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PHOTODEGRADATION OF TEBUCONAZOLE IN AQUEOUS SOLUTION AND PHYTOTOXIC EFFECTS

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Abstract

Tebuconazole (TEB) is a fungicide largely used in agriculture that contributes to the environmental contamination of water resources, soil, and living organisms. Advanced oxidation processes (AOPs) are excellent tools to mitigate environmental contamination by TEB. Hence, this study aimed to evaluate the catalytic photodegradation of TEB in an aqueous solution using $TiO_2 \cdot SiO_2 \cdot AgNO_3$ as a catalyst and to evaluate the phytotoxic effects of its photoproducts. A factorial planning and response surface methodology was executed using a central composite model containing 2 variables (pH and catalyst concentration) in 5 levels, totaling 10 experiments. The analyses were performed in triplicate. The results showed better photodegradation efficiency at low catalyst concentrations and slightly acidic medium concentrations with photodegradation rates up to 84.96%, or in the absence of catalyst and near photodegradation neutrality of 65.89%. Thus, the experiments indicate the potential use of photolysis to degrade TEB without the use of catalysts and, in this way, develop a low-cost and environmentally friendly TEB degradation technique. The TEB and its photoproducts were phytotoxic for lettuce and onion seeds. However, it was non-phytotoxic for cucumber seeds even when there was photodegradation with UV irradiation and the presence of the photocatalyst. Hence, special attention must be given to the phytotoxicity effects of TEB when it is applied to the agricultural systems, avoiding the environmental contamination of the water resources, soil, and live organisms.

Key words: test organisms, catalyst, fungicide, germination index, photolysis

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1. Introduction

The contamination of the water resources and the environment by agrochemicals is common, mainly due to agricultural practices (Khamdahsag et al., 2018). More than 300,000 tons of agrochemicals are used in Brazil every year and these compounds can reach the surface and groundwater (Chaves and De Souza, 2015).

Tebuconazole (TEB) is a triazole applied in intensive cultivation, most of the time in rice crops and its presence in water resources was detected in many

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countries of the world such as Spain (Herrero-Hernández et al., 2013), Lebanon (Kouzayha et al., 2012), Greece (Papadakis et al., 2015), Colombia (Mojica and Guerrero, 2013) and France (Togola et al., 2014) and also in several Brazilian states because of their agricultural activities (Britto et al., 2015; Caldas et al., 2010; Chicati et al., 2012; Demoliner et al., 2010; Donato et al., 2015; Mattos et al., 2008; Silva et al., 2009).

Tebuconazole presents moderate mobility potential, however, its mobility increases when in subsurface soil layers or inceptisols (Mosquera-Vivas et al., 2018). The TEB causes endocrine disorders in humans, such as a decrease in progesterone secretion in the placenta (Rieke et al., 2014), cytotoxic effects with apoptosis in renal and fetal cells (Mesnage et al., 2014), inhibition of testosterone secretion, and inhibition of androgen receptor (Roelofs et al., 2014). Similar activities take place in animal health where anti-androgenic and feminized effects in male rats are observed such as fetal testosterone reduction and increase in progesterone levels (Taxvig et al., 2007), reduction of acetylcholinesterase and butyrylcholinesterase activities in adult bulls (*Bostaurus l.*) (Kolesárová et al., 2013), bioaccumulation and decreased immunity in frogs (*Pseudacris regilla*) from Pacific Ocean (Smalling et al., 2013) and bioaccumulation in adults zebrafish (*Danio rerio*) (Andreu-Sánchez et al., 2012) and development of fibrosis in the myocardium in rats (Othmène et al., 2020).

According to IUPAC, the TEB can be appointed as 1-(4-chlorophenyl)-4,4-doimethyl-3-(1,2,4-triazol-1-ylmethyl) pentan-3-ol. It presents class III toxicity, moderate toxicity, and class II environmental risk, which is very dangerous to the environment (Andrade et al., 2011; Silva et al., 2015).

Advanced Oxidation Processes (AOPs) have shown promising results on the degradation of recalcitrant compounds and agrochemicals (Alaton and Dogruel, 2004; Teixeira et al., 2005). These technologies are based on the generation of a strong type of oxidant species. These oxidants can degrade a range of recalcitrant substances efficiently (Marmitt et al., 2009; Schneider et al., 2014). Photolysis and heterogeneous photocatalysis stand out among the AOPs due to their efficiency and easy operation (Bessegato et al., 2012; Duca et al., 2020; Schneider et al., 2014).

Toxicity tests using bioindicators are used to identify pollutants present in the environment and their toxicity effects and biological response, mainly in water and soil (Hillis et al., 2011; Ronco et al., 2004). The most used agrochemicals are fungicides (Herrero-Hernández et al., 2013), and the superior plants have been used to determine the phytotoxicity according to their initial steps of growing (Foti et al., 2005). The germination index (GI) indicates the effects of substances on the radicular growth of the plants (Charles et al., 2011; Himanem et al., 2012; Young et al., 2012) where the relative growing inhibition indicates the phytotoxic effect of the evaluated substance (Foti et al., 2005; González et al., 2003). In this way, this research aimed to evaluate the catalytic photodegradation of TEB using $TiO_2 \cdot SiO_2 \cdot AgNO_3$ in aqueous suspension and to evaluate the phytotoxic effects of its photoproducts.

2. Material and methods

2.1. Reagents and chemicals

TEB was purchased from Sigma Aldrich (São Paulo, Brazil), methanol, and HPLC grade acetonitrile from Mallinckrodt (Phillipsburg, New Jersey, USA) and formic acid (98-100 % purity), and phosphoric acid (85 % purity) from Merck (Darmstadt, Germany). All chemicals used in experiments were P.A. grade. The ultrapure water used in experiments and solutions was prepared in a lab with a Millipore aid system (Bedford, MA, USA). SPE Strata cartridges C18-E (200 mg) were used to pre-concentrate samples and their clean-up steps (Phenomenex, Torrance, CA, USA). A TEB stock solution containing 1,000 $mg \cdot L^{-1}$ in methanol and an intermediate solution containing 100 $mg \cdot L^{-1}$ was prepared for analytical procedures.

2.2. Determination of TEB concentration

The determination of TEB concentration was done by applying the methodology according to Caldas et al. (2010) and a chromatograph Waters 2996 aid (Water pump 600 and photodiode detector, Rheodyne 20 µL of loop injector, λ 210-400 nm), a column of BDS Hyperclone C18 5 µm 130A Phenomenex (250×4.6 mm); acetonitrile: water pH 3 (52:48, v/v) was used as mobile phase. Water pH was adjusted with H3PO4 solution (1:1 v/v); the flow-rate of 0.8 mL min^{-1} for 8 min, 1.2 $mL \cdot min^{-1}$ for 14 min and 0.8 $mL \cdot min^{-1}$ for 15 min applied in analytical procedures. TEB was prepared for the calibration curve (1-1,000 $\mu g \cdot L^{-1}$ TEB; r>0.99; LOQ: 0.001 $mg \cdot L^{-1}$ TEB). TEB aqueous solution was prepared by dilution of a commercial TEB (Rival 200 EC). The experiments were executed in triplicate.

2.3. Photodegradation experiments

The photodegradation experiments were carried out with a stainless steel photoreactor aid with 316 mL capacity (UV Water Sterilizer) connected to an external tank with 684 mL capacity (totaling 1 L of work solution); UV OSRAM PURITEC Hg vapor low-pressure lamp 6 W as a UV light source (5.581-$7.66.10^{18}$ photons flux); and underwater recirculation pump (SARLO BETTER S90) applying 0.5 $L \cdot min^{-1}$. The photodegradation experiments were executed using an aqueous solution containing 5 $\mu g \cdot L^{-1}$ of TEB prepared by dilution of a commercial TEB (Rival 200 EC). The pH was set with TECNOPON mPA 210 pH meter, hydrochloric acid solution, and sodium hydroxide solution aid. The catalyst made from Titanium Dioxide, Silicon Dioxide, and Silver Nitrate ($TiO_2 \cdot SiO_2 \cdot AgNO_3$) was utilized in all experiments.

The experiments were conducted at room temperature for 40 min under UV light irradiation and recirculation. The sample collection was carried out with 20 mL sampling at zero and 40 min. The experiments were conducted with the photoreactor system as shown in Fig. 1. The sampling was executed in 0 and 40 min of photodegradation treatment.

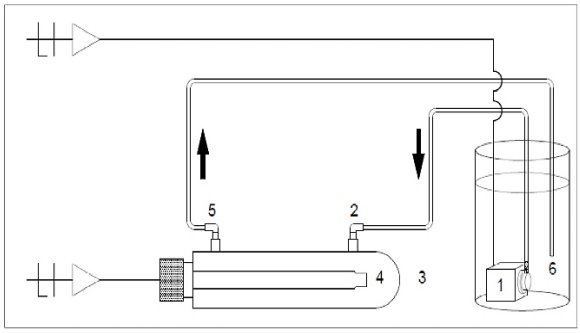

Fig. 1. Photoreactor system: (1) recirculation pump, (2) inlet, (3) photoreactor, (4) UV source, (5) outlet, and (6) external tank

2.4. Design of the experiments

The experiments were managed by employing an experimental design containing two fixed parameters: pH (5.6-8.4) and catalyst concentration (0-100 $mg \cdot L^{-1}$). Five levels of significance were tested (-1.41, 1.00, 0.00, 1.00, and 1.41). The matrix comprises a group of ten experiments (Table 1).

Table 1. Experimental design using the central composite design (CCD) for 2 factors in 5 levels to TEB photocatalytic degradation

Experiment (n)	***TiO_2·SiO_2·$AgNO_3$ (mg s^{-1})***	***pH***
1	-1.00 (14.5)	-1.00 (6.0)
2	-1.00 (14.5)	1.00 (8.0)
3	1.00 (85.5)	-1.00 (6.0)
4	1.00 (85.5)	1.00 (8.0)
5	-1.41 (0.0)	0.00 (7.0)
6	1.41 (100)	0.00 (7.0)
7	0.00 (50.0)	-1.41 (5.6)
8	0.00 (50.0)	1.41 (8.4)
9 (C)	0.00 (50.0)	0.00 (7.0)
10 (C)	0.00 (50.0)	0.00 (7.0)

C: Central point

2.5. Phytotoxicity study

The phytotoxicity tests were performed using a treated work solution that presented the higher degradation of the fungicide. Lettuce seeds (*Lactuca sativa*), onion seeds (*Allium cepa*), and cucumber seeds (*Cucumis sativus*) were used as bioindicators. According to US Environmental Protection Agency (EPA) (EPA U.S. 1996), these species are shown to be the best bioindicators for these kinds of substances and the toxicity tests followed the work of Zucconi et al. (1981) with modification and Mendes et al. (2016, 2021). The treated work solutions containing the TEB and/or its photoproducts were diluted (10x) and homogenized (10 min) (Mendes et al., 2016, 2021). According to Zucconi et al. (1981), a dilution adjustment is made because the contaminants are typically discharged in the water resources and soils after passing through a dilution. Also, the Environmental Protection Agency recommends diluting 10x to simulate the natural dilution that occurs in hydric resources (EPA, 1996). Next, this diluted solution was added to lettuce, onion, and cucumber seeds previously placed on filter paper in Petri dishes. The experiments were executed using 5 mL of the diluted solution and 10 seeds of each seed species in triplicate. The Petri dishes were sealed with Parafilm® aid to promote the gas changes and to inhibit the humidity losses. The dishes containing lettuce and cucumber seeds were incubated at 25 °C for 48 h according to Mendes et al. (2016, 2021) and the dishes containing onion seeds at 25 °C for 168 h, according to Bernardes et al. (2015).

The number of seeds was counted, and the radicular length was measured with a digital pachymeter aid (150 mm) after the incubation time. The relative germination index (*RGI*) was calculated according to Eq. (1) (Mendes et al., 2016, 2021; Zucconi et al., 1981), and the Root Elongation (*RE*) according to Eq. (2), and the Germination Index (*GI*) according to Eq. (3).

$$RGI\ (\%) = [(GSSD) / (GSCD)] \times 100 \quad (1)$$

$$RE\ (\%) = [(\Sigma RLSD) / (\Sigma RLCD)] \times 100 \quad (2)$$

$$GI\ (\%) = [RGI\ (\%) \times RE\ (\%)]/100 \quad (3)$$

where: *GSSD* is germinated seeds in sample dishes; *GSCD* – germinated seeds in control dishes; *ΣRLSD* – the sum of root length in sample dishes; *ΣRLCD* – the sum of root length in control dishes.

2.6. Experimental design for phytotoxicity test

The univariate experimental design was implemented using the experiments of photodegradation and a control group (absence of catalyst and UV irradiation with TEB) as treatments. The *GI* of the bioindicator was used as a response variable (lettuce, onion, and cucumber seeds). Each treatment was carried out with 3 replicates. The outliers were disregarded applying the studentized residual technique. The variables were normalized and analysis of variance (ANOVA) was performed considering F-test ($p<0.05$) and posteriorly Duncan Test ($p<0.05$).

3. Results and discussion

3.1. Catalytic photodegradation experiments

The degradation efficiencies obtained in photo experiments are shown in Table 2. The results present the interference of the pH and catalyst concentration on TEB degradation. The higher presence of

$TiO_2 \cdot SiO_2 \cdot AgNO_3$ in work solution demonstrated a negative influence on TEB degradation: lower than 60 % using concentrations higher than 50 $mg \cdot L^{-1}$ of catalyst.

The most efficient photodegradation was obtained using 14.5 $mg \cdot L^{-1}$ catalysts (Experiment 1, Table 2): 84.96 % degradation. The experiment without catalyst reached 65.89 % degradation in 40 min under UV irradiation (Experiment 5), higher than all other experimental results that used a catalyst. These results show that the increase catalyst concentration results in lower photodegradation. Similar behavior was found by Schneider et al. (2014) in their research, in which the efficiency of the experiments using a high concentration of TiO_2 led to lower degradation results. The presence of the catalyst makes the aqueous medium turbid and inhibits the UV light propagation. The TEB concentration also must be considered. The photodegradation results depend on the substrate concentration once the molecules compete for the photons (Pourata et al., 2009) and the UV irradiation (Devi and Murthy, 2008).

The efficiency obtained in the photodegradation experiment was plotted in Fig. 2. It shows the response surface considering the results obtained in photodegradation experiments (Table 2) as a function of pH and catalyst concentrations. The response surface demonstrates the photodegradation process behavior (Pd), according to the mathematical model Eq. (4):

$$Pd\ (\%) = 0.0024x2 + 0.6964y2 + 215.4218 - 1.7533x - 25.4636y + 0.1926xy \quad (4)$$

where: "*Pd*" is the photodegradation (*%*), "*x*" is the catalyst concentration, and "*y*" is the pH.

Table 2. The efficiency obtained in photodegradation experiments of TEB in 40 min of treatment

Experiment (n)	***$TiO_2 \cdot SiO_2 \cdot AgNO_3$ ($mg \cdot L^{-1}$)***	***pH***	***Photodegradation (%)***
1	14.5	6	84.96
2	14.5	8	57.61
3	85.5	6	56.38
4	85.5	8	56.38
5	0	7	65.89
6	100	7	54.87
7	50	5.6	63.03
8	50	8.4	48.15
9	50	7	60.33
10	50	7	54.17

The best results were reached in pH 5.6 and 7.0, however, all of the experiments presented degradations higher than 48 % (Fig. 2). Similar results were encountered by Bastidas et al. (2013) for the photocatalytic degradation of organophosphate insecticides. According to Antonopoulou and Konstantinou (2014), pH 3 presented a better condition to DEET (N, N-dimethyl-*m*-toluamide) photocatalytic degradation using TiO_2 as a catalyst. Our results show the low concentration of $TiO_2 \cdot SiO_2 \cdot AgNO_3$ or its absence, and neutral up to acid pH, enhance the conditions for TEB photodegradation.

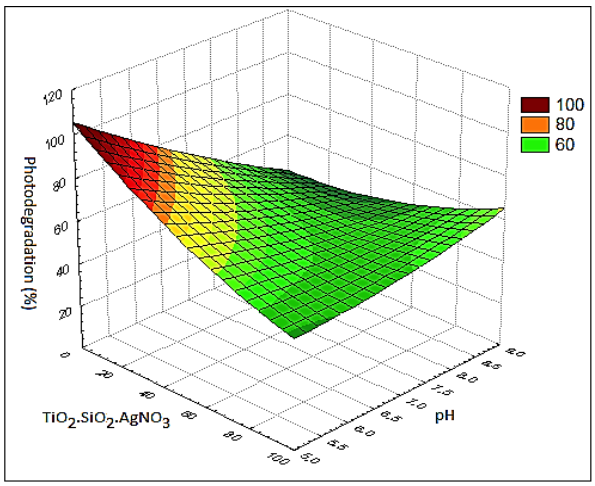

Fig. 2. Response surface for the photodegradation experiments as a function of pH and catalyst concentrations

Usually, acid mediums are indicated for AOPs. The pH interferes with these techniques modifying the solubility and adsorption of the catalyst. In this way, while taking into account the results shown in Fig. 2, the photolysis acid of TEB is economically viable besides being environment-friendly (Menezes et al., 2016). The photodegradation without catalyst use is interesting since the separation of catalyst frequently restricts the photocatalytic degradation. Therefore, the TEB degradation is possible using only UV irradiation in lightly pH acid: a typical condition in water resources and in accordance with the Brazilian standards of treated wastewater released into nature (pH 5-9) (Brazil, 2011).

3.2. Phytotoxicity studies

The phytotoxicity tests were executed to evaluate the effects of TEB and its photoproducts in the water bodies, because of the importance of bioavailable substances in water and soil (Hillis et al., 2011): the main destination of fungicides used in agriculture (Herrero-Hernández et al., 2013). Thus, the toxicity tests have been used in toxicological assessment for different compounds (Eze et al., 2021; Sobrero and Ronco, 2004) and adopted as efficiency monitoring of AOPs (Garcia et al., 2009; Palácio, 2009). This evaluation is possible due to the submersion of the seeds in a solution containing TEB and its photoproducts, which germinate under this environmental stress (Gerber et al., 2017; Guidoni et al., 2018; Souza et al., 2005).

The root's elongation is a very important parameter to be observed because this is the first part of the plant in contact with the medium and the substances absorbed by the roots (Kapustka, 1997). The differences of the responses obtained between the three species of seeds to evaluate the TEB and its photoproducts are the result of the lack of correlation

physiology between them (Méndez et al., 2009; Santos 2008). The onion and lettuce seeds are phenotypically sensitive and put across contaminants in the environment (Cuchiara et al., 2012; Grisi et al., 2011; Magiero et al., 2009).

In this way, the phytotoxicity tests were implemented with three treatments: the first was a treated work solution without catalyst (0UVT40); the second a treated work solution containing 14,5 $mg \cdot L^{-1}$ of catalyst in slightly acidic medium (145UVT40 - best photodegradation result), and in the third, a control group was established as a reference (absence of catalyst and UV irradiation containing TEB). Table 3 shows the phytotoxic effects of TEB and its photoproducts. The phytotoxic effects of TEB and its photoproducts were analyzed through the Germination Index (GI) using lettuce, onion, and cucumber seeds. According to Zucconi et al. (1981), *GI* values under 80 % are considered phytotoxic. Therefore, the TEB, catalyst, and their photoproducts had an effect on all seeds analyzed.

The *GI* was lower than 70 % for lettuce and onion seeds indicating phytotoxicity to all treatments. The assessment with those bioindicators denotes that the phototreatment does not reduce the potential of phytotoxicity, once the *GI* has shown results without a significant difference when compared to the control group (Mendes et al., 2016, 2021; Zucconi et al., 1981). Garcia et al. (2009) evaluated the photocatalytic degradation of textile effluents using the TIO_2 system and found similar phytotoxic effects using *Lactuca sativa* germination, where there was an increase in toxicity only at the end of the process after 4 h of irradiation, creating a less toxic product. However, studies undertaken by Palácio (2009) evaluated the effects of the AOPs and electrocoagulation followed by photocatalytic degradation in the presence of TiO_2 in the treatment of textile effluents, which corroborated high toxicity to *Lactuca sativa*, even though the effluent was treated for 6 hours. The phytotoxic characteristic of TEB can be attributed to the presence of triazoles that were not photodegraded in the step before the phytotoxicity test. These triazoles directly impact the development of plants, mainly in the roots, by inhibiting their growth. The inhibition is caused by negative effects on enzymatic metabolism, biochemical mechanism, and nitrogen fixation. Also, the phytotoxic character is greater in seeds more sensitive to changes and stresses, as shown in this study in onion and lettuce seeds (Ahemad and Khan, 2012; Shishatskaya et al., 2018).

The *GI* values found in this study for onion seeds were higher than those presented by Bernardes et al. (2015), in spite of all treatment shown phytotoxicity on onion seeds. They evaluated the phytotoxic potential of TEB in five different concentrations between 12.5 $mg \cdot L^{-1}$ and 200 $mg \cdot L^{-1}$. In this study, the germination of *Allium cepa GI* was below 50 %, showing that the TEB caused higher macroscopic changes in the roots, even in lower concentrations, showing a phytotoxic character depending on the concentration employed, affecting the percentage of germination, the germination index and the cell division in the onion seeds, indicating phytotoxic and cytotoxic actions.

The phytotoxicity test using cucumber seeds showed that the phototreated experimental solution using a catalyst (145UVT40) is less phytotoxic than the phototreated work solution without a catalyst (0UVT40). The treatment 145UVT40 proves that the presence of the catalyst with phototreatment promotes the degradation of some toxic substances, thus not inhibiting the development of the tested seeds in their entirety. Moreover, cucumber seed are considered to be more tolerant in terms of the presence of chemical agents that act as growth inhibitors for the other seeds (Tao et al., 2016).

The treatment 0UVT40 demonstrates a significant decrease in the *GI* of 59.70 % (values under 80 % are considered phytotoxic when compared to the control group) (Zucconi et al., 1981). The results display that the treatments only with photolysis generated phytotoxic photoproducts. The non-phytotoxicity identified on the control group and 145UVT40 for *Cucumis sativus* bioindicator can be attributed to the non-generation of phytotoxic composts, normally generated by the oxidation reactions in these kinds of processes (Bessegato et al., 2012; Santana et al., 2003; Schneider et al., 2014). Moreover, the main reason for obtaining significant data in the phytotoxicity test with *Cucumis sativus* is its sensitivity, showing excellent stability and reproducibility to effects applicable in ecological risk assessments, having been demonstrated by Wang et al. (2001), who observed the method of Germination Index and growth of the root of *Cucumis sativus* in control in comparison with tests in the presence of xenobiotics.

The significant means of *GI* found between the treatments for the cucumber seeds and the non-significant means for the onion and lettuce seeds are due to the toxic effects of certain substances that are not only identified in the germination test (*GI*), but also can be detected through the germination speed or other parameters of the seed growth process (Cuchiara et al., 2012; Ferreira and Borghetti, 2004).

Table 3. Germination Index (%) using lettuce, onion, and cucumber seeds for TEB photoproducts in treated work solution

Treatment	***Germination Index (%)***		
	Lettuce Seeds	***Onion seeds***	***Cucumber seeds***
Control group	63.14±7.76[a]	57.61±23.05[a]	126.70±9.61[a]
0UVT40	62.53±13.84[a]	69.90±10.44[a]	59.70±7.98[b]
145UVT40	54.25±15.07[a]	64.37±10.64[a]	84.72±18.08[a]

Mean ± Standard error. Different letters in the column indicate significant differences (Duncan test: $p<0.05$)

4. Conclusions

The results show that the TEB photodegradation in a slightly acidic medium and lower catalyst concentrations or its absence is more efficient than photodegradation in high catalyst concentrations. Also, the experiment confirms the potential of the photolysis application to degrade TEB without the use of catalysts and in this way, lowering the costs and contributing to sustainable development.

The TEB and its photoproducts were phytotoxic for lettuce and onion seeds, despite the UV irradiation and photocatalyst presence. On the other hand, the TEB was non-phytotoxic for cucumber seeds when it was exposed to UV irradiation and the presence of the photocatalyst.

For future works, we recommend assessing the phytotoxicity effects of $TiO_2 \cdot SiO_2 \cdot AgNO_3$ raw catalyst and in other concentrations on lettuce, onion, and cucumber seeds. Hence, special attention must be given to the phytotoxicity effects of TEB when it is applied to the agricultural systems, avoiding the environmental contamination of the water resources, soil, and live organisms.

Acknowledgments

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