

Study of solar photo-Fenton system applied to removal of phenol from water

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ABSTRACT

This study evaluated the use of a Fenton's reaction in a falling film solar reactor (FFR), as a possible advanced oxidation process for the mineralization of the organic compound phenol in water. Preliminary tests were carried out to evaluate phenol degradation by photolysis and to select the optimal residence time in which to carry out the process using a solar photo-Fenton system. The variables studied were the initial phenol concentration (100 to 300 mg L⁻¹), the [Phenol]:[H₂O₂] mass ratio (1.0 to 2.0) and the [H₂O₂]/[Fe²⁺] molar ratio (5 to 10). Phenol degradation of 99% and chemical oxygen demand (COD) reduction of 97% were obtained under the following reaction conditions: phenol concentration = 200 mg L⁻¹, mass ratio [Phenol]:[H₂O₂] = 1.5 and molar ratio [H₂O₂]/[Fe²⁺] = 7.5. Overall mineralization was achieved using the solar photo-Fenton process to destroy phenol and COD. The solar photo-Fenton process using a FFR appears to be a viable method for removing phenols in wastewaters on an industrial scale.

Key words | falling film reactor, phenol, solar fenton

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INTRODUCTION

Phenolic compounds are considered to be hazardous pollutants because of their high toxicity and bioaccumulation effect. There are several sources of phenolic compounds such as phenol manufacturing plants, the pulp and paper industry, the pharmaceutical industry, wood processing plants, pesticide manufacturing and industrial waste from extraction and processing of fossil fuels (Malato *et al.* 2003). Due to their toxicity and consequent health hazards, phenolic compounds have been placed in the list of priority pollutants by the US Environmental Protection Agency (Zhou *et al.* 2011).

Advanced oxidation processes (AOPs) are among the existing processes for water treatment that can be employed for removal of phenol. They are considered to have potential due to their high degradation capacity, complete mineralization or oxidation to very low concentrations and the production of environmentally friendly by-products. AOPs can be defined as processes that involve the in-situ generation of highly reactive species, such as hydroxyl radicals, which are very powerful oxidizers ($E^0 = 2.80$ V). These reactive species lead to the destruction of various organic pollutants in water and wastewater treatment operations.

The breakdown of phenolic and related compounds in water and wastewater using AOPs has been studied since 1964 on a laboratory scale (Eisenhauer 1964; Kochany & Bolton 1992; Lipczynska-Kochany *et al.* 1995; Zhu *et al.* 1996; Esplugas *et al.* 2002), a comprehensive review of the subject was published by Busca *et al.* (2008).

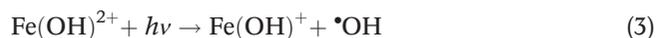
Hydroxyl radicals used in water and wastewater treatment can be generated by several processes including H₂O₂/UV, O₃/UV, Fenton's reagent, O₃/H₂O₂/UV, heterogeneous photocatalysis and, more recently, the solar photo-Fenton process (Araujo *et al.* 2007; Malato *et al.* 2009; Vilar *et al.* 2009).

In the Fenton process, hydrogen peroxide reacts with Fe(II) salts forming radicals according to Equation (1).



Oxidized iron (III) is quickly reduced by the action of ultraviolet radiation in the sunlight, to regenerate ferrous ion. The photolysis of hydrogen peroxide and of intermediate organic chelates of iron (III) can also occur according

to Equations (2)–(6) (Pignatello & Sun 1995).



The use of solar radiation for the photocatalytic oxidation of organic contaminants in wastewater is a fast developing application. The combination of solar light and catalysts has proven to be a promising option (Silva *et al.* 2004; Lapertot 2006; Xu *et al.* 2007). The main purpose of sunlight as a source of radiation is to reduce the operating costs of a photo-Fenton system when applied to an industrial scale. Appropriate design of a solar reactor is important to ensure an efficient solar photo-Fenton process. There are two main types of solar reactors for wastewater treatment, namely concentrating and non-concentrating. Non-concentrating solar reactors are more effective in wastewater treatment in comparison with concentrating solar reactors (Malato *et al.* 2007). Non-concentrating solar reactors/collectors are static systems with no solar tracking mechanism; they usually use parabolic or flat-plate technology, static devices oriented towards the equator with a specific inclination which depends on the latitude of the site (Tanveer & Guye 2013).

Different types of non-concentrating solar reactors/collectors have been developed including the non-concentrating falling film reactor (FFR). In this reactor the fluid falls slowly over a tilted plate which faces the sun and is open to the atmosphere. FFR uses both direct and diffuse components of solar light and its operating costs are usually low (Golisch *et al.* 1997; Blanco-Galvez *et al.* 2007). Conventional photo-reactors operate with lamps immersed in the solution under treatment; on the other hand solar reactors FFR work under a lower light intensity and thus require a larger illuminated area. They will only be effective during daytime and will be dependent on atmospheric conditions. These are factors which have to be taken into consideration when designing a full-scale treatment plant. The radiant energy used for enhancing the conventional

homogeneous Fenton process comes from the sun, and so it is generated at zero cost.

The aim of the present work has been to evaluate the efficiency of a solar photo-Fenton process using a FFR reactor for the removal of phenol in water.

MATERIALS AND METHODS

Photo-Fenton experiments were carried out under natural sunlight in a pilot solar FFR reactor installed at Universidade Federal do Rio de Janeiro (Figure 1) in Brazil. The solar plant consists of a photocatalytic system comprising a flat surface made of high-density polyethylene 1.37 m long, 0.82 m wide and 10 cm thick, resulting in an illuminated area of 0.98 m², mounted on a fixed platform with an inclination of 22° (local latitude).

The phenol solution was pumped from the feed tank (TQ2) to the FFR reactor using a centrifugal pump at a maximum flow rate of 200 L h⁻¹. This tank was equipped with a mechanical stirrer, pH sensor (TECNOPON, Model: mPA-210P), temperature sensor and three metering pumps for the addition of H₂SO₄, H₂O₂ and NaOH. The plant can be operated in a batch or continuous mode. The treated phenol solution was collected in TQ3. Tank TQ1 was not used in this work.

The intensity of solar UV radiation was measured by a global UV radiometer (KIMO, Model: SL 100) that provided data in terms of incident W/m².

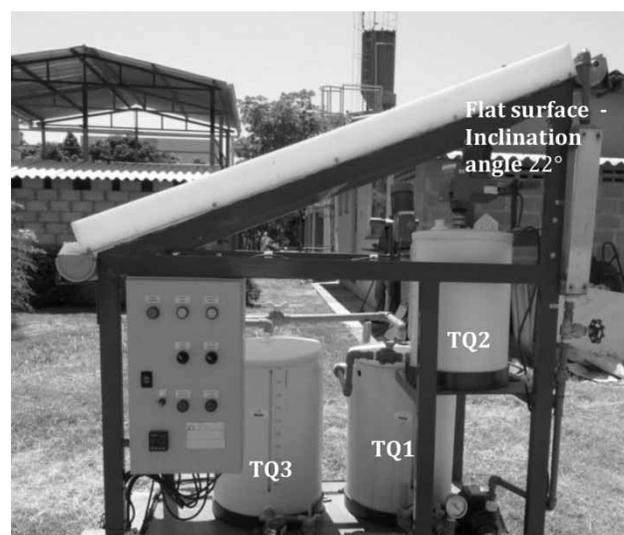


Figure 1 | Falling film reactor (FFR).

The average accumulated energy was estimated using the equation below (Malato *et al.* 2002).

$$Q = Q_{n-1} + \Delta t_n UV \frac{A}{V_t}; \quad \Delta t_n = t_n - t_{n-1}$$

In this equation, t_n is the experimental time for each sample, A is the radiation collecting surface of the photo-reactor, V the total pilot plant volume and UV the ultraviolet radiation average measured during time interval Δt_n .

The experiments were carried out using a statistical factorial design (2^3); the independent variables were: [phenol]₀, mass ratio [phenol]₀:[H₂O₂]₀ and molar ratio [H₂O₂]/[Fe²⁺].

Iron sulfate salt was manually added and pH adjusted to 3.0 with H₂SO₄ and monitored during the solar photo-Fenton reaction. The phenol solution was pumped to the FFR reactor and the solar photo-Fenton reaction started. Hydrogen peroxide concentration was automatically controlled by the addition of a commercial H₂O₂ solution (50% w/v). Samples were collected at different times to evaluate the degradation process. The reaction was stopped after the required time. The treated phenol solution was neutralized with 10 mol/L NaOH to pH 10.0 to quench the oxidation reaction by terminating the production of [•]OH radicals, releasing excess H₂O₂ as O₂ (Papadopoulos *et al.* 2007), and leading to iron precipitation.

Phenol analysis was measured using Folin–Ciocalteu reagent according to Queiroz *et al.* (2002). In this method a phenol solution reacts with 10% v/v Folin–Ciocalteu

reagent and 7.5% w/v sodium carbonate; the color obtained was analyzed using a spectrophotometer (Hach model DR-2800) at 460 nm. H₂O₂ concentration was determined by reaction with ammonium metavanadate and measurement of the characteristic absorbance at 450 nm, according to Nogueira *et al.* (2005). Chemical oxygen demand (COD) was measured according to *Standard Methods* (2005). Iron concentration was determined by colorimetry with 1,10-phenantroline according to *Standard Methods* (2005).

RESULTS AND DISCUSSION

Experiments were carried out from September to December 2011 between 9 am and 4 pm. The influence of direct photolysis with solar radiation on the phenol degradation was studied for comparison. After 5 hours of treatment, no significant phenol degradation was observed. The average accumulated energy in all experiments was 643 kJ L⁻¹.

Experiments with the solar Fenton process were carried out according to a statistical factorial design 2^3 (where 2 represents the number of levels of each variable and 3 the number of variables) with four replicates at the central point and the results were analyzed using a Design Expert 6.0.4 computer program, as shown in Table 1.

Phenol degradation increased from 52 to 97% after a reaction time of 60 min under different experimental conditions. After 120 and 240 min reaction time almost all phenol was removed under the experimental conditions tested. This result indicates that the solar Fenton process is

Table 1 | Phenol removal under different experimental conditions

Test	[Phn] ₀ (mg L ⁻¹)	[Phn] ₀ : [H ₂ O ₂]	[H ₂ O ₂]/[Fe ²⁺]	% Phenol removal			
				60 min	120 min	180 min	240 min
E1	100	1.0	5	52.3	97.7	98.8	99.0
E2	300	1.0	5	77.6	97.3	99.5	99.7
E3	100	2.0	5	95.3	99.3	99.6	99.9
E4	300	2.0	5	95.5	99.6	99.8	99.8
E5	100	1.0	10	62.7	95.7	97.1	98.6
E6	300	1.0	10	64.8	97.8	99.4	99.8
E7	100	2.0	10	96.8	98.8	99.2	99.2
E8	300	2.0	10	90.6	91.0	99.6	99.9
E9 (PC)	200	1.5	7.5	90.9	99.2	99.6	99.9
E10 (PC)	200	1.5	7.5	91.6	99.4	99.6	99.6
E11 (PC)	200	1.5	7.5	91.2	98.9	99.4	99.8
E12 (PC)	200	1.5	7.5	90.4	98.9	99.5	99.8

very effective for the degradation of phenol in water. The central point replicates showed a small variation indicating good reproducibility of the results with a standard deviation of 0.32%.

The statistical significance of the independent variable effect was visualized graphically in the Pareto chart (Figure 2). Most of the independent variables and their interactions had a significant effect and it can be seen that the mass ratio $[\text{Phenol}]_0:[\text{H}_2\text{O}_2]$ was the variable that most influenced phenol removal, followed by the initial phenol concentration ($[\text{Phenol}]_0$). It was also observed that the ratio of hydrogen peroxide and ferrous ion, as an isolated variable on its own, did not have a significant effect on the outcome, but it did affect the effect of the other variable $[\text{Phenol}]_0$.

The effect of H_2O_2 dosage is very important in the phenol degradation by an AOP process. Figures 3(a) and 3(b) show the response surface graphics of phenol removal as a function of the $[\text{Phenol}]_0$ and $[\text{Phenol}]_0:[\text{H}_2\text{O}_2]$ mass ratio, for different $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ molar ratios.

Figure 3(a) shows that phenol degradation was very high (about 96%) with an increase in both $[\text{Phenol}]_0:[\text{H}_2\text{O}_2]$ and $[\text{Phenol}]_0$. However, when using a $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ ratio of 10.0 (Figure 3b) the initial phenol concentration shows a smaller influence on phenol removal. Although the effect of $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ molar ratio by itself does not have a statistically significant effect in the factorial design, it shows a significant interaction with $[\text{Phenol}]_0$. It is possible that the very large effect of the H_2O_2 concentration obscured the

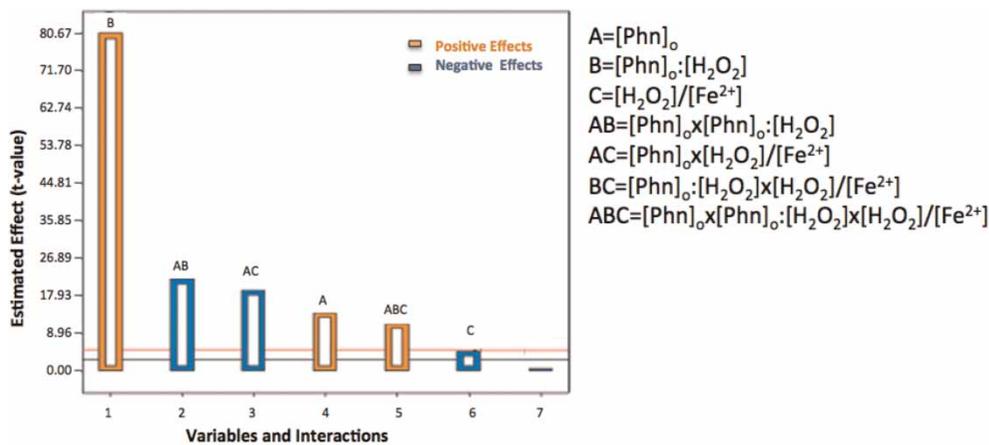


Figure 2 | Pareto chart of the standardized effects.

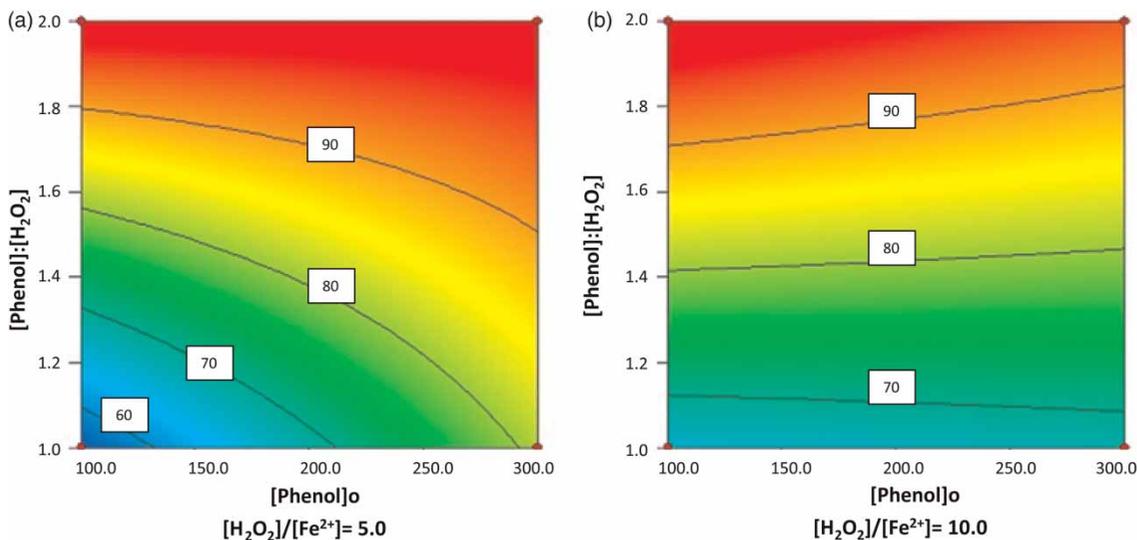
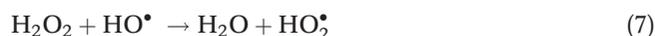


Figure 3 | Contours of the estimated response surface for phenol removal as a function of $[\text{Phenol}]_0$ and $[\text{Phenol}]_0:[\text{H}_2\text{O}_2]$. (a) $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}] = 5.0$ and (b) $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}] = 10.0$.

effect of $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ molar ratio for $[\text{Phenol}]_0:[\text{H}_2\text{O}_2]$ mass ratio = 1:2 at high $[\text{Phenol}]_0$ concentrations.

Phenol degradation is influenced by the stoichiometric relationship between pollutant concentration (phenol) and primary oxidant (H_2O_2) and the relationship between hydrogen peroxide and catalyst (Fe^{2+}). Excessive H_2O_2 and Fe^{2+} react with $\cdot\text{OH}$ according to Equations (7) and (8), competing with phenol and consequently reducing treatment efficiency.



As seen in Figure 4 hydrogen peroxide dose $[\text{Phenol}]_0:[\text{H}_2\text{O}_2]$ molar ratio is the most affecting variable in the process. If the $[\text{Phenol}]_0:[\text{H}_2\text{O}_2]$ mass ratio increases from 1.0 to 2.0, phenol removal is very effective after a reaction time of about 60 min (experiments E3 and E7).

A comparison of experiments E1 and E5 shows that phenol degradation and the reaction rate increase for a reaction time of up to 60 min with a decrease in ferrous ion concentration, after which phenol removal was the same for both experiments.

Similar results were obtained for COD removal. An analysis of residual H_2O_2 was carried out because it can affect COD removal; in these experiments none was found. An increase in hydrogen peroxide and ferrous ion concentration results in effective COD removal. After 60 minutes reaction time COD removal was about 35% in test E1 ($[\text{Phenol}]_0 = 100 \text{ mg L}^{-1}$, $[\text{Phenol}]_0:[\text{H}_2\text{O}_2] = 1.0$ and $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}] = 5.0$) and about

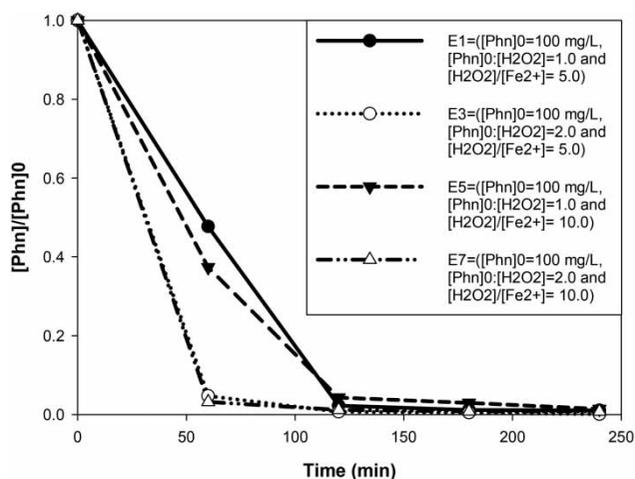


Figure 4 | Phenol removal in the solar photo-Fenton process at 120 min reaction time. Conditions: $[\text{Phenol}]_0 = 100 \text{ mg L}^{-1}$.

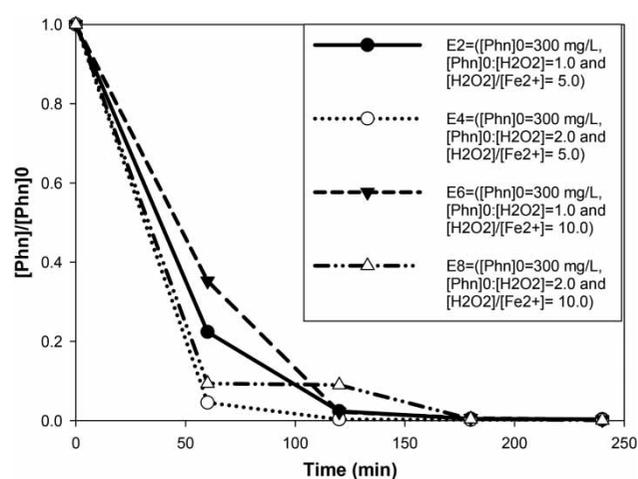


Figure 5 | Phenol removal in the solar photo-Fenton process for a reaction time of 120 min. Conditions: $[\text{Phenol}]_0 = 300 \text{ mg L}^{-1}$.

95% in test E7 ($[\text{Phenol}]_0 = 100 \text{ mg L}^{-1}$, $[\text{Phenol}]_0:[\text{H}_2\text{O}_2] = 2.0$ and $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}] = 10.0$).

Figure 5 shows the results for tests carried out at the initial phenol concentration of 300 mg L^{-1} . In these experiments the phenol degradation was faster when the ratio, $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ decreased from 10.0 to 5.0. In this case it seems that an increase in Fe^{2+} concentration promoted the breakdown of phenol, according to the reaction described in Equation (1). Furthermore, higher concentrations of phenol and ferrous ion lead to the formation of more iron carboxylate complex species ($\text{Fe}(\text{RCO}_2)^{2+}$). These complex species are photochemically active species in the presence of UV radiation, enabling the regeneration of ferrous ions and mineralization of organic radicals according to Equation (5).

The $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ ratio is normally an important variable in the Fenton reaction. At a $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ equimolar ratio, more Fe^{3+} is generated in the course of the reaction and this may lead to some $\text{Fe}(\text{OH})_3$ precipitation even at $\text{pH} = 3$, which will hinder the process.

The differences in the UV-visible absorption spectra for a phenol solution are shown in Figure 6. The degradation process in the presence of H_2O_2 involves $\cdot\text{OH}$ radicals generated by the photolysis of H_2O_2 . Hydroxyl radicals are very strong oxidizing agents (2.80 V) and are involved in the fast degradation of phenol.

CONCLUSIONS

The solar photo-Fenton process appears to be an effective method for removing phenol from waters and wastewaters.

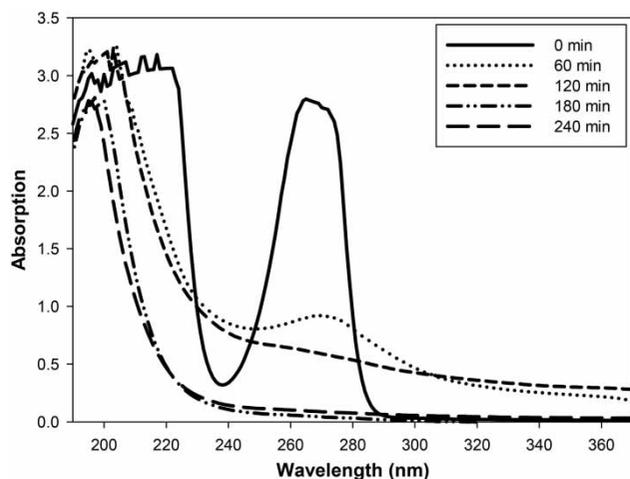


Figure 6 | UV/visible spectra of a phenol solution at different reaction times. Conditions: E_4 ([phenol] $_0$ = 300 mg L $^{-1}$, [Phenol] $_0$:[H $_2$ O $_2$] = 1.0 and [H $_2$ O $_2$]/[Fe $^{2+}$] = 5.0).

The experimental factorial design showed that the initial concentration of hydrogen peroxide was very important for the efficiency of the process. H $_2$ O $_2$ generates highly reactive •OH radicals and is the reagent primarily responsible for oxidizing and mineralizing phenol in water. Phenol and COD removal decreased for all runs at the lower initial concentration of hydrogen peroxide ([Phenol] $_0$:[H $_2$ O $_2$] = 1.0). The greatest phenol degradation was obtained with [Phenol] $_0$: [H $_2$ O $_2$] = 2.0. When H $_2$ O $_2$ concentration exceeded the optimum value the amount of phenol degradation was reduced.

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