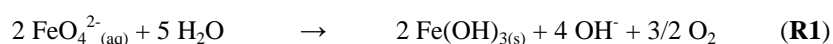
Concerning the byproducts from ferrate decomposition in water, XRD analysis exhibits both amorphous and crystalline phase. The crystalline phase is identified as magnetite (Fe_3O_4) (Fig. S3). The presence of this mixed valence iron oxide in decomposed ferrate is beneficial since Fe_3O_4 is efficient in heterogeneous photo-Fenton process (Huang W et al. 2017). On the other hand, amorphous iron oxides/hydroxides undergo leaching which is an advantage for homogenous Fenton-type reactions (Prucek et al. 2009). Usually, ferrate is decomposed into hematite (Miklos et al. 2018), thus the presence of magnetite in the decomposition byproducts from the ferrate mixture is a new finding reported for the first time here. Regarding the low number of publications devoted to the control of iron oxide formation from ferrate decomposition, such a research field would be of high interest in the future.

3.1.2. Stability of ferrate in solution

The stability of ferrate solution (0.04 g L^{-1} , $\text{pH} = 10.0$) is investigated in the dark and under UVA irradiation (Fig. S4A). From the UV-visible spectra, a decrease of the characteristic absorption band of ferrate centered at 505 nm (Licht et al. 2001; Rush et al. 1996) is observed upon ageing the solution. This decrease is accelerated under UVA irradiation suggesting a photo-induced decomposition. After adjusting the pH to acidic values ($\text{pH} = 5.0$), the stability of ferrate rapidly decreases and almost the complete decomposition is observed after 2 min (Fig. S4A). This is explained by considering the short lifetime of ferrate species in acidic media in which they are much more reactive (Rush and Bielski 1996; Sharma 2002). Similarly, pure ferrate solution (0.04 g L^{-1}) exhibits the same tendency (Fig. S4B).

At higher concentrations, the stability of ferrate mixture solution slightly decreases (Fig. S4C). This is due to the increase of nucleation sites since ferrate decomposes into solid iron species (R1) which favor

decomposition/precipitation of ferrate (Miklos et al. 2018; Wang et al. 2016). In addition, in the presence of BPA, complete decomposition of ferrate is obtained within several minutes probably due to the high reactivity toward electron rich moieties (Fig. S4D).



3.2. Degradation of BPA

3.2.1. Oxidation process by ferrate and its valorization under UVA

The degradation of BPA by oxidation in the presence of ferrate is very fast (Fig. 2). No pH adjustment is performed, and pH of the solution is measured at 10. The fast BPA degradation in Fig. 2 is due to its high oxidation potential and fast kinetic since the time of reaction between ferrate and most of organic pollutants containing electron rich moieties is ranging from seconds to minutes (Sharma 2002). Moreover, ferrate acts through direct oxidation, *i.e.* 1 or 2 electrons transfer (Han et al. 2015; Sharma et al. 2016). The effect of ferrate concentration on the degradation extent of BPA is shown in Fig. 2A. As expected, the removal extent of BPA increases with the ferrate concentration and reaches approximately 85% after 120 min in the dark at 0.4 g L⁻¹ of ferrate (Fig. 2A). However, the maximum degradation extent tends to a limit with a large excess of ferrate (Fig. 2B). Indeed, self-decomposition of ferrate (R1) becomes more important at higher concentration and it is not favorable to BPA removal (Han et al. 2015). To study the ferrate-mediated heterogeneous photo-Fenton process, the concentration of 0.04 g L⁻¹ was chosen for the following parts of the work in order to better observe negative/positive effects of tested parameters.

UVA irradiation was also turned on during the degradation of BPA to improve the oxidation process. Indeed, the ferrate decomposition leads to the production of H₂O₂ in our experimental conditions (Fig. S5), which is in accordance to the literature (Lee et al. 2014; Sharma et al. 2015). Although UVA irradiation can trigger photochemical activation of H₂O₂ to produce hydroxyl radicals (HO[•]) (Huang W et al. 2018), the effect of irradiation on the BPA degradation by ferrate oxidation exhibits a negligible increase, from 53% to 58% after 60 min (Fig. S6). To improve BPA degradation extent, the irradiation of the solution is applied once the ferrate is fully decomposed (*i.e.* after 60 min) for 2 main reasons: (i) solid iron oxides/hydroxides from ferrate have different physico-chemical properties compared to those of synthetic oxides/hydroxides (Batarseh et al. 2007; Miklos et al. 2018; Wang et al. 2016) and (ii) decomposed ferrate contains crystallized magnetite (section 3.1.1). This ferrate-mediated heterogeneous photo-Fenton process, in presence or absence of H₂O₂ is reported in Fig. 3,

where different steps can be identified. The first one corresponds to the fast degradation of BPA in the presence of ferrate (from 0 to 60 min). A second step starting from 60 min corresponds to the effect UVA radiation which triggers photo-Fenton process, thus BPA further degrades, especially in the presence of 1 mM H₂O₂. In other words, the BPA degradation is assigned to Fe(III) photolysis (R2) and reactivity of photogenerated Fe(II) with H₂O₂ (R3). However, this new combined oxidation treatment is efficient only at pH ≤ 4.0 (Fig. 3).



For comparison, classical heterogeneous photo-Fenton experiments are conducted at pH = 4.0 using different synthetic iron oxides/hydroxides, namely goethite and hematite (Fig. S7) while a previous work using magnetite is already reported (Huang W et al. 2017). It is clear that ferrate-mediated photo-Fenton oxidation is more advantageous due to (i) the first degradation stage of BPA by ferrate (until t = 60min) and (ii) the more efficient heterogeneous photo-Fenton process. This second stage is almost two times more efficient than in classical heterogeneous processes and it is due to the presence of oxides with different physico-chemical properties (Batarseh et al. 2007; Miklos et al. 2018; Wang et al. 2016).

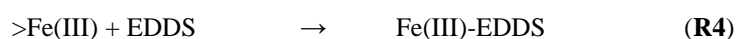
3.2.2. Valorization of ferrate using natural and non-toxic compounds

In order to design a sustainable process for wastewater treatment, the decrease of pH in the ferrate-based treatment could be operated using compounds of natural origin. Ascorbic acid (AA) is an excellent candidate since it is an antioxidant substance contained in many fruits and vegetables. In addition, AA has reducing and complexing properties that are able to improve the iron cycle (Hou et al. 2016, 2018; Huang X et al. 2017). Different amounts of AA are added to ferrate/BPA system after 60 min, then the solution was left for next 30 min before addition of H₂O₂ (1 mM) (Fig. 4). The initial 60 min reaction and induction time of 30 min were necessary to avoid degradation of AA by ferrate and to allow efficient reduction of Fe(III) into Fe(II). The Fe(II) released in solution is stabilized by the formation of Fe(II)-ascorbate complex, thus improving the iron cycle (Hou et al. 2016, 2018; Huang X et al. 2017). The use of AA obviously improves the ferrate-mediated oxidation process (Fig. 4). Control experiments are performed with only AA and H₂O₂ (Fig. S8) and no degradation of BPA was observed. The efficient removal of BPA was assigned to enhanced photolysis of Fe(III) and Fenton reactions (R2 and R3). The difference between dark (Fig. 4A) and irradiated systems (Fig. 4B) was

the net contribution of UVA light which accelerates the BPA removal extents from +10 to +20 % according to the AA concentration. This enhancement obtained under UVA is explained by considering the photolysis of Fe(III) into Fe(II) which is reported in Fig. 5. After addition of 1 mM of AA after 60 min, the concentration of Fe(II) increases up to 12.5 μM at $t > 90$ min. Then, the concentration drops after the addition of 1 mM of H_2O_2 due to its consumption by the Fenton reaction (R3). Under UVA, the decrease of Fe(II) concentration is less pronounced due to its renewal from Fe(III) photolysis (R2). An interesting point is that under UVA and beyond 180 min, the degradation reaction still continues (Fig. 4A) which is consistent to the constant increase of Fe(II) under UVA (Fig. 5). On the other hand, in the dark, the degradation efficiency reaches its limit after 180 min (Fig. 4B) with no more change in Fe(II) concentration suggesting that H_2O_2 is the limiting reactant (R3).

By comparison, similar experiments are performed using lower concentration of ferrate (0.01 g L^{-1} ; Fig. S9). Briefly, even if the concentration of produced Fe(II) is approximatively 2 times less than in the system containing 0.04 g L^{-1} of ferrate, the maximum BPA degradation extent was approximatively unchanged (around 95%). At 0.04 g L^{-1} of ferrate, when AA concentration increased to 1.0 mM, the initial pH of 10.0 decreased to 4.6 which is more beneficial for Fenton-based processes (Fig. 4). However, at higher concentration (1.5 mM), it is possible to see a negative effect on the BPA degradation (Fig. 4) which is due to a significant quenching effect on generated hydroxyl radicals by the antioxidant.

Although the use of AA is a promising way to valorize the ferrate decomposition byproducts, it is necessary to investigate another strategy since acidic pH cannot be considered for viable wastewater treatment. Therefore, one key parameter is the use of iron complexing agent to increase the pH of the ferrate-mediated heterogeneous photo-Fenton process at environmentally relevant conditions. EDDS is an efficient iron complexing agent and a harmless substitute to EDTA. Different amounts of EDDS were added to the ferrate/BPA system after 60 min followed by addition of H_2O_2 (1 mM) 30 min later (Fig. 6). Prior to the addition of EDDS, the pH was fixed at 6.0 ± 0.2 while the UVA irradiation was turned on once EDDS was just added to the solution in order to improve the dissolution of Fe(III) (R4 and R5). Indeed, EDDS leads to the formation of a soluble and reactive form of iron at near neutral pH. Moreover, Fe(III)-EDDS complex could modify the redox potential of iron since this soluble complex can contribute to both oxidative and reductive steps of Fenton-like chemistry (Huang et al. 2013).



The total iron concentration increased from 20 to 40 μM in presence of 50 μM of EDDS under UVA (Fig. 6A). The concentration of Fe(II) follows a similar trend. After addition of H_2O_2 , the concentration of iron decreases (Fig. 6A) due to the consumption of soluble Fe(II) and Fe(III) species by the (photo)Fenton-based processes. Concerning the BPA degradation, the combination of EDDS and UVA irradiation at $t = 60$ min followed by addition of H_2O_2 at $t = 90$ min in the ferrate/BPA system (Fig. 6B) improved the BPA degradation extent after 180 min compared to the ferrate alone (+20 %). The optimal EDDS concentration was found to be 50 μM since either low amount (20 μM) or excess of EDDS (200 μM) limited the BPA degradation. This is explained by the lower quantity of iron transferred in solution at lower EDDS concentration while the involvement of this organic ligand at higher concentration is detrimental due to the reactivity with hydroxyl radicals. The pH which was monitored during the BPA degradation in the photochemical ferrate/EDDS/ H_2O_2 system slightly increased from 6.0 to 6.7. Although the valorization of oxidation by ferrate using EDDS appeared less efficient than in the case of ascorbic acid, the strong advantage of the ferrate-mediated heterogeneous photo-Fenton process is the possible use at circumneutral pH and thus, its potential application to real wastewater treatment.

3.2.3. Application to municipal wastewater treatment

In order to investigate the feasibility of the above ferrate-mediated heterogeneous photo-Fenton oxidation process, treatment of municipal wastewater spiked by BPA is performed using the optimal conditions described above (the photochemical system using 0.04 g L^{-1} of ferrate with 1 mM H_2O_2 in the presence of either 1 mM AA or 50 μM EDDS) (Fig. 7). The pH after the first oxidation step by ferrate is adjusted at 6.7. It was worth noting that the efficiency of oxidation by ferrate was not affected by the WW matrix since BPA degradation extents reached also 45% after 300 min. This indicates that ferrate has a better reactivity towards BPA than humic substances which account for most of the organic matter in WW. Due to the presence of other components in WW playing the role of scavengers (Table S1), the observed degradation extents of BPA are logically lower than in the synthetic water. By increasing the concentration of AA and EDDS, slight increase in the BPA degradation is obtained (Fig. 7). It is interesting to observe that, in WW, the ferrate-mediated heterogeneous photo-Fenton treatment in presence of AA is more affected than using EDDS, compared to the degradation extents of BPA obtained in synthetic water. Indeed, in synthetic water, almost 100% of BPA was removed by the AA-enhanced treatment (Fig. 4A) while in WW, a maximum of 63% degradation extent is observed (Fig. 7A). On the other hand, for the EDDS-enhanced treatment, 68% (Fig. 6B) and 60% (Fig. 7B) of BPA is degraded in synthetic

water and WW, respectively. These results can be explained by the non-selective reactivity of AA which does not react exclusively with iron species in the treated wastewater, while EDDS is rather selective in the formation of Fe(III) complexes. In addition, the organic matter present in wastewater probably has a complexation/stabilization effect on aqueous iron (Garcia Ballesteros et al. 2017). Therefore, the EDDS-enhanced ferrate-mediated heterogeneous photo-Fenton treatment is considered as the most viable for municipal WW treatment in our experimental conditions.

4. Conclusions

In this work, we investigated for the first time the combination of two oxidation processes in an innovative one called ferrate-mediated heterogeneous photo-Fenton process. In our experimental conditions, oxidation by ferrate only removed 45% of bisphenol A (BPA). Since ferrate was decomposed in solid iron oxides species, including crystallized magnetite, their valorization in different heterogeneous photo-Fenton processes were performed for the first time. Under UVA, which is a part of solar radiation, and in presence of either ascorbic acid or EDDS which are natural origin and non-toxic compounds, we designed an environmentally friendly and sustainable wastewater treatment. Indeed, UVA is known to trigger Fe(III) photolysis while AA and EDDS are able to reduce Fe(III) into Fe(II) and to efficiently complex Fe(III), respectively. In our experimental conditions, almost complete degradation of BPA in synthetic water was observed using AA-enhanced ferrate-mediated photochemical system while 68% BPA removal was obtained using EDDS in this new treatment method. However, this latter ferrate-mediated heterogeneous photo-Fenton process was the most viable for real WW treatment since it can be used at circumneutral pH and the effect of WW matrix has a smaller impact. Therefore, the application of the EDDS-enhanced treatment was the most promising for municipal WW spiked by BPA with a degradation extent of 60%. This work highlighted a new possibility to consider wastewater treatments *via* a modified process based on oxidation by ferrate which is a promising and innovative strategy in the enhancement of persistent organic pollutants degradation in water.

Acknowledgements

Authors acknowledge financial support from the CAP 20-25 I-site project and the Fédération des Recherches en Environnement (FRE) through the CPER “Environment” founded by the region AURA, the French government and the European Commission (FEDER). OM also acknowledges the financial support for the post-doctoral provided by University Clermont Auvergne.

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