

Heterogeneous photodegradation of methylene blue with iron and tea or coffee polyphenols in aqueous solutions

Claudio Kendi Morikawa and Makoto Shinohara

ABSTRACT

Recently, we developed two new Fenton catalysts using iron (Fe) and spent tea leaves or coffee grounds as raw material. In this study, Fe-to-tea or Fe-to-coffee polyphenol complexes were successfully tested as heterogeneous photo-Fenton catalysts. The photodegradation efficiency of methylene blue solutions with Fe-to-polyphenol complexes was higher than that of homogeneous iron salts in the photo-Fenton process. Furthermore, the tested Fe-to-polyphenol complexes could be reused by simply adding H₂O₂ to the solutions. After three sequential additions of H₂O₂, the conventional catalysts FeCl₂·4H₂O and FeCl₃ removed only 16.6% and 53.6% of the dye, while the catalysts made using spent coffee grounds and tea leaves removed 94.4% and 96.0% of the dye, respectively. These results showed that the complexes formed between Fe and chlorogenic acid, caffeic acid, gallic acid and catechin, which are the main polyphenols in tea and coffee, can be used to improve the photo-Fenton process.

Key words | coffee polyphenols, methylene blue, photodegradation, photo-fenton, tea polyphenols

Claudio Kendi Morikawa (corresponding author)
Makoto Shinohara
National Agriculture and Food Research
Organization,
Postal 514-2392 Mie, Tsu, Ano,
Kussawa 360,
Japan
E-mail: ckm@affrc.go.jp

INTRODUCTION

Extensive application of synthetic dyes can cause considerable environmental pollution, making it a serious public concern. Among the various types of dyes, methylene blue (MB) is used in dyes, paint production and wool dyeing. MB is also used in microbiology, surgery, and diagnostics (Milani *et al.* 1992; Belaz-David *et al.* 1997) and as a sensitizer in the photo-oxidation of organic pollutants (Nubbe *et al.* 1995). Textile dyes should be removed before discharge to avoid water pollution (Babu *et al.* 2007). Among the advanced oxidation processes that are available, the Fenton and photo-Fenton processes are environmentally friendly techniques for the removal of dyes from aqueous solutions (Chacon *et al.* 2006). However, when the pH is high, iron (Fe) precipitates, and Fe sludge accumulates, reducing the efficiency of the process. The cost of treating Fe sludge is high and is frequently the limiting factor in the practical application of these processes.

On the other hand, coffee and tea drinks are the most consumed beverages in the world. Coffee grounds and tea dregs, which are waste materials of the tea and coffee industry, are produced daily in large amounts throughout the world. In Europe, America, and Japan, large amounts of coffee grounds are discharged from the food industry. Although part of them is

reused as compost and animal feed, most of the tea and coffee grounds are burned as waste, which results in the production of carbon dioxide, which is a greenhouse gas. In Japan, approximately 400,000 and 600,000 tons of coffee grounds and tea wastes, respectively, are produced every year. These wastes are usually mixed with common garbage (Tokimoto *et al.* 2005; Mussatto *et al.* 2011; Cruz *et al.* 2012) and burned. These wastes are highly pollutant due to the presence of organic material that demands a great quantity of oxygen in order to degrade (Silva *et al.* 1998). In addition, caffeine, tannins, and polyphenols present in these materials confer a toxic nature to them (Mussatto *et al.* 2011). Therefore, finding strategies that add value to the utilization of these wastes is of much interest. The chemical composition of these residues indicates that they have several applications. In particular, efforts are being made to implement adequate disposal approaches and potential reuses, including as horticultural or animal feed, biodiesel, fuel pellets, or activated carbon (Silva *et al.* 1998; Yang *et al.* 2003; Oliveira & Franca 2009; Mussatto *et al.* 2011). In an *in vitro* experiment, tea polyphenols were used to synthesize nanoscale zero-valent iron (Fe⁰) particles (Mallikarjuna *et al.* 2009) and heterogeneous Fenton catalysts (Morikawa 2013). Spent tea leaves have been tested

as a new non-conventional and low-cost adsorbent for the removal of basic dyes from aqueous solutions (Hameed 2009). The objectives of this study were: (1) to compare the Fe catalysts made using spent tea leaves and coffee grounds with homogeneous Fe salts as photo-Fenton catalysts; (2) to test chlorogenic acid, caffeic acid, catechin and gallic acid, which are the main polyphenols in coffee and tea beverages, as a model for the photo-Fenton process; and (3) to test the reusability of those materials.

MATERIAL AND METHODS

Materials

Light source

A 1.2 A/28 W LED (light-emitting diode) unit light source was used in the photo-Fenton experiments. The light unit was continuously supplied using a near-UV LED ($\lambda = 375$ nm) unit, 15 cm \times 15 cm in size (CCS Inc., ISC-150 \times 150-UU375, Kyoto, Japan) located 13.5 cm away from the bottom of the glass beaker. The light intensity of UV radiation at 1 cm from the bottom of the glass beaker was measured using an Asahi Spectra spectroscope HS-100S (Tokyo, Japan), and the UV intensity was set to 10 W m⁻². Figure 1 shows the spectra of the near-UV LED used in the kinetic experiments.

Chemicals

All chemicals used in this study were prepared using deionized water from a Millipore system with a resistance of 18.2 M Ω cm⁻¹. L(+)-Ascorbic acid (AsA) and anhydrous

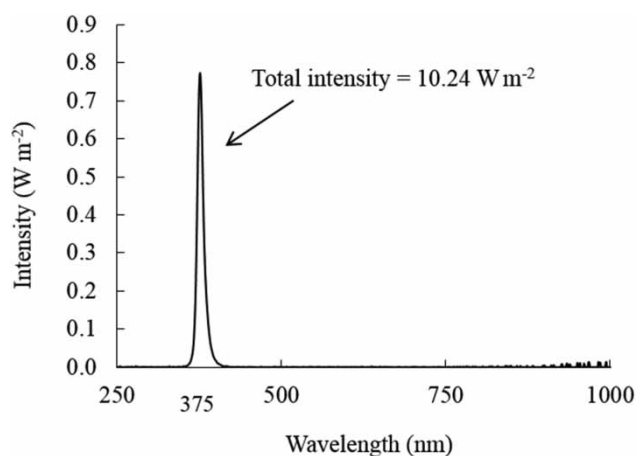


Figure 1 | Light irradiation spectra of the near-UV LED ($\lambda = 375$ nm) used in all photocatalytic experiments.

ferric chloride (FeIII) were obtained from Kanto Chemical Co., Inc. (Japan). Caffeic acid (3,4-dihydroxycinnamic acid) (CA), chlorogenic acid (CGA), (+)-catechin ((+)-3,3',4',5,7-flavanpentol) (CTh), citric acid (CTA), ferrous chloride tetrahydrate (FeII), 1,10-phenanthroline monohydrate and 35% hydrogen peroxide (H₂O₂) were obtained from Wako Pure Chemical Industries (Japan). MB was obtained from Merk KGaA (Japan). Spent tea leaves and coffee grounds were collected from Ajinomoto General Foods Inc. in Suzuka, Japan.

Synthesis of iron catalysts from spent tea and coffee grounds

Iron was reacted with the tea or coffee polyphenols by mixing 88 g of used tea leaves or coffee grounds with 12 g of FeIII and 300 mL of water, heated to 98 °C for 24 h in an autoclave (ALP Co. Ltd, TR-24S, Tokyo, Japan), then dried at room temperature. Subsequently, the materials were ground (Sansho Industry Co., Hammer Crusher NH-34, Osaka, Japan) to obtain fine particles smaller than 1 mm before use. The Fe catalyst developed using tea extract was named TEA-Fe, and that developed from coffee extract was named CAF-Fe.

Stock solutions preparation

Stock solutions of TEA-Fe and CAF-Fe were prepared by dissolving 2 and 5 g of each catalyst in 1 L of deionized water and filtering using a single sheet of filter paper (Advantec, 5A, Tokyo, Japan). The obtained solutions contained 0.9 mM L⁻¹ and 2.25 mM L⁻¹ Fe as TEA-Fe and CAF-Fe catalysts. FeII stock solutions containing 0.9 mM L⁻¹ and 2.25 mM L⁻¹ Fe were prepared by dissolving 178.9 mg and 447.3 mg, respectively, into 1 L of deionized water. Fe³⁺ stock solutions containing 0.9 mM L⁻¹ and 2.25 mM L⁻¹ Fe were prepared by dissolving 145.9 mg and 364.9 mg, respectively, into 1 L of deionized water. The 0.1 M L⁻¹ and 1 M L⁻¹ H₂O₂ stock solutions were prepared by mixing 9.72 mL and 97.2 mL of 35% H₂O₂ with 1 L of deionized water, respectively.

Stock solutions of Fe-to-chlorogenic acid (Fe-CGA), Fe-to-caffeic acid (Fe-CA), Fe-to-gallic acid (Fe-GA), Fe-to-catechin (Fe-CTh), Fe-to-ascorbic acid (Fe-AsA) and Fe-to-citric acid (Fe-CA) complexes were prepared with deionized water. Separate amounts of 180.16 mg of CA, 3,54.31 mg of CGA, 290.26 mg of CTh, 170.12 mg of GA, 192.12 mg of CTA and 176.12 mg AsA were each mixed with 162.21 mg L⁻¹ of FeIII. Each solution had an Fe-to-polyphenol ratio of 1:1 mmol L⁻¹. AsA and CTA were tested because they have

high antioxidant activity and iron chelation ability, respectively.

Treatments

Photo-Fenton test

The efficiency of the newly developed 'green' catalysts to degrade 0.016 mM L⁻¹ MB solution under light was compared to that of FeII and FeIII catalysts. FeII, FeIII, TEA-Fe and CAF-Fe were tested in the photo-Fenton process.

Nine treatments were studied under continuous light: (1) H₂O₂ (H₂O₂/hv); (2) TEA-Fe (TEA-Fe/hv); (3) TEA-Fe and H₂O₂ (TEA-Fe/H₂O₂/hv); (4) CAF-Fe (CAF-Fe/hv); (5) CAF-Fe and H₂O₂ (CAF-Fe/H₂O₂/hv); (6) FeCl₂·4H₂O (FeII/hv); (7) FeCl₂·4H₂O and H₂O (FeII/H₂O₂/hv); (8) FeCl₃ (FeIII/hv); (9) FeCl₃ and H₂O₂ (FeIII/H₂O₂/hv). Two concentrations of iron (0.018 and 0.045 mM) as FeII, FeIII, TEA-Fe, and CAF-Fe catalysts and 10 mM L⁻¹ of H₂O₂ were tested under light (hv). Treatments 2 and 4 were performed to evaluate the absorption capacity of TEA-Fe and CAF-Fe. All experiments were performed in a 25 °C room. Solution pH was not adjusted for any treatment.

Fe-to-polyphenol model and reusability tests

CGA, CA, CTh, CTA, AsA and GA, which are the main polyphenols in coffee and tea beverages, were reacted with Fe and used for an Fe-to-polyphenol model test. TEA-Fe and CAF-Fe were used as controls. Eleven treatments were studied under continuous light: (1) H₂O₂ only (H₂O₂/hv); (2) TEA-Fe; (3) CAF-Fe; (4) FeCl₃ and H₂O₂ (FeIII/H₂O₂/hv); (5) FeCl₂·4H₂O and H₂O₂ (FeII/H₂O₂/hv); (6) Fe-CGA and H₂O₂ (Fe-CGA/H₂O₂/hv); (7) Fe-CA and H₂O₂ (Fe-CA/H₂O₂/hv); (8) Fe-GA and H₂O₂ (Fe-GA/H₂O₂/hv); (9) Fe-CTh and H₂O₂ (Fe-CTh/H₂O₂/hv); (10) Fe-CTA and H₂O₂ (Fe-CTR/H₂O₂/hv); (11) Fe-AsA and H₂O₂ (Fe-AsA/H₂O₂/hv). Solutions containing 0.1 mM L⁻¹ of iron as TEA-Fe, CAF-Fe, FeII, FeIII, Fe-CGA, Fe-CA, Fe-GA, Fe-CTh, Fe-CTA and Fe-AsA catalysts and 10 mM L⁻¹ of H₂O₂ were tested under light (hv). All experiments were performed in a 25 °C room. Solution pH was not adjusted for any treatment.

Methods

Photo-Fenton test

For each treatment, 48.5 mL of 0.0164 mM L⁻¹ MB dye stock solution was transferred to an 80 mL beaker placed

in a reactor chamber. Then, 0.5 mL of 1 M L⁻¹ H₂O₂ and 1 mL of 0.9 mM L⁻¹ or 2.25 mM L⁻¹ Fe stock solutions as catalyst material were added to the solution depending on the treatment. The glass beakers containing the treatment solutions were placed on a magnetic stirrer and continuously stirred at 120 rpm in a reactor chamber. The experiments were conducted under identical conditions at room temperature (25 °C). The measurements were performed every 5 min over a total reaction time of 30 min. The absorbance of MB was determined spectrophotometrically with a Hitachi Gene Spec III (Tokyo, Japan) at 650 nm. The changes to pH of the solution were measured by a pH meter (Horiba, Horiba F-52, Kyoto, Japan).

Fe-to-polyphenol model and reusability tests

The objective of these tests was to evaluate the role of tea and coffee polyphenols on the photodegradation of MB by CAF-Fe and TEA-Fe catalysts in the photo-Fenton process and the reusability of those materials. The reusability test was carried out by four sequential additions of H₂O₂ and MB to the solutions which had the same initial Fe concentration as the catalysts, under continuous light irradiation. An irradiation box attached to a spectrophotometer (Multiscan FC, Thermo Scientific, Tokyo, Japan) was used. Figure 2 shows the schematic steps for these experiments. First, 80 µL of 0.0164 mM L⁻¹ MB, 10 µL of 100 mM L⁻¹ H₂O₂ and 10 µL of 1 mM of iron as

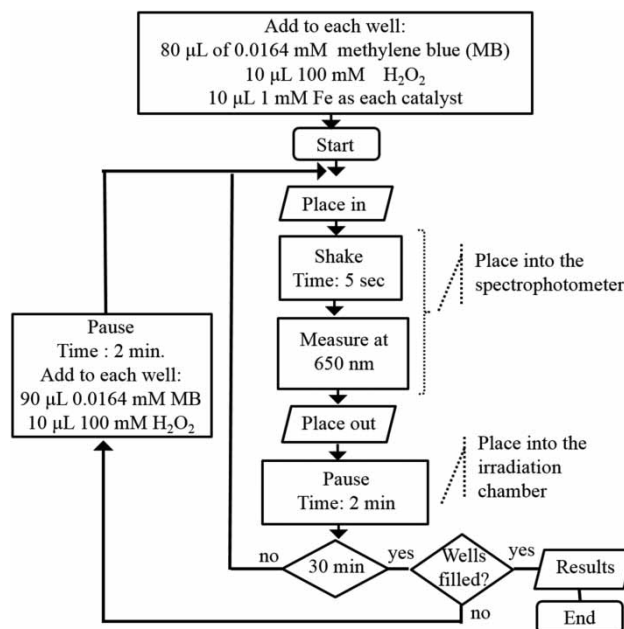


Figure 2 | Schematic diagram of experimental protocol for the Fe-to-polyphenol model and reusability tests.

TEA-Fe, CAF-Fe, FeII, FeIII, Fe-CGA, Fe-CA, Fe-GA, Fe-CTh, Fe-CTA and Fe-AsA catalysts were added to 96-well microplates with a total volume capacity of 400 μL . The spectrophotometer was programmed to place the microplate in the irradiation box and measure the absorbance of MB (650 nm) after every 2 min of reaction, shaking the samples automatically for 5 sec before each measurement. After each 30 min of reaction, 90 μL of 0.0164 mM L^{-1} MB and 10 μL of 100 mM H_2O_2 were added three times until the wells had filled. After each MB addition, the absorbance measurements were repeated.

Colour removal efficiency and first-order reaction rate calculations

The colour removal efficiency (η) was calculated as in Equation (1).

$$\eta(\%) = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

C_0 and C are the concentration of MB at initial and given time t , respectively.

The kinetics of the reaction was fitted using apparent first-order kinetics as in Equation (2).

$$\ln\left(\frac{C_0}{C}\right) = k_1 t \quad (2)$$

where k_1 is the apparent first-order reaction rate constant, t is the reaction time, and C_0 and C are the initial and final concentration values of the dye solution, respectively.

Fe analysis

The total iron on the samples was determined by ICP-AES (inductively coupled plasma atomic emission spectroscopy; iCAP 6000, Thermo Scientific, Tokyo, Japan). The concentration of ferrous (Fe^{2+}) of the samples was measured by the 1,10-phenanthroline method while the concentration of ferric (Fe^{3+}) in samples was calculated by subtracting Fe^{2+} from total Fe of each sample.

RESULTS AND DISCUSSION

Photo-Fenton test

The advantage of the Fenton process is the complete destruction of pollutants to harmless compounds, for

example, carbon dioxide and water. However, on occasion, the Fenton process leads to the formation of intermediates that can be more toxic than the initial compounds. There are two drawbacks when implementing the Fenton reaction in water treatment. First, the working pH for the highest efficiency of the Fenton reaction occurs at pH 2.8–3.0 (Zhang *et al.* 2005, 2006). Thus, an adjustment to pH is necessary to obtain an efficient reaction. Second, the amount of Fe^{2+} ions decreases as solution pH increases. At pH higher than 4, almost all the Fe species are insoluble, such as Fe_2O_3 or other colloidal hydroxide compounds (Salgado *et al.* 2013). The reactivity of the Fenton reaction (without Fe ligands) thus decreases at a pH greater than 4. The highest reactivity of the Fenton reaction (i.e., at pH = 3) is related to the $[\text{Fe}(\text{OH})]^{2+}$ species (Figure 3). The use of light may be able to increase the effectiveness of the Fenton process, the so called photo-Fenton process, at higher pH and also at the usual pH range for the Fenton reaction.

The colour removal of MB was negligible in the following treatments: (1) $\text{H}_2\text{O}_2/h\nu$; (2) TEA-Fe/ $h\nu$; (4) CAF-Fe/ $h\nu$; (6) FeII/ $h\nu$; (8) FeIII/ $h\nu$. For both initial iron concentrations, the colour removal efficiency of MB was close to 0.9% in the $\text{H}_2\text{O}_2/h\nu$ treatment and around 20.0% after 30 min of reaction in the FeII/ $h\nu$ and FeIII/ $h\nu$ treatments. In addition, for an initial Fe concentration of 0.018 mM L^{-1} , the colour removal efficiency was 5.0% and 11.0% after 30 min of reaction for TEA-Fe/ $h\nu$ and CAF-Fe/ $h\nu$ treatments, respectively. And, for an initial Fe concentration of 0.045 mM L^{-1} , it was 11.0% and 5.0% for TEA-Fe and CAF-Fe/ $h\nu$ treatments, respectively. In our experiments, the low ability of TEA-Fe and CAF-Fe catalysts to remove colour under light implies that the adsorption of dye by these catalysts was not the factor accounting for the removal

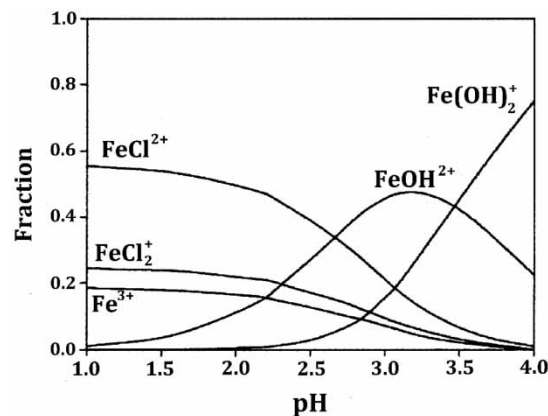


Figure 3 | Speciation of 0.5 mM Fe(III) between pH 1 and 4 at 25 °C and an ionic strength of 0.2 M kg^{-1} in the presence of 0.1 M NaCl (Machulek *et al.* 2012).

of colour observed in the treatments. The low capacity of H_2O_2 under light to remove dye from water in our experiments was unexpected. H_2O_2 is one of the most powerful oxidants known and is completely harmless because H_2O_2 is a natural metabolite of many organisms which have the ability to convert H_2O_2 into oxygen and water. From our results, H_2O_2 alone did not have the ability to produce hydroxyl radicals for efficient dye photodegradation and needed to be used in combination with ferrous salts.

Figure 4 shows a comparison between the effects of catalysts on the photodegradation of MB under near-UV light. The photodegradation of MB using TEA-Fe and CAF-Fe catalysts was clearly higher than that of Fe^{2+} and Fe^{3+} under light irradiation. MB was completely decomposed within 30 min by TEA-Fe and CAF-Fe catalysts in the presence of H_2O_2 and light.

For the TEA-Fe/ H_2O_2 / $h\nu$ treatments, light irradiation enhanced the reaction when the initial concentration of Fe was 0.018 mM L^{-1} rather than 0.045 mM L^{-1} . The colour removal efficiency of MB was close to 98.0% and 81.4% after 30 min of reaction for TEA-Fe/ H_2O_2 / $h\nu$ and CAF-Fe/ H_2O_2 / $h\nu$, respectively, for an initial Fe concentration of 0.018 mM L^{-1} . In addition, for an initial Fe concentration of 0.045 mM L^{-1} , the colour removal efficiency was close to 96.1% and 97.8% after 30 min of reaction for TEA-Fe/ H_2O_2 / $h\nu$ and CAF-Fe/ H_2O_2 / $h\nu$, respectively.

The pH value is an important factor that affects the photo-Fenton reaction. Figure 5 shows the changes in pH over 30 min of reaction under UV light. A drastic drop in pH occurred after the addition of H_2O_2 and Fe catalysts. Slight acidification was observed when H_2O_2 was added but it was minimal compared to when the Fe catalysts

were added. For both Fe catalyst concentrations, solution pH mostly decreased in the TEA-Fe/ $h\nu$ and CAF-Fe/ $h\nu$ treatments. This drop in pH is attributed to the higher organic acid content of spent tea leaves and coffee grounds in addition to the fragmented organic material forming organic acids. For 0.018 mM L^{-1} Fe, the final solution pH of the treatments CAF-Fe/ H_2O_2 / $h\nu$, TEA-Fe/ H_2O_2 / $h\nu$, FeII/ H_2O_2 / $h\nu$ and FeIII/ H_2O_2 / $h\nu$ were 4.9, 4.6, 5.1 and 5.0, respectively, while for 0.045 mM L^{-1} Fe, values were 4.6, 4.3, 4.7 and 4.7, respectively. When solution pH is high, iron precipitates as $\text{Fe}(\text{OH})_3$ and will decompose into H_2O_2 , thus reducing the efficiency of the Fenton process (Perez *et al.* 2002). The higher capacity of the heterogeneous catalysts CAF-Fe and TEA-Fe to remove MB from solution compared with the homogeneous FeII and FeIII catalysts cannot be explained by the precipitation of Fe because all treatments had similar pH at the end of the reaction.

Table 1 shows the kinetic parameters from the colour removal values, such as the apparent first-order reaction rate constant (k_1) and half-life time ($t_{1/2}$). The results clearly showed that the combination of iron and tea or coffee polyphenols can greatly accelerate the MB photodegradation reaction under UV irradiation. The k_1 values for the 'green' iron catalysts (TEA-Fe and CAF-Fe) were significantly higher than those for the Fe^{2+} and Fe^{3+} catalysts. The photo-Fenton process using TEA-Fe achieved a rate constant k_1 of 9.77×10^{-2} and $9.45 \times 10^{-2} \text{ min}^{-1}$ and a $t_{1/2}$ value of 3.9 min.

The removal efficiency of MB after 30 min of reaction time can be ranked as the following decreasing order for the 0.018 mM Fe initial rate: TEA-Fe/ H_2O_2 / $h\nu$ >

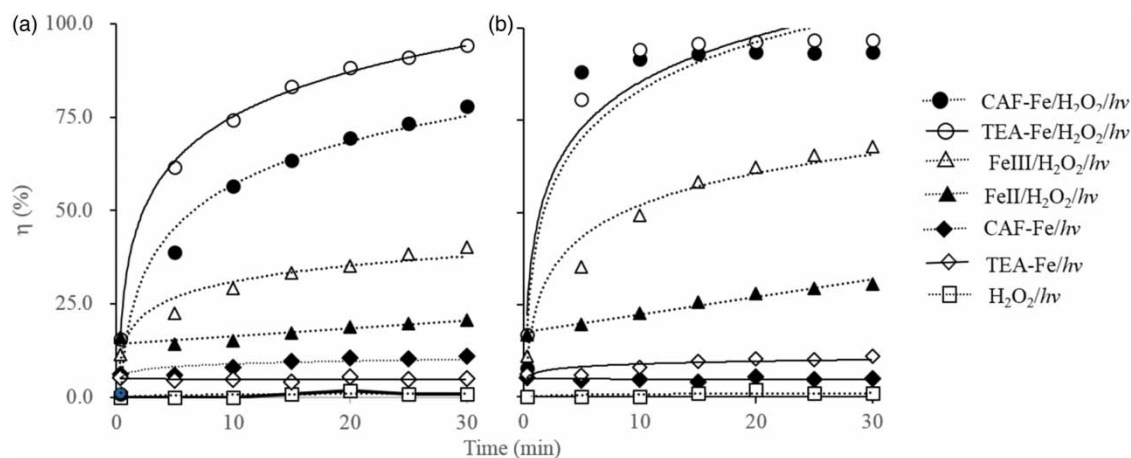


Figure 4 | Colour removal efficiency of MB (0.016 mM L^{-1}) after treatments under near-UV light irradiation (375 nm , 10 W m^{-2}). Except for the H_2O_2 / $h\nu$ treatment, all other treatments contained (a) 0.018 mM L^{-1} and (b) 0.045 mM L^{-1} of iron as FeII, FeIII, CAF-Fe and TEA-Fe catalysts. All treatments received the same amount of H_2O_2 , i.e., 10 mM L^{-1} . CAF-Fe = Fe-to-coffee extract; TEA-Fe = Fe-to-tea extract; FeII = $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$; FeIII = FeCl_3 .

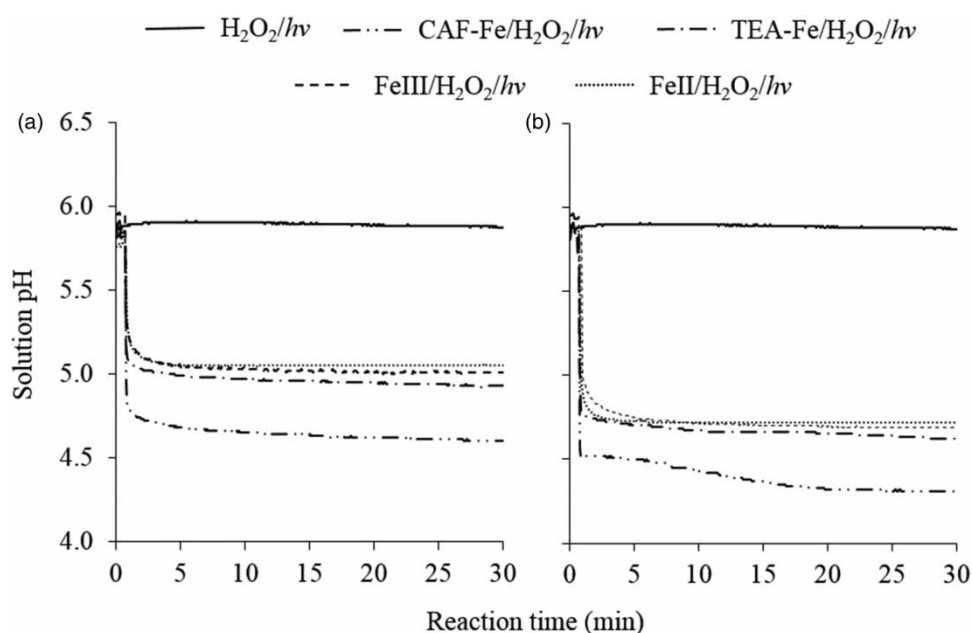


Figure 5 | Changes to solution pH during treatments in near-UV light irradiation (375 nm , 10 W m^{-2}). Except for the $\text{H}_2\text{O}_2/h\nu$ treatment, all other treatments contained (a) 0.018 mM L^{-1} and (b) 0.045 mM L^{-1} of Fe as FeII, FeIII, CAF-Fe and TEA-Fe catalysts. All treatments received the same amount of H_2O_2 , i.e., 10 mM L^{-1} . CAF-Fe = Fe-to-coffee extract; TEA-Fe = Fe-to-tea extract; FeII = $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$; FeIII = FeCl_3 .

Table 1 | Colour removal as apparent first-order reaction rate constant (k_1) and half-life time for the oxidation of MB ($t_{1/2}$) for the treatments

Treatment	0.018 mmol L ⁻¹ Fe		0.045 mmol L ⁻¹ Fe	
	$k_1 \times 10^{-2}\text{ min}^{-1}$	$t_{1/2}\text{ (min)}$	$k_1 \times 10^{-2}\text{ min}^{-1}$	$t_{1/2}\text{ (min)}$
$\text{H}_2\text{O}_2/h\nu$	0.35	–*	0.35	–
TEA-Fe/ $h\nu$	0.79	–	0.98	–
CAF-Fe/ $h\nu$	0.49	–	0.71	–
TEA-Fe/ $\text{H}_2\text{O}_2/h\nu$	9.77	1.7	9.45	0.6
CAF-Fe/ $\text{H}_2\text{O}_2/h\nu$	5.03	4.7	11.53	0.6
FeII/ $\text{H}_2\text{O}_2/h\nu$	0.80	–	4.63	3.4
FeIII/ $\text{H}_2\text{O}_2/h\nu$	0.73	–	3.56	7.5

*Over 30 min. of reaction; CAF-Fe = Fe-to-coffee extract; TEA-Fe = Fe-to-tea extract; FeII = $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ and FeIII = FeCl_3 .

$\text{CAF-Fe}/\text{H}_2\text{O}_2/h\nu > \text{FeIII}/\text{H}_2\text{O}_2/h\nu = \text{FeII}/\text{H}_2\text{O}_2/h\nu > \text{TEA-Fe}/h\nu > \text{CAF-Fe}/h\nu > \text{H}_2\text{O}_2/h\nu$. In addition, the follow decreasing order was observed for the 0.045 mM Fe initial rate: $\text{CAF-Fe}/\text{H}_2\text{O}_2/h\nu > \text{TEA-Fe}/\text{H}_2\text{O}_2/h\nu > \text{FeII}/\text{H}_2\text{O}_2/h\nu > \text{FeIII}/\text{H}_2\text{O}_2/h\nu > \text{TEA-Fe}/h\nu > \text{CAF-Fe}/h\nu > \text{H}_2\text{O}_2/h\nu$.

Fe-to-polyphenol model and reusability tests

To evaluate the role of Fe-to-polyphenol complexes of CAF-Fe and TEA-Fe catalysts on the photo-Fenton process, CGA,

CA, CTh, CTA, AsA and GA, which are the main polyphenols in coffee and tea beverages, were reacted with Fe and compared with the FeII, FeIII, TEA-Fe and CAF-Fe catalysts in the photo-Fenton process. The reusability of all materials was tested by sequential additions of H_2O_2 and MB.

Figure 6 shows a comparison of the reusability between FeII, FeIII, CAF-Fe and TEA-Fe to remove MB from aqueous solutions after three sequential additions of H_2O_2 . The rate of photodegradation of MB increased in response to the heterogeneous CAF-Fe and TEA-Fe catalysts compared to the homogeneous iron salts. After four cycles, the catalysts FeII and FeIII removed only 16.6% and 53.6% of the dye, while the new catalysts CAF-Fe and TEA-Fe removed 94.4% and 96.0% of the dye, respectively.

As shown in Figure 7, the Fe-CTA and Fe-AsA complexes showed a lower ability to remove MB and reusability than TEA-Fe and CAF-Fe catalysts. After four cycles, Fe-CTA and Fe-AsA complexes removed only 58.5% and 74.3% of the dye, while the Fe-GA removed 85.6% the dye.

As shown in Figure 8, Fe-CGA, Fe-CA, Fe-GA, Fe-CTh, CAF-Fe and TEA-Fe catalysts showed similar patterns of MB degradation and reusability. Fe-CA, Fe-CTh, Fe-CTh and Fe-CGA removed 90.1%, 96.4% and 97.6% of dye, respectively. The removal efficiency of MB could be ranked as follows: $\text{FeII} < \text{FeIII} < \text{Fe-CTA} < \text{Fe-AsA} < \text{Fe-GA} < \text{Fe-CA} < \text{CAF-Fe} < \text{TEA-Fe} = \text{Fe-CTh} = \text{Fe-CGA}$.

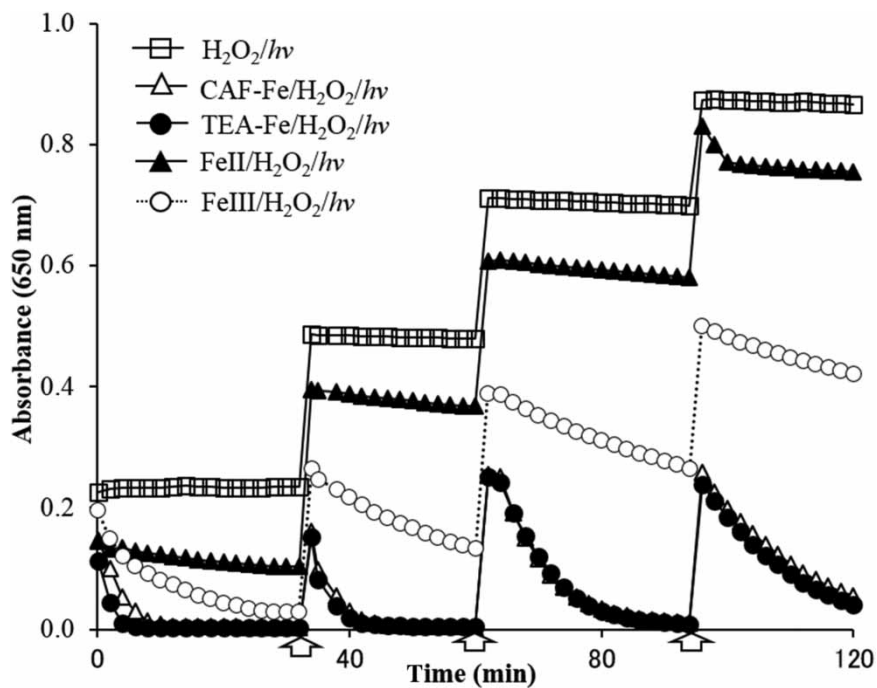


Figure 6 | Effect of sequential addition of hydrogen peroxide (H_2O_2) to solutions during the photodegradation of MB under continuous near-UV light irradiation (375 nm , 10 W m^{-2}). Arrows indicate the time when H_2O_2 and MB were added to the solutions. CAF-Fe = Fe-to-coffee extract; TEA-Fe = Fe-to-tea extract; FeII = $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$; FeIII = FeCl_3 . (Initial conditions: 0.1 mM Fe , $10 \text{ mM H}_2\text{O}_2$, pH was not adjusted.)

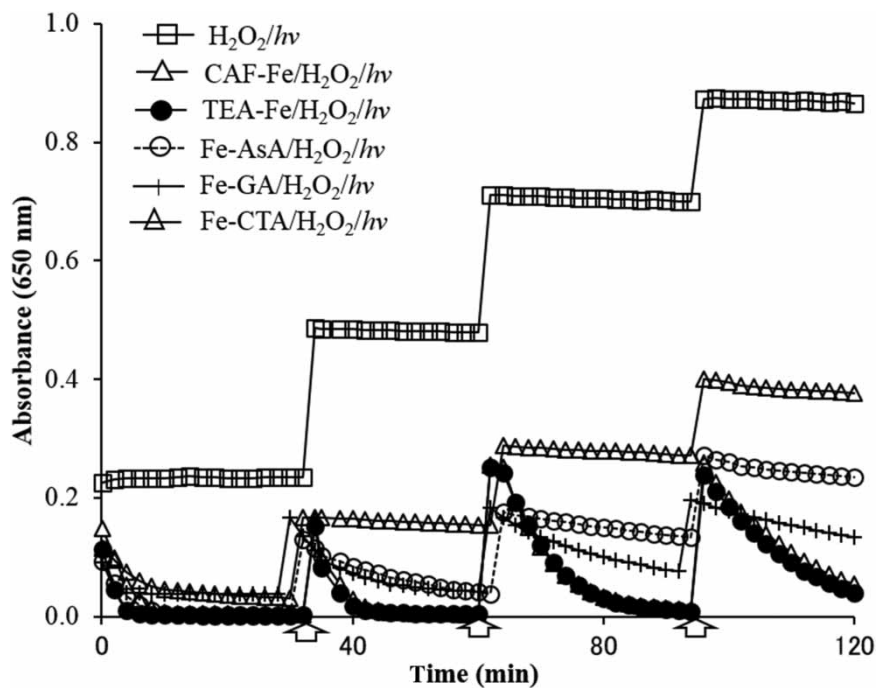


Figure 7 | Effect of sequential addition of hydrogen peroxide (H_2O_2) to solutions on the degradation of MB under light irradiation (375 nm , 10 W m^{-2}). Arrows indicate the addition of H_2O_2 and MB to the solutions. CAF-Fe = Fe-to-coffee extract; TEA-Fe = Fe-to-tea extract; Fe-AsA = Fe-to-ascorbic acid; Fe-GA = Fe-to-gallic acid; Fe-CTA = Fe-to-citric acid. (Initial conditions: 0.1 mM Fe , $10 \text{ mM H}_2\text{O}_2$, pH was not adjusted.)

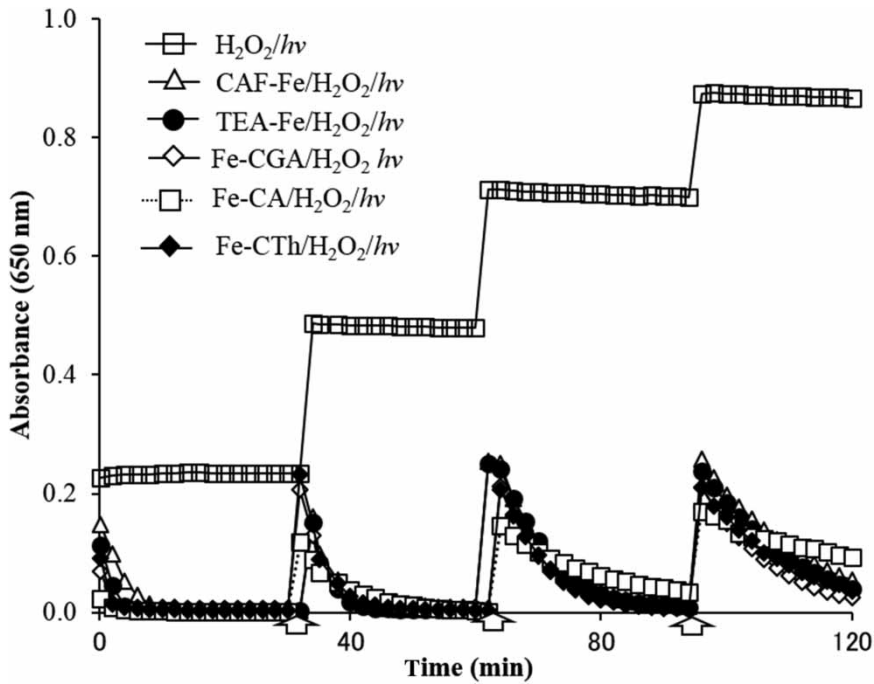


Figure 8 | Effect of sequential addition of hydrogen peroxide (H_2O_2) to solutions on the degradation of MB under light irradiation (375 nm , 10 W m^{-2}). Arrows indicate the addition of H_2O_2 and MB to the solutions. CAF-Fe = Fe-to-coffee extract; TEA-Fe = Fe-to-tea extract; Fe-CGA = Fe-to-chlorogenic acid; Fe-CA = Fe-to-caffeic acid; Fe-CTh = Fe-to-catechin. (Initial conditions: 0.1 mM Fe , $10 \text{ mM H}_2\text{O}_2$, pH was not adjusted.)

Fortunately, the catalysts made using spent tea leaves and coffee grounds could be reused in the photo-Fenton process, with a slight decline in efficiency. Similar results were found for the following Fe-to-polyphenol complexes: Fe-CGA, Fe-CA, Fe-GA and Fe-CTh (Figures 7 and 8). As shown in Figure 8, the

tea and coffee polyphenols most effectively photodegraded MB. Those polyphenols probably contributed to the photo-Fenton process by reducing Fe^{3+} to Fe^{2+} and/or served as electron donors to maintain the activity of Fe in the reduced state in the photo-Fenton cycle. In our experiments, as shown in Figure 9,

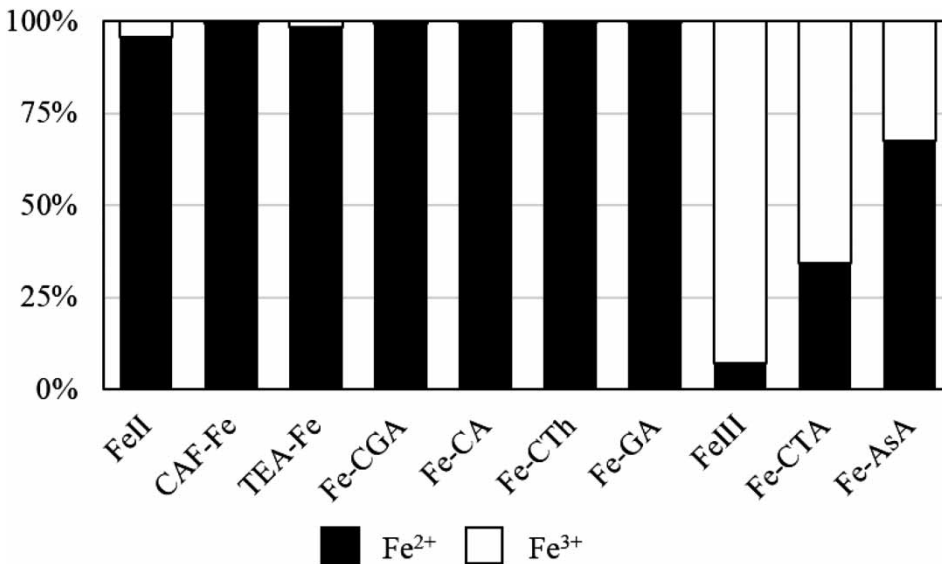


Figure 9 | Percentage of Fe^{2+} and Fe^{3+} in 1 mM L^{-1} of Fe of each solution before the kinetic experiments. Solutions: FeII = $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$; CAF-Fe = coffee extract; TEA-Fe = Fe-to-tea extract; FeIII = FeCl_3 ; Fe-CA = Fe-to-caffeic acid; Fe-CGA = Fe-to-chlorogenic acid; Fe-CTh = Fe-to-catechin; Fe-GA = Fe-to-gallic acid; Fe-CTA = Fe-to-citric acid; Fe-AsA = Fe-to-ascorbic acid.

the TEA-Fe and CAF-Fe solutions contained 95.1% and 98.5% of Fe in a reduced form, respectively, implying that the reduction of Fe^{3+} that generates Fe^{2+} by the tea or coffee polyphenols appeared to contribute to the generation of $\cdot\text{OH}$.

The hydroxyl radical is produced via the photo-Fenton reaction in the presence of organic substances like malonic acid (Sun *et al.* 2010), oxalic acid (Li *et al.* 2007) and catechin (Wang *et al.* 2014). In our study, the tea and coffee polyphenols tested increased the photodegradation of MB under light irradiation. These results indicate that the polyphenols used were involved in the increased generation of $\cdot\text{OH}$ under light irradiation. Furthermore, it was not necessary to adjust the reaction's pH. Normally, these substances interact with iron, thereby reducing the generation of $\cdot\text{OH}$ (Lopes *et al.* 1999). The antioxidant activity of polyphenols, which involves the prevention of $\cdot\text{OH}$ formation and lipid peroxidation, has been correlated with their iron-chelating properties (Guo *et al.* 1996; Kondo *et al.* 1999; Liu *et al.* 2000). However, in our experiments, the antioxidant activity of tea and coffee polyphenols was not observed.

In previous work, we noted a higher generation of hydroxyl radicals and the high content of active Fe^{2+} of the TEA-Fe and CAF-Fe catalysts as being responsible for the high $\cdot\text{OH}$ generation observed (Morikawa 2013). The reducing and chelating functions of tea and coffee polyphenols were proposed as a mechanism to produce a stable Fenton reaction. From the results obtained in this work, we propose that the tea and coffee polyphenols are involved in the process of hydroxyl radical production although more detailed studies are necessary to elucidate the actual mechanism. Sun *et al.* (2010) demonstrated that the degradation of malachite green (MG) in the presence of malonic acid and ethylenediaminetetraacetic acid was decreased in the Fenton system in the dark because of the interaction between malonic acid and iron species. However, degradation occurred again after irradiation with visible light. According to those authors, for the Fenton system with malonic acid, electrons can transfer from the excited MG to the Fe^{3+} /malonic complex, and the formed Fe^{2+} species reacts with H_2O_2 to give $\cdot\text{OH}$, leading to the degradation of MG. Similarly, the degradation of MG in the presence of malonic acid in the Fenton system could be initiated by the addition of hydroquinone in the dark or under visible light irradiation because hydroquinone can also energetically react with Fe^{3+} to produce Fe^{2+} and sustain the Fenton cycle via the reaction of Fe^{2+} with H_2O_2 . The photodegradation of MB by H_2O_2 under near-UV LED irradiation light was significantly higher in the presence of Fe^{3+} compared with that in the presence of Fe^{2+} . This result could be explained by the continuous reduction of Fe^{3+} to Fe^{2+} in the presence of

H_2O_2 and light, thereby promoting the generation of more radicals under light irradiation. The Fenton reaction can be greatly accelerated via UV light irradiation due to photolysis of ferric species, which enhances the generation of Fe^{2+} with a concomitant production of $\cdot\text{OH}$ radicals (Spuhler *et al.* 2010).

One of the advantages of the green catalysts developed versus conventional Fe salts is their reusability as Fe fertilizers. In previous work, we demonstrated that 'green' Fe catalysts we had developed could be used as an Fe fertilizer in agriculture (Morikawa & Saigusa 2008, 2011) and in the Fenton process to degrade pollutants or disinfect pathogens, such as *Escherichia coli* (Morikawa 2013).

The enhancement of MB photodegradation by tea and coffee polyphenols is interesting from the point of view of the use of light in water treatment. The effectiveness of near-UV LED illumination to increase Fe's photocatalytic activity is also very interesting and could lead to innovative sustainable water treatment. Traditional UV lamps contain mercury that is hazardous to the environment. Near-UV LEDs have a long operating life and are more environmentally friendly than traditional mercury UV lamps. The use of LED light as a 'clean reagent' may provide a 'green' method to promote chemical reactions in the future. The developed approach to the photo-Fenton method is safe for the environment and is expected to be applied in water treatment processes for agricultural and industrial uses. Therefore, the developed method is expected to contribute to the effective use of tea and coffee wastes from the beverage industry by creating a novel application method for these food waste materials.

CONCLUSIONS

Compared to the conventional Fenton reagent Fe^{2+} , which requires acidic conditions (pH ~ 3), TEA-Fe and CAF-Fe catalysts are effective at higher pH (pH ~ 5). This is an important consideration in full-scale applications since acidifying an aquifer is typically impractical. All of the results using the new 'green' iron catalysts were obtained under controlled laboratory conditions. The effectiveness of these new materials to catalyse the Fenton and photo-Fenton reactions could be influenced by many factors such as the presence of scavengers under natural conditions, light intensity, and wavelength. Therefore, more detailed studies that assess the effectiveness of these developed 'green' iron catalysts on the catalysis of photo-Fenton processes at a large scale and under natural conditions are required. From the obtained results we propose that the tea and coffee

polyphenols created were involved in the process of hydroxyl radical production in the photo-Fenton process.

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