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# Innovative frontiers: Advancing technologies for pesticide elimination in grape seeds

## Üzüm çekirdeklerinde pestisit içeriğinin azaltılması için yenilikçi teknolojiler

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### Abstract

Grape seeds, a valuable by-product of winemaking, are rich in bioactive compounds with significant economic potential. However, pesticide residues in grape seeds pose risks to human health and product quality. This study explores innovative technologies including cold plasma, ultrasound, aqueous ozone, and gaseous ozone to eliminate pesticide residues from grape seeds. Cold plasma treatment emerged as highly effective, completely eliminating certain pesticides like Triadimenol and Azoxystrobin. Ultrasound treatment also showed promising results, particularly in reducing Pyrimethanil residues. Aqueous ozone treatment achieved moderate reductions, while gaseous ozone exhibited the least efficacy. Factors influencing efficacy included pesticide type, treatment duration, and matrix characteristics. Future research should focus on optimizing parameters to enhance pesticide removal while minimizing impacts on product quality. These findings indicate the importance of tailored approaches for pesticide elimination, contributing to safer agricultural practices and consumer health.

**Keywords:** Grape seed, Pesticide elimination, Cold plasma, Ultrasound, Ozone treatment

### Öz

Üzüm çekirdekleri, şarap üretimi sırasında ortaya çıkan değerli bir yan üründür ve biyoaktif bileşikler açısından zengin olmalarıyla dikkat çekerler. Ancak, bu çekirdeklerde bulunan pestisit kalıntıları, insan sağlığı ve ürün kalitesi açısından ciddi bir endişe kaynağıdır. Bu çalışma, üzüm çekirdeklerinden pestisit kalıntılarını azaltmak için soğuk plazma, ultrason, sulu ozon ve gaz ozon gibi yenilikçi teknolojileri araştırmaktadır. Yapılan deneylerde, özellikle soğuk plazma işleminin Triadimenol ve Azoksistrobin gibi belirli pestisitleri tamamen ortadan kaldırdığı gözlemlenmiştir. Diğer taraftan, ultrason işlemi özellikle Pirimetanil kalıntılarını azaltmada etkili olmuştur. Sulu ozon ve gaz ozon işlemleri ise daha az etkili bulunmuştur. Bu bulgular, pestisitlerin ortadan kaldırılması için özelleştirilmiş yaklaşımların önemini vurgulayarak, daha güvenli tarımsal uygulamalara ve tüketici sağlığına katkıda bulunmaktadır.

**Anahtar kelimeler:** Üzüm çekirdeği, Pestisit, Soğuk plazma, Ultrases, Ozon uygulamaları

## 1 Introduction

Grape pomace, a valuable by-product of winemaking, has gathered considerable attention due to the significance of its grape seeds, constituting about 25% of the pomace [1]. Beyond being a simple by-product, grape seeds hold remarkable economic potential, containing cellulose, oil, protein, and various bioactive compounds such as polyphenols [2]. This composition includes grape seeds as valuable resources for the development of nutraceuticals and cosmetics [3]. The multi-layered health benefits associated with grape seeds, including antioxidative, anti-inflammatory, anticancer, and neuroprotective properties, underscore their importance in promoting overall well-being [4,5].

Pesticides play a pivotal role in controlling pests and diseases in vineyards yet their improper use can lead to the exceeding of safe levels, posing threats to the environment, grape quality, processed products, and human health [6–8]. This concern is further emphasized by the fact that a significant percentage of tested grapes, over 86% according to a recent European Union report, showed pesticide residues, with more than 68% having multiple residues [9]. The European Union has established maximum permitted pesticide levels in vegetable products, with grape residue limits typically ranging between 0.01 mg/kg and 5 mg/kg, depending on the specific pesticide [10].

The application of pesticides to grapevines prior to harvest tends to accumulate in grape seeds due to their high lipid solubility [11]. Furthermore, residues of pesticides present on the surface of grapes can transfer to the seeds throughout the processing stages for various products [12,13]. Specifically, in the production of cold-pressed grape seed oil, which involves traditional solvent extraction and refining processes without high-temperature treatments, elevated levels of pesticide residues may be observed [11]. Food producers involved in the industrial production of grape seed oil using the cold-press technique face a notable obstacle, as levels of pesticide residues may exceed the maximum residue limit (MRL). This issue becomes a critical concern, potentially endangering human health and

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complicating the preservation of essential nutrients during the cold-press process.

Traditional methods such as washing, chlorine-based chemical sanitization, and thermal processing are commonly used to remove pesticides from food. However, washing is only partially reliable for eliminating water-insoluble pesticides like hexachlorocyclohexane and endosulfan [14]. Moreover, the effectiveness of these methods varies based on factors such as residue location, polarity, time, and temperature [15,16]. Chemical sanitization, though effective, has raised concerns due to the potential generation of carcinogenic by-products, leading to its prohibition in some regions [17]. Although rigorous thermal treatments can guarantee products free of pesticides, they have the potential to negatively affect the physicochemical, nutritive, and organoleptic properties [18]. As an alternative, researchers are exploring non-thermal advanced oxidation methods for removing pesticide residues from agricultural products. Recent advancements in non-thermal and novel techniques, such as ozone, ultrasounds and cold plasma, have shown promise in modifying the negative impacts of pesticides in food [19–22].

In this investigation, grape seeds were obtained from grapes treated with pesticides, including Azoxystrobin, Triadimenol, Boscalid, Tetrahydrophthalimide, Fluopyram, Cyprodinil, Metalaxyl and isomer mix and Pyrimethanil. Significantly, the analysis shows that the pesticide content exceeds the established maximum residual limits (MRL) within the grape seeds. To eliminate these residues, innovative technologies such as cold plasma, ozone, and ultrasound were employed.

## 2 Materials and methods

The material for this study comprises Misket grape seeds sourced by a local company (İstanbul, Türkiye) which produces grape seed powder and oil. In this study, the samples analyzed are naturally contaminated products determined to be pesticide-laden through quality control analyses conducted during the routine purchasing process of the company that uses grape seeds as raw material. All chemicals used for analyses were purchased from Sigma-Aldrich (St Louis, MO).

### 2.1 Emerging technologies applied

In this study, various innovative technologies were employed as methods to eliminate pesticide residues from grape seeds. These included cold plasma, ultrasound, aqueous ozone, and gaseous ozone treatments.

### 2.1.1 Cold plasma application

The experimental setup for this study involved the utilization of an Atmospheric Cold Plasma Jet. Specifically, the plasma jet utilized in the research was the Plasmatek A5 with a power capacity of 600W. The cold plasma operated at a frequency of 40 kHz, and a power input of 600W was employed during the experimental procedures. Additionally, dry air was supplied at a controlled rate of 10 L/min to facilitate the atmospheric cold plasma jet application. The 5 gr of grape seed samples were weighed in a petri dish and placed under the jet outlet. The treatment time was determined as 15 min which was tested highest treatment time for food products in the literature.

### 2.1.2 Ultrasound application

The ultrasound treatment was administered using the Bandelin HD4100 Ultrasonic Homogenizer, paired with the TS106 probe for enhanced precision. To commence the procedure, the 50 grams of seed samples were suspended in water at a ratio of 5/100 (w/v). The ultrasonication process involved pulsing at intervals of 10 seconds on and 5 seconds off, conducted at room temperature for a duration of 15 minutes while maintaining a precise 75% amplitude (20 kHz, ultrasonic power ranging from 30 to 150 W). Following the ultrasonication process, the seed samples underwent a careful filtration step and were subsequently subjected to air-drying to complete the process. This method ensures the effective application of ultrasound for decrease of pesticide residues in the treatment of seed samples.

### 2.1.3 Aquas ozone application

Aquas ozone was generated by a custom-made ozone generator (PCS Electronics, İstanbul, Turkey). The ozone was generated at a controlled flow rate of 2 L/min, ensuring a stable and efficient production with at least 2 ppm concentration. Subsequently, a total of 100 grams of seed were immersed in this ozone-enriched solution, maintained at room temperature. The immersion duration was set as 30 minutes allowing for the exploration of the impact of ozone exposure on the seeds.

### 2.1.4 Gaseous ozone application

The experimental setup for the application of gaseous ozone comprised an oxygen concentrator, an ozone generator, a fumigation chamber, and an ozone destructor. The gaseous ozone generator is integrated with an oxygen concentrator to enhance the ozone concentration. The ozone generation system, utilizing an oxygen concentrator, achieved a purity level of 95% through the swing adsorption principle, effectively separating oxygen, nitrogen, and other gases at a constant temperature. To produce gaseous ozone, a corona discharge ozone generator from PCS Electronics in Istanbul was employed. Operating with a power consumption of 500 W and utilizing purified dry oxygen feed gas, this ozone generator yielded an output of 10 g/h. This comprehensive system ensures the controlled and efficient generation of gaseous ozone for various applications. The 100 grams of seed samples were exposed to gaseous ozone for 30 min in the chamber and then kept in a sealed bag for pesticide analysis.

### 2.2 Pesticide analysis

### 2.2.1 Pesticide extraction

In the preparation process for LC-MS/MS analysis, the grape seed samples were ground with the help of a grinder. The QuEChERS (quick, easy, cheap, effective, rugged, and safe) method was employed one-step buffered acetonitrile (MeCN) extraction, incorporating salting-out liquid–liquid partitioning with MgSO to remove water from the sample. For this, 10 g of the homogenized samples were carefully transferred into a 50 mL centrifuge tube. To validate the process, recovery studies were conducted by introducing specific volumes of the working standard solution into blank samples, followed by the addition of 20 mL of ACN. The tube underwent a vigorous 3-minute vortex, and a well-defined phase separation was achieved by introducing 3 g of NaCl. Following immediate capping, the tubes underwent an additional 2-minute vortex and were then centrifuged for 5 min at 3800 rpm. The upper layer, amounting to 1 mL, was precisely transferred to a 2 mL centrifuge tube. After a 1-minute vortex and a subsequent 1-minute centrifugation at 10,000 rpm, the resulting upper layer was subjected to filtration through a membrane with a pore size of 0.22 µm. Finally, the filtered content was transferred into an auto-sampler vial, ready for LC-MS/MS analysis.

### *2.2.2 Chromatographic analysis*

AOAC Official Method 2007.01 was used to analyze the pesticide residues on grape seed samples with some modifications. The concentration of pesticides was determined using the LC-MS/MS system (Agilent), which featured an ESI source. Chromatographic separation was achieved employing a C18 column (15 cm long, 3.0 mm id, 3µm particle size) with a flow rate of 0.3 mL/min, and the injection volume was set to 10µL. The gradient elution with an initial condition of 25% MeOH in 5 mM formic acid solution was taken linearly in 15 min to 90% MeOH in 5 mM formic acid solution and held for 15 min [23].

## 3 Results and discussion

The seed samples were naturally contaminated with 8 different pesticides which were Pyrimethanil, Metalaxyl and isomer mix, Cyprodinil, Fluopyram, Tetrahydrophthalimide, Boscalid, Triadimenol and Azoxystrobin. The concentration of the pesticides was indicated in Table 1. These pesticides were determined over the maximum residual limit which is stated in the Turkish Food Codex.

**Table 1.** The pesticide levels of naturally contaminated grape seeds

| Pesticide | Concentration (mg/kg) | MRL* (mg/kg) |
|---|---|---|
| Pyrimethanil | 0.28±0.01 | 0.020 |
| Metalaxyl and isomer mix | 0.21±0.004 | 0.010 |
| Cyprodinil | 0.13±0.005 | 0.020 |
| Fluopyram | 0.066±0.001 | 0.010 |
| Tetrahydrophthalimide | 0.056±0.002 | 0.050 |
| Boscalid | 0.043±0.001 | 0.010 |
| Azoxystrobin | 0.024±0.001 | 0.010 |

*MRL (maximum residue level as stated in the Turkish Codex)

In this study, emerging methods to eliminate pesticides were evaluated specifically focusing on Pyrimethanil, Metalaxyl and its isomer mix, Cyprodinil, Fluopyram, Tetrahydrophthalimide, Boscalid, Triadimenol, and Azoxystrobin, all of which were found to exceed the Maximum Residue Limits (MRLs).

Cold plasma treatment is one of the promising techniques to eliminate or reduce pesticide residues on food products [24]. Jet air cold plasma treatment involves the use of non-thermal plasma to eliminate pesticide residues on the surface of fruits and vegetables. In this study jet air cold plasma applied to grape seed samples resulted in a significant amount of elimination in the aforementioned pesticides as shown in Figure 1. Triadimenol and Azoxystrobin were completely eliminated by cold plasma treatment, while Tetrahydrophthalimide exhibited a moderate level of resistance, with a reduction rate of 59%. Azoxystrobin's numerous functional groups make it vulnerable to attack by active chemical species resulting from cold plasma. Photodegradation likely occurs through multiple pathways, including photo-isomerization, hydrolysis, and cleavage of various bonds [25]. Additionally, Boscalid demonstrated the second highest resistance, with a reduction rate of 65%. Similar results were observed for the dissipation efficacy of boscalid and imidacloprid on blueberries by plasma treatment. A two-minute plasma treatment achieved removal efficiencies surpassing 20% across all applied voltages. Notably, after five minutes at 80 kV, removal efficiencies for boscalid and imidacloprid reached 75% and 80%, respectively [26]. In another study conducted by Misra et al. [27], applied cold plasma treatment to strawberries contaminated with a mixture of pesticides, achieving maximum reductions of 69%, 45%, 71%, and 46% for azoxystrobin, cyprodinil, fludioxonil, and pyriproxyfen, respectively, after 300 s of treatment at 80 kV. Except for pyriproxyfen, all other pesticides reached concentrations below the permitted MRL following plasma treatment. Since the cold plasma treatment was applied for 15 min in this study, all pesticides were determined under the MRL. The longer the treatment time, the more elimination rate was achieved [28]. These findings emphasize the variability in pesticide susceptibility to cold plasma treatment, highlighting the need for further research to better understand resistance mechanisms and treatment effectiveness.

Ultrasound treatments, an eco-friendly technology in the food industry, are utilized for pesticide decontamination, as indicated by Bhargava et al. [29]. In this study, ultrasound treatment demonstrated the highest effectiveness in dissipating pesticides as seen in Figure 1. Similarly, cold plasma treatment successfully eliminated Triadimenol and Azoxystrobin, with Pyrimethanil also completely removed from the grape seed samples. Boscalid exhibited greater resistance to ultrasound treatment compared to cold plasma treatment, achieving only a 58% elimination rate. This suggests that while ultrasound can effectively reduce the concentration of Boscalid, it may not be as efficient as cold plasma treatment in eliminating this particular pesticide. Ultrasonication was observed to effectively remove pesticide residues from food products through reactive oxygen and cavitation processes. However, it was noted that certain pesticides, such as Boscalid, exhibited higher resistance to ultrasonication compared to cold plasma treatment. The findings align with previous research, such as that performed by Cengiz et al. [30] and Lozowicka et al. [31]. Cengiz et al. have demonstrated the efficacy of low-intensity electric current and ultrasound in reducing pesticide levels in tomatoes, while Lozowicka et al. found the ultrasonic treatment to be particularly effective in removing pesticide

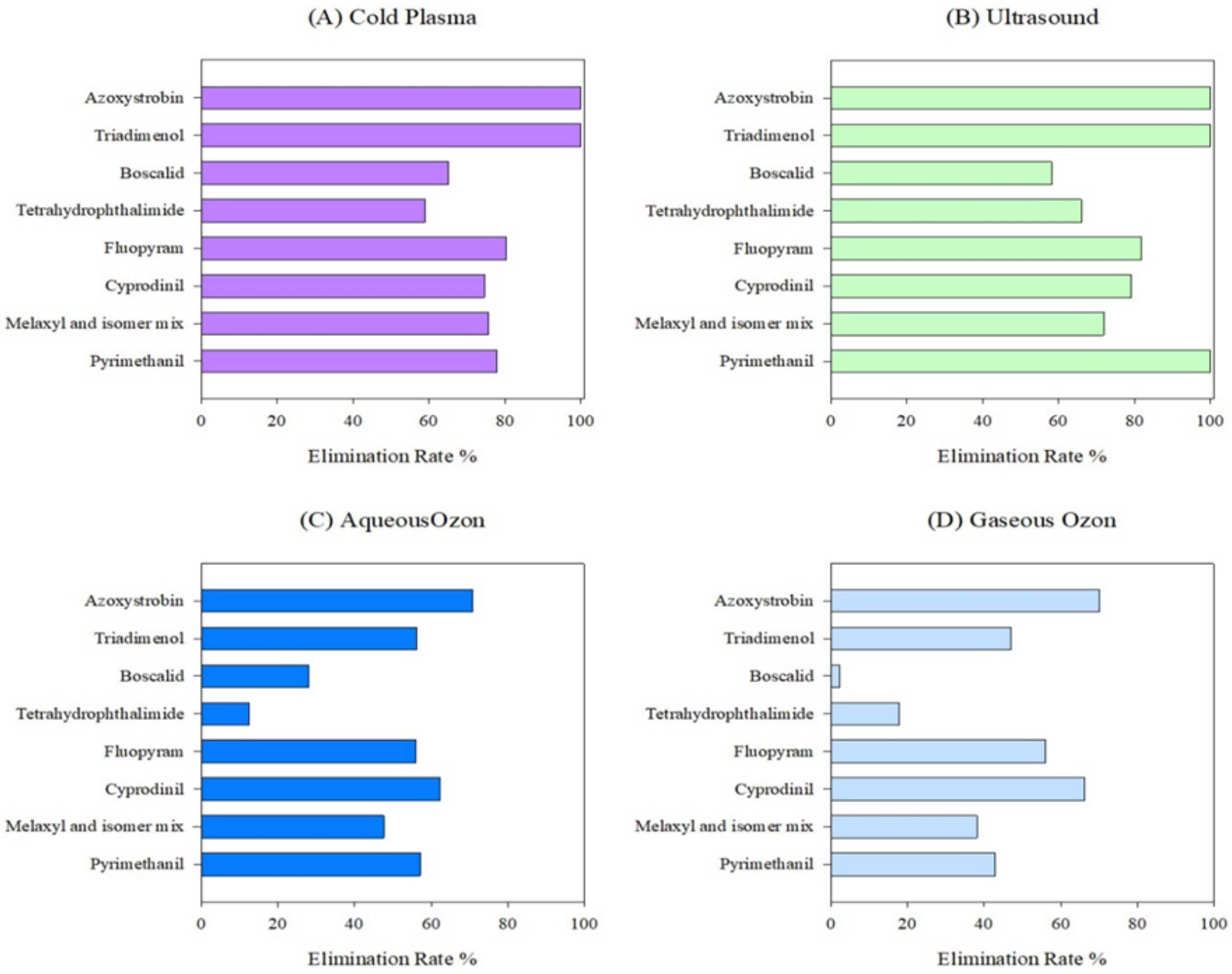

**Figure 1.** Elimination rate of pesticide, determined grape seed by different emerging technologies including (A) Cold Plasma, (B) Ultrasound treatments, (C) Aqueous Ozon and (D) Gaseous Ozone

residues from strawberries. Furthermore, Zhou et al. [32] investigated the efficacy of sole ultrasonic washing on the dissipation of various pesticides in rape and grapes, using a commercial ultrasonic dishwasher. Their study highlighted the considerable impact of surface characteristics on dissipation efficiency, noting higher reductions in grape samples due to their increased surface area. Similarly, [33] examined the influence of ultrasonic washing on pesticide residues in pakchoi. They observed that increasing ultrasonic power and decreasing frequency enhanced pesticide reduction, albeit at the expense of the vegetable's vitamin C content and physical integrity. The effectiveness of ultrasound treatment in pesticide dissipation is influenced by factors such as the commodity's surface area, treatment conditions (ultrasonic power and frequency), and pesticide resistance. Optimizing these parameters is crucial for maximizing treatment efficiency and effectively managing pesticide residues in agricultural products.

Aqueous ozone treatment offers an economically feasible and efficient method for reducing pesticides from food products. Since ozone undergoes degradation into harmless oxygen, making it environmentally friendly, is commonly used during fruit and vegetable processes [34]. The treatment with ozonated water resulted in the reduction of pesticide residues, including Pyrimethanil, Cyprodinil, Fluopyram, Triadimenol, and Azoxystrobin, by 57%, 62%, 56%, 56%, and 70% respectively. However, unlike cold plasma and ultrasound treatments, the complete elimination of any pesticide on grape seeds was not achieved. Moreover, Tetrahydrophthalimide showed the greatest resistance to aqueous ozone treatment in this study, with the lowest 12% elimination rate observed. In contrast, Al-Dabbas et al. [35] reported substantial reductions of 98% in chlorpyrifos and 87% in cypermethrin levels in tomato fruits after washing with ozonated water containing 0.4 ppm ozone for 30 minutes.

In a study conducted by Rodrigues et al. [36] two ozone treatments, bubbling ozone in water at concentrations of 1 and 3 mg/L, effectively removed residues of the fungicides azoxystrobin, chlorothalonil, and difenoconazolein tomatoes, with the 3 mg/L treatment achieving the highest reduction of 70–90% of the pesticides. Another study examined the use of low levels of dissolved ozone (1.4–2.0 mg/L) to eliminate residues of four pesticides (methylparathion, parathion, diazinon and cypermethrin) on Brassica rapa vegetable surfaces. Notably, ozone exhibited considerable effectiveness in removing cypermethrin, with removal rates exceeding 60% [37]. Furthermore, the efficiency of pesticide removal was found to be closely linked to the levels of dissolved ozone and temperature. The efficacy of ozone treatment is depending on several factors, including concentration, temperature and application duration, as evidenced in this study. Consequently, the complete elimination of the expected pesticides was not achieved in these tested conditions for our study, emphasizing the importance of selecting parameters to achieve broad dissipation while minimizing adverse effects on product quality.

In the conducted study, it was found that the application of gas ozone exhibited the least efficacy relative to other treatments under investigation. It was observed that Boscalid exhibited the minimum reduction among the tested pesticides when exposed to gas ozone. This indicates the highest degree of resistance among all tested pesticides. This result seems to be consistent with other research which found storage in the gaseous ozone did not accelerate the decline of boscalid residues on table grapes [38]. Although none of the pesticides used in the study were completely eliminated by gas ozone, noteworthy reductions were evident. Specifically, Azoxystrobin demonstrated the most significant decrease at 70 %, followed closely by Cyprodinil at 66 %. These results suggest that while gas ozone shows promise as a pest control agent, its effectiveness varies depending on the specific pesticide being targeted. The fact that Boscalid exhibited the least reduction emphasizes the variability in susceptibility among different pesticides to gas ozone treatment. A study conducted to remove difenoconazole and linuron from carrots reported that as ozone concentration and treatment duration increased, the percentages of pesticide removal also increased [39].

In another study showed by Kusvuran and colleagues, on lemon, orange, and grapefruit, they highlighted the significant impact of the matrices on the efficacy of gas ozone application. They observed that the removal efficiency of pesticide residues with ozone was notably influenced by the structural properties of the pesticides as well as the characteristics of the matrices [40]. The diminished efficacy of gaseous ozone in eliminating pesticides could be attributed to the matrices effect, particularly evident in grape seeds due to their smaller surface area and thicker coating. This limited contact with ozone gas could explain the reduced effectiveness observed in pesticide elimination. It is clear that achieving optimal results necessitates a nuanced understanding of the specific characteristics of the target residues and matrices involved.

## 4 Conclusion

This study aimed to evaluate various emerging technologies for removing pesticide residues from naturally contaminated grape seeds. While specific conditions are known to be necessary for effective treatment, this research underscores the importance of considering the type of pesticide involved due to variations in resistance levels. Among the tested methods, cold plasma application emerged as the most powerful, demonstrating remarkable efficacy in pesticide elimination. Ultrasound treatment also proved successful in significantly reducing pesticide residues. Although ozone treatments exhibited comparatively lower efficacy, both applications achieved a moderate level of pesticide elimination. These findings highlight the complexity of pesticide removal processes and emphasize the necessity of tailored approaches based on pesticide type and food matrices. Further research in this area could lead to the development of more efficient and targeted pesticide removal strategies, benefiting agricultural practices and consumer safety.

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## Conflict of interest

The author declares that no conflicts of interest exist regarding the research and content of this study.

**Similarity rate (iThenticate):** 11%

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