A new perspective for Dissolved Organic Matter in water potabilization: Exploitation before removal

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ABSTRACT

The Dissolved Organic matter (DOM) has been demonstrated to contribute to water self-cleaning and waste-derived substances similar to DOM have already been tested as Fe(III) complexants to degrade compounds of emerging concern (CECs) via photo-Fenton process at pH 5–6. On the other sideDOM has to be removed during natural water potabilization because it negatively affects taste and smell and yields toxic disinfection by-products. In the present work, the DOM exploitation before removal has been explored for the first time. In particular, DOM has been developed as an iron complexing agent for the photo-Fenton degradation of caffeine (taken as representative CEC) in water matrix. The effect of pH, DOM concentration and Fe(II) concentration on the process has been studied. The formation of DOM-Fe(III) complexes has been demonstrated through potentiometric and fluorescence measurements. Promising results for caffeine degradation have been obtained, also when applying the method to a riverine water sample.

1. Introduction

Dissolved Organic Matter (DOM) can be considered an environmentally ubiquitous substance featuring multifaceted physical-chemical characteristics [3,19,38,44]. The presence in its structure of both polar and nonpolar functionalities and of complexing moieties makes DOM capable of interacting with organic (including non-polar) compounds as well as with metal ions, affecting their environmental mobility, reactivity and bioavailability [2,15,16,36,67,78].

Aquatic DOM has been studied for several years for its contribution to the water self-cleaning capability, since the presence of phenolic and quinone groups promote, under sunlight, the formation of reactive species able to attack organic compounds of anthropogenic origin [10–12,31,55,58,6,60,73]. Based on this, in recent years it has been considered the possibility to introduce in polluted water, waste derived substances very similar to DOM in order to promote water photo cleaning ("waste cleaning waste" approach) [4,5,8,53]; moreover DOM-like substances have been also tested as chelating agents for iron (III) to allow running iron-mediated oxidative degradation of pollutants [28–30].

On the opposite side, when natural waters undergo potabilization in order to be used for human consumption, the presence of DOM negatively influences the water quality in term of taste (and smell at high concentration) [40,72]; in addition, DOM can react during disinfection processes leading to toxic by-products [9,24,37,39,75]. Efforts have been therefore made to eliminate DOM in the water pretreatments before chlorination [7,48,49,62,66,79].

Considering that also surface waters can be used for human consumption, an additional issue, appeared in the last decades, is represented by the so-called contaminants of emerging concern (CECs), that are substances of anthropogenic origin present in solution at very low concentration that could affect the water quality and threat environmental and human health through chronic toxicity, biomagnification, endocrine disruption, etc,…. [22,34,71,76]. The presence of CECs in natural waters (especially in surface ones) is mainly linked to the effluents of wastewater treatment plants (WWTP) that treat urban wastewater and/or industrial waters before their return to water bodies. A characteristic common to many CECs is that they are recalcitrant to biological treatments which are the most applied in WWTP. The effective removal of CECs from wastewater is increasingly a pressing imperative and water utilities need suitable technologies to determine and eliminate CECs from effluents of WWTP. In recent years, in addition to adsorption on activated carbon and membrane treatments, advanced oxidation processes (AOPs) have been proposed [14,45–47,61]. Among AOPs, the photo-Fenton process is based on the activation of hydrogen peroxide by iron salts to generate hydroxyl radicals able to oxidize

organic pollutants; the main limitation is that this process requires acidic pH (around 3) to be operated [42,57]. To overcome this problem several studies dealt with the search of iron ligands able to form photoactive complexes, in order to run photo-Fenton processes at pH closer to neutrality [1,18,20,21,32,45,65].

As far as we know, there have been no studies considering the exploitation of DOM as an auxiliary in the removal of CECs, before water potabilization treatments, that include DOM elimination.

In the present study we considered the water potabilization before delivery of drinking water and in particular we focused our attention on the following evidences reported in the literature (and already mentioned):

1. DOM contributes, under natural solar light, to water self-cleaning process;
2. DOM features complexing properties towards metal ions;
3. The potabilization treatments include the removal of DOM because it can affect water taste and smell and, if chlorination is applied, it could form harmful chlorination by-products.

Based on these premises, we explored the possibility to boost the self-cleaning capability of natural water by means of DOM-assisted photo-Fenton process at circumneutral pH values, upon addition of H_2O_2, together with a small amount of Fe(II), if not yet present, to degrade CECs eventually present.

The aim is not to propose the use of DOM-assisted photo-Fenton process as an alternative to other treatments, rather to exploit DOM already present in natural water as a complementary contribution to CECs abatement, prior to DOM removal in water potabilization treatments. This could facilitate the final water refinement before its delivery, that in many real cases is performed by means of adsorption on activated carbon followed by reverse osmosis or nanofiltration [23].

Caffeine has been taken as model CEC and the effect of several experimental parameters (pH, DOM concentration, iron concentration and oxidation state) on its abatement has been explored.

Beside a synthetic water sample, preliminary experiments have also been performed on riverine water samples.

2. Experimental

2.1. Chemicals

Caffeine (≥99%), iron (II) sulphate heptahydrate (≥99%), sodium phosphate monobasic monohydrate (≥99%), sodium phosphate dibasic dodecahydrate (≥99%), ammonium iron (II) sulfate hexahydrate (Mohr's salt, 99%), potassium chloride (≥99%), o-phenanthroline (99%), acetic acid (>99%), and ammonium acetate (≥98%) were purchased from Sigma-Aldrich. Hydrogen peroxide solution (30%) was purchased from ITW reagents. Iron (III) sulfate monohydrate (≥76%) was purchased from Fluka and Suwannee River DOM (SR-DOM) (product code 2R101N) was purchased from the International Humic Substances Society (IHSS). 2-Propanol and chromatographic UHPLC-grade acetonitrile (ACN) were purchased from Carlo Erba Reagents. Potassium hydroxide solution 0.2 mol/L used as titrant was prepared by diluting Merck (Darmstadt, Germany) concentrated product and its concentration was assessed by standardization against potassium hydrogen phthalate (Sigma-Aldrich). All aqueous solutions, if not differently specified, were prepared using ultrapure water Millipore Milli-Q™ (TOC < 2 ppb, 18.2 MΩ cm).

2.2. Caffeine quantification

Caffeine concentration was determined by HPLC model MERK HITACHI L-6200 Intelligent Pump coupled with a UV-Vis L-4200 detector and equipped with a RP-18 (5 µm) LIChrospher® 100 Merck (125 ×4 mm) reverse phase column. Analyses were performed using isocratic

conditions (12/88, ACN/ultrapure water) and caffeine absorbance was monitored at 272 nm. An injection loop of 20 µL of volume was used for all samples. Irradiated samples containing hydrogen peroxide were quenched with methanol right after sampling to stop dark degradation of caffeine by Fenton reaction; to do so, 100 µL of methanol were added to 500 µL of sample directly inside the HPLC vial. Vials were stored in the fridge until analysis.

2.3. Absorbance, fluorescence, and DOC measurements

Solutions absorbance was measured using a UV-Vis CARY 100 Scan UV–visible spectrophotometer and a pair of 1 cm optical path quartz cells using ultrapure water as reference. Fluorescence was measured using a Varian Cary Eclipse Fluorescence Spectrophotometer with slits opening at 10 nm for both excitation and emission. Before recording the fluorescence, all samples were diluted to obtain an absorbance of 0.1 at 254 nm.

The measurement of DOC was carried out with a Shimadzu TOC-VCSH Total Organic Carbon Analyzer, equipped with an ASI-V auto-sampler and fed with zero-grade air. DOC values were determined as the difference between total carbon (TC) and inorganic carbon (IC).

2.4. Irradiation setup

2.4.1. Photo-Fenton processes
Caffeine solutions were irradiated in closed Pyrex glass cells using a Solar Box CO.FO.ME.GRA (Milano) irradiating device equipped with a xenon lamp and a filter with cutoff at 340 nm; 20 mL of solution were placed inside each cell and solutions were maintained under magnetic stirring during the irradiation. Different amounts of DOM; Fe(III) salts and H_2O_2 were added. Caffeine degradation kinetics were obtained by sampling from the same cell at the different irradiation times.

2.4.2. H_2O_2 photolysis
Hydrogen peroxide was added to caffeine aqueous solutions to study caffeine oxidation both in the dark and under irradiation (analogous instrumental set-up adopted for photo-Fenton process).

2.4.3. pH-metric titrations
Alkalimetric titrations were carried out on 50 mL of a solution of SR-DOM 40 mg/L and on 50 mL of a solution containing the same amount of SR-DOM and 10 mg/L of Fe(III). The titrant was KOH standard solution 0.2 mol/L. In this set of experiments, iron concentration was higher than the one used in the degradation tests for the sole purpose of getting more evident results. Measurements were carried out at 25 °C and with an ionic strength of 0.1 mol/L, KCl was used as ionic medium. In order to avoid O_2 and CO_2 contamination during the titration, a stream of purified N_2 was bubbled in the titration cell. Titrando 888 (Metrohm, Herisau, Switzerland) was used to perform the titrations in DET (Dynamic Equivalence point Titration) modality and the maximum accepted signal drift was settled at 0.5 mV/min. The electrode couple was calibrated in terms of H^+ concentration by titrating a $5 \cdot 10^{-3}$ mol/L HCl solution at the working ionic strength (0.1 mol/L) with standard KOH.

3. Results and discussions

3.1. Preliminary tests

Preliminary tests were run to assess the stability of caffeine under different experimental conditions. Caffeine concentration was 5 mg/L for all experiments described in this work.

At first, the stability of caffeine irradiated in MilliQ water at pH 6.0 (adjusted using 0.1 M phosphate buffer) was investigated. The irradiation was run in triplicates and in each case caffeine degradation was inferior to 3% after 180 min of irradiation and therefore direct photolysis was considered to be negligible. Caffeine degradation in the

presence of hydrogen peroxide both in dark conditions and under irradiation was also measured; as shown in Fig. S1, caffeine degradation was negligible in the dark but was around 30% after 3 h when under irradiation due to partial photolysis of H_2O_2. The concentration of added hydrogen peroxide was 51 mg/L corresponding to the double of the stoichiometric concentration required for caffeine full mineralization.

DOM is known to generate upon irradiation reactive oxidant species such as singlet oxygen, triplet excited states, hydroxyl radical and hydrogen peroxide [26,59]. To verify the possible involvement of such species in the degradation of caffeine under the studied conditions, caffeine was irradiated for 180 min in the presence of Suwannee River DOM (SRDOM) added at the concentration of 40 mg/L. As reported in Fig. S2, caffeine degradation after 180 min in the sole presence of SRDOM was around 10% but, when both SRDOM and H_2O_2 were added, caffeine degradation profile was similar to the one obtained in the sole presence on hydrogen peroxide. SRDOM was therefore only able to partially induce caffeine degradation but its presence resulted not influent when H_2O_2 was also added in the reaction medium.
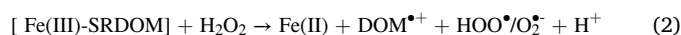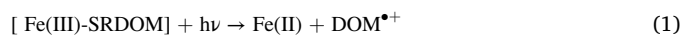
3.2. Circumneutral photo-Fenton in the presence of SRDOM

SRDOM was used as an iron interacting agent with the goal of increasing the photo-Fenton working pH from strongly acidic values, at which it is classically performed, to circumneutral pH values therefore avoiding acidification and post-treatment neutralization of the treated water. Indeed, it is known that DOM can complex the Fe(III) suppressing hydrolysis and precipitation processes [33,51] allowing to keep Fe(III) available for the photo-Fenton reactions. DOM can also reduce the Fe(III) to Fe(II), ability that promotes Fenton reaction, but this process is favored in acidic solutions, a condition quite far from the one used in this work ([25,52].

At first, three series of parallel experiments at different pH values were performed to evaluate the influence of the pH on the degradation of caffeine. Iron(II), hydrogen peroxide, and SRDOM concentrations were fixed to 1 mg/L, 51 mg/L, and 40 mg/L respectively while the solution pH was adjusted to 5.0, 6.0, and 7.0. The concentration of caffeine against irradiation time for the different pH values is reported in Fig. 1A. While very similar results were obtained at pH 5.0 and 6.0, at pH 7.0, the degradation of caffeine was much slower. Such a drastic change in treatment efficiency over a narrow pH range is not unusual for photo-Fenton processes carried out in the presence of iron complexing agents. *Subramanian e Madras,* working with saccharic acid as chelating agent, reported a drastic drop in methylene blue degradation rate when pH was raised from 4.0 to 5.0 due to less efficient Fe(II) regeneration [69]. In the present work, the efficiency drop was observed to take place between pH 6.0 and 7.0, i.e. 2 units of pH higher, therefore showing how SRDOM

could significantly increase the working pH range compared to saccharic acid. Since pH 6.0 represented an optimal compromise between the required acidification of treated water and system performances, all following experiments were performed at this pH.

Then, the role of SRDOM concentration on the system performances at pH 6.0 was evaluated. To do so, different concentrations of SRDOM ranging from 5 to 40 mg/L were added to the photo-Fenton system while iron and hydrogen peroxide concentrations were maintained the same as before. The results, reported in Fig. 1B, show a clear dependence of the caffeine degradation rate on the concentration of added SRDOM. In particular, almost complete degradation was achieved after 180 min of irradiation in the presence of SRDOM 40 mg/L (black squares) and slightly slower degradation was achieved in the presence of 10 and 20 mg/L of SRDOM (red triangles and blue dots respectively). These results can be explained by taking into account the formation of photo-active SRDOM-Fe(III) complexes that accelerate the photo-reduction of Fe(III) to Fe(II) both via photochemical and dark processes (reactions 1 and 2), typically representing the rate-limiting step in the iron catalytic cycle of Fenton processes [70].

$$[Fe(III)\text{-}SRDOM] + h\nu \rightarrow Fe(II) + DOM^{\bullet+} \tag{1}$$

$$[Fe(III)\text{-}SRDOM] + H_2O_2 \rightarrow Fe(II) + DOM^{\bullet+} + HOO^{\bullet}/O_2^{\bullet-} + H^+ \tag{2}$$

Such effect has been already studied for a variety of organic iron-complexing molecules such as oxalate [13], EDTA [80] or EDDS [77] and it has been recently hypothesized the effect of NOM in a study on UVC-H_2O_2 degradation of acetaminophen [43].

3.3. Evidences on the formation of Fe(III)-SRDOM complex

The capability of SRDOM to form stable complexes with Fe(III) allowing to maintain Fe(III) in solution at circumneutral pH has been confirmed by fluorescence measurements and by alkalimetric titrations.

The formation of complexes of organic ligands with paramagnetic elements such as Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} is reported in the literature to quench fluorescent emission of the ligand via intramolecular energy transfer promoting non-radiative relaxation pathways [68]. Such an effect has also been observed for DOM and the fluorescence attenuation of Suwannee river fulvic acid due to the formation of complexes with Fe(III) has been observed [74].

To gather experimental evidence over the formation of Fe(III)-SRDOM complexes in the system under study, the fluorescence excitation-emission matrices (EEMs) of SRDOM both in the absence (Fig. 2A) and in the presence of increasing iron(III) concentrations, i.e. 1, 5, and 10 mg/L, (Figs. 2B to 2D) have been recorded.

The interpretation of the EEM spectra was performed following the fluorescence regional integration (FRI) method [17,63], that divides the
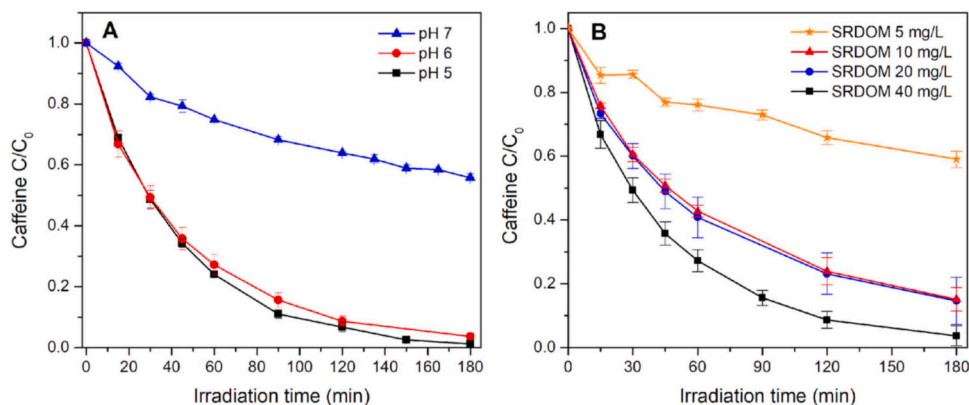

Fig. 1. A) Caffeine concentration over irradiation time at pH 5.0 (black), 6.0 (red), and 7.0 (blue) in the presence of Fe(II) 1 mg/L, H_2O_2 51 mg/L, and SRDOM 40 mg/L. B) Caffeine concentration over irradiation time at pH 6.0 in the absence of SRDOM (orange) and in presence of SRDOM 5 mg/L (orange), 10 mg/L (red), 20 mg/L (blue), and 40 mg/L (black). Iron and H_2O_2 concentrations were 1 mg/L and 51 mg/L respectively.
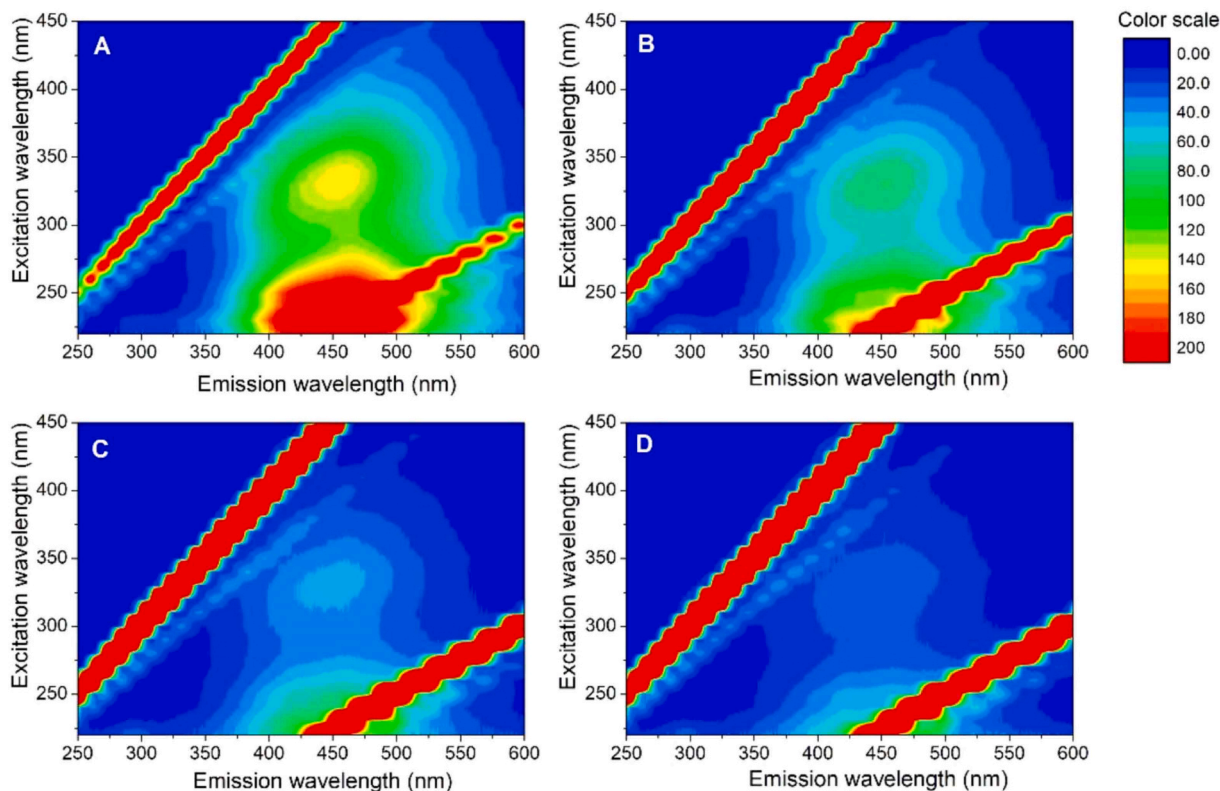
Fig. 2. Normalized fluorescence excitation-emission matrices (EEMS) of SRDOM 40 mg/L recorded at pH 6.0 in the presence of increasing iron (III) concentration: 0 mg/L (A), 1 mg/L (B), 5 mg/L (C), and 10 mg/L (D) of added iron.

EEM spectra into five regions, characteristic of specific components of DOM (aromatic proteins, microbial by-products, humic and fulvic-like).

The EEM recorded for the sole SRDOM 40 mg/L exhibits the classical fluorescence associated with humic and fulvic acids as it can be seen in Fig. 2A. When iron is added a significant fluorescence decrease is observed when increasing iron content, in agreement with the hypothesis of Fe(III)-SRDOM interaction.

Additional evidence on the formation of Fe(III)-SRDOM complexes was obtained via alkalimetric titrations that were carried out on solutions of SRDOM in the absence and in the presence of Fe(III). The
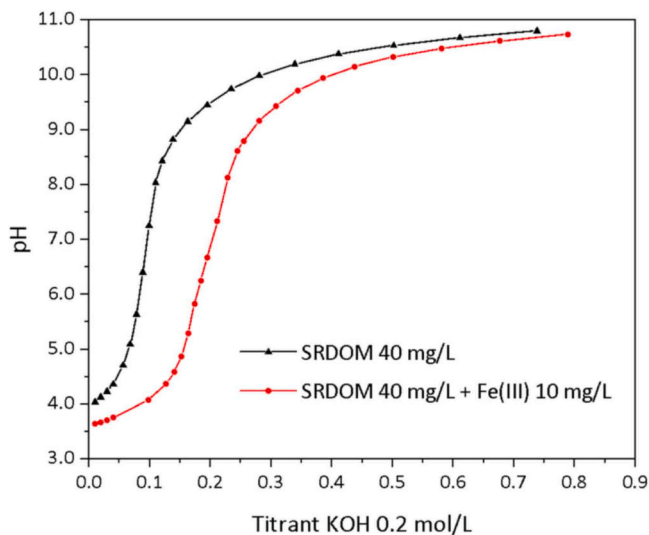

Fig. 3. Alkalimetric titrations of 40 mg/L Suwannee River DOM solution (black line) and 40 mg/L Suwannee River DOM solution with Fe(III) 10 mg/L (red line). Ionic strength 0.1 mol/L (medium KCl). Temperature 25 °C.

resulting titration curves are reported in Fig. 3. It can be seen that for the same amount of titrant added, the pH of the solution containing the Fe (III) was lower than that containing only DOM. This could be due to both hydrolysis of the metal cation and protons released by DOM during the coordination of Fe(III). Based on the formation constants of Fe(III) hydrolytic species, in the working pH range (3.6 – 10.8), Fe(III) should be present as the solid species $Fe(OH)_3(s)$, but turbidity was observed only before the start of the titration procedure, suggesting that when the deprotonation of DOM occurs coordination the Fe(III) took place avoiding the precipitation of $Fe(OH)_3(s)$. The potentiometric results are in accordance with those reported by Pandeya, 2000 who studied the interaction of Fe(III) with fulvic acids. Moreover, it is well known that donor groups of DOM, in particular carboxyl and hydroxyl groups, can coordinate metal cations ([27,35,41,50], p. 10; [51]). Being protogenic functionalities, their interaction with metal cations provides the release of H^+ coherently with the obtained results.

3.4. Effect of iron concentration and oxidation state

Iron is commonly detected in natural waters under the form of Fe(II) and Fe(III) cations and its concentration typically ranges from fractions of ppm to tens of ppm depending on the composition of the minerals in contact with the water body, the pH, and the presence of complexing agents. Ideally, if the natural iron concentration of the water body is high enough, it would be possible to perform the photo-Fenton treatment without external iron addition. To investigate the useful iron concentration range and its most active oxidation state, a series of tests were performed. In Fig. 4A is reported the caffeine degradation catalyzed by iron(II) (red curve) or iron(III) (black curve) both added at the concentration of 1.0 mg/L; the other water matrix constituents were maintained unchanged (SRDOM 40 mg/L, H_2O_2 51 mg/L, pH 6.0). As expected, the use of iron(II) as starting cation led to much faster caffeine degradation and nearly complete caffeine removal was achieved after
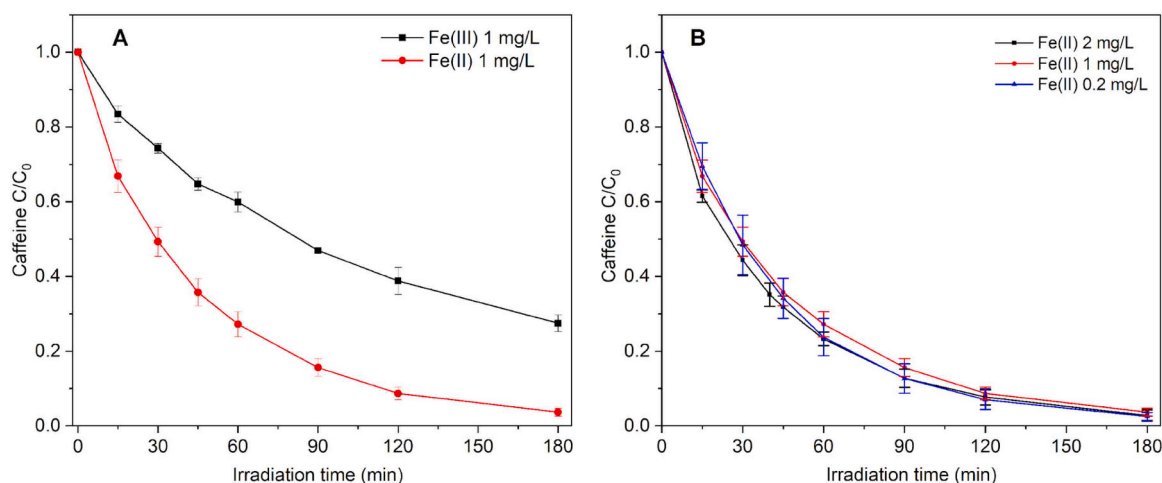
Fig. 4. A) Caffeine concentration over irradiation time at pH 6 in the presence of Fe(II) 1.0 mg/L (red) and Fe(III) 1.0 mg/L (black). B) Caffeine concentration over irradiation time at pH 6–0 in the presence of Fe(II) 2.0 mg/L (black), 1.0 mg/L (red) and 0,20 mg/L (blue). In both series of experiments, the concentration of hydrogen peroxide and SRDOM was 51 mg/L and 40 mg/L respectively.

3 h of irradiation. On the contrary, when using iron(III), the degradation significantly slowed down (~30% of residual caffeine after 3 h) as Fe(II) needed to be formed through reactions 1 and 2. This behavior confirms the crucial role of Fe(II) in the activation of hydrogen peroxide to form hydroxyl radicals. Then, the effect of three different Fe(II) concentrations, i.e. 0.20, 1.0 and 2.0 mg/L, on the kinetic of caffeine degradation was also studied and the results are shown in Fig. 4B. No significant difference was observed in the three cases meaning that the treatment could be performed efficiently with 0.20 mg/L of added iron. This result is particularly interesting considering that such concentration of total iron could already be present in natural waters.

3.5. Caffeine degradation in real water matrix

To start exploring the efficiency of the treatment in real water matrices, a preliminary trial was performed on a sample of the Stura river (Piedmont region, northwest of Italy) whose composition is reported in Table S1. The sample was vacuum filtered using 0.45 μm filters, buffered at pH 6.0, and H_2O_2 and caffeine were added in the same concentration used in all previous experiments. To assess the contribution of H_2O_2 photolysis compared to photo-Fenton, experiments were run either in the absence or in presence of added Fe(II) 1 mg/L. Fig. 5 reports the results obtained in Stura river water, compared with the ones obtained in MilliQ-water spiked with SRDOM 5.0 mg/L previously displayed. It can be seen that no caffeine degradation in buffered Stura water took place (red dots); when H_2O_2 51 mg/L was added (green triangles) about 20% caffeine depletion was observed after 180 min of irradiation. This result was considerably lower than the one observed for the photo-Fenton experiment, where iron was also added in the medium (blue diamonds).

The DOM concentration measured for the Stura river sample was 3.94 mg/L. It can be seen that despite DOM concentration being slightly lower in the real water sample, caffeine degradation was comparable with the one observed working in MilliQ water. This result is rather surprising when taking into account that the natural sample contained around 20 mg/L of bicarbonate anions that typically act as hydroxyl radical scavengers.

In order to explain the observed behavior, the fluorescence matrix of Stura water was recorded (Fig. S3). Opposed to what was observed for SRDOM EEM, no signal was present in the humic and fulvic acids region, while a very weak signal was detected in the aromatic protein region (mainly tryptophan like). At the same time is not surprising the absence of such a signal in the SRDOM fluorescence matrix, since SRDOM is commercially available in the form of lyophilized powder and the
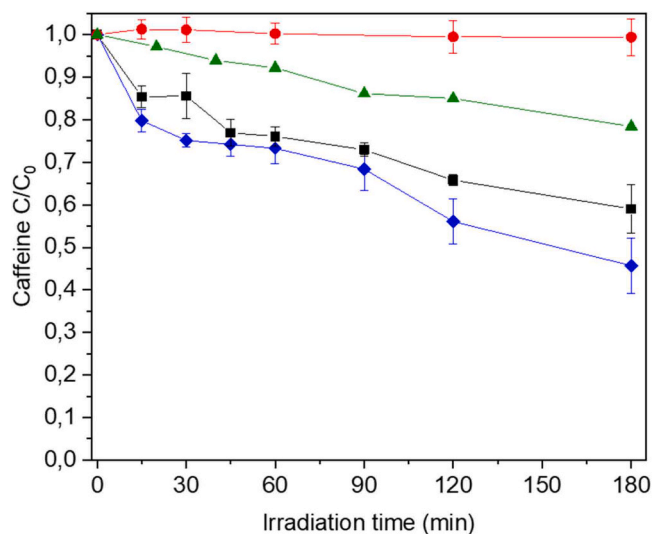

Fig. 5. Caffeine photolysis in Stura river water (red dots); caffeine degradation in Stura river water in the presence of H_2O_2 51 mg/L (green triangles); caffeine degradation at pH 6.0 during photo-Fenton treatment performed in Stura river water (blue diamonds) and in ultrapure water spiked with SRNOM 5 mg/L (black squares).

desalination steps required for the preparation of these materials typically cause the loss of the low MW fractions of DOM that have often been reported in the literature to be the most photo-active ones [54,56]. This result underlines the need of further investigation on the composition of organic components of the natural water matrix, to get insights on its role in the process; in the present case it could be hypothesized that, with regard to caffeine degradation, the ability of NOM to form stable iron complexes would prevail over its photo-sensitizing properties.

4. Conclusions

The efficient caffeine degradation by means of Photo-Fenton treatment at pH 6 was efficiently performed at very low Fe ions concentration. The presence of DOM was confirmed as fundamental to maintain Fe (III) in solution as complex, also when working with a real riverine water sample.

This latter aspect opens to the exploitation of natural DOM in lagooning basins, used as pretreatment facilities for water treatment

plants, for example when river water is used for human consumption [64]. Indeed, hanks to the aid of natural solar light, the addition to the basin of a very low amount of iron, if not already present, and a reduced amount of H_2O_2, would enhance the DOM assisted-CECs photo--degradation with a positive effect on the further potabilization treatments. Considering that the classical Fenton/photo-Fenton processes are run at pH 2.8, the shift from such a strongly acidic pH value to pH 6 represents a notable improvement. At the moment, an optimal scenario in which to use the approach proposed in this work, would be in the presence of those natural waters having a native slightly acidic pH. In fact, many natural waters that are also rich in DOM, have a pH around 6 or lower (e.g. Suwannee River in USA, Rio Negro in Brazil, black rivers in Scotland) and would not therefore require pH adjustment.

DOM can therefore be reconsidered as a powerful and natural available auxiliary for CECs abatement in water for human consumption before its removal from water during the potabilization treatments.

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CRediT authorship contribution statement

Bianco Prevot Alessandra: Conceptualization, Methodology, Supervision, Writing – original draft, Writing – review & editing. **Berto Silvia:** Investigation, Writing – original draft, Writing – review & editing. **Urbano Antela Kevin:** Investigation. **Salucci Roberto:** Investigation, Methodology. **Palma Davide:** Conceptualization, Data curation, Methodology, 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.2024.111879.

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