



Short communication

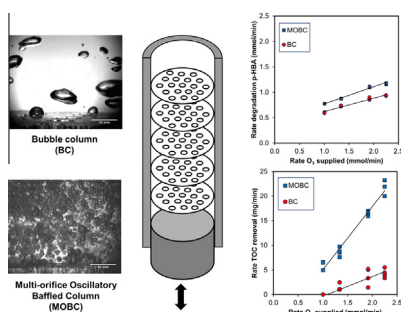
Intensification of ozonation processes in a novel, compact, multi-orifice oscillatory baffled column

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HIGHLIGHTS

- Water ozonation intensification in a multi-orifice oscillatory baffled column.
- Higher rates of ozone utilisation in a highly compact device.
- MOBC ozonation reactor is benchmarked against a bubble column.
- MOBC allows a significant reduction in reactor volume.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel approach for the intensification of ozonation of water and wastewater is presented using a highly efficient and compact multi-orifice oscillatory baffled column (MOBC) ozonation contactor. The MOBC uniquely yielded full (i.e. 100%) use of the ozone supplied with a very short (2.25 min) liquid contact time under continuous operation and reducing the need of further gas–liquid contacting equipment downstream from the MOBC. The increased performance of the MOBC ozonation reactor was benchmarked against a bubble column (BC) design and resulted in 20% increase on the rate of *p*-hydroxybenzoic acid (*p*-HBA) degradation, 75% increase in the rate of mineralisation of *p*-HBA per mole of ozone consumed, and 4.5–5.0-fold increase in the rate of mineralisation of *p*-HBA per mole of ozone supplied. This results from the very small size of bubbles (few hundreds of microns) and enhanced gas–liquid mass transfer and hold-up generated in the presence of small fluid pulsations and orifice baffles.

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1. Introduction

Ozonation is a mature advanced oxidation process increasingly applied to the treatment and purification of water and wastewater, including the oxidation of micro-contaminants and the inactivation of virus and bacteria [1–7]. Nevertheless, current ozonation technologies can be economically unattractive when they are

applied at industrial scale due to the high rate of ozone supply needed to treat contaminated water, the extended contacting time required in the reactor and the bulky size of the installed equipment. Ozone contacting often relies on conventional gas–liquid reactor designs such as bubble columns, packed columns, stirred tank reactors, air-lift reactors, or static mixers or venturi injectors systems usually combined with very bulky gas–liquid holding tanks [8–13]. These approaches require large footprint equipment and high ozone supply demands.

Oscillatory baffled columns (OBCs) are an emerging multiphase mixing technology that can effectively intensify many multiphase chemical and biological processes [14–16]. In OBCs, the eddy

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mixing obtained with small fluid pulsations and periodic restricting baffles, distributed in an elongated column, results in the generation of strong radial mixing within the chambers defined by successive baffles. The intense mixing generated is very effective in tuning the bubble size of the dispersed phase and in increasing the contact between immiscible phases (gas–liquid or liquid–liquid) [16,17]. Previous dissolution studies of oxygen, carbon dioxide and ozone in water [14–16,18–20] showed that the mass transfer rates in OBCs is several orders of magnitude higher than in other contactors. The dissolution of oxygen in water in a 26 mm internal diameter OBC was 6-fold faster compared to a bubble column (BC) [18]. The ozone–water mass transfer rate in a semi-batch 25 mm internal diameter OBC equipped with single-orifice baffles was 3-fold higher than in a BC [20]. Reis et al. described a 1–2-fold increase in oxygen mass transfer rate using an oscillating mesotube comparatively to a 50 mm internal diameter oscillatory flow reactor [15,21]. However, an investigation on the effectiveness of ozonation of wastewater in a pilot-scale OBCs, which may lead to full industrial scale reactors, has not been reported.

The novel ozonation reactor concept herein presented is based on a multi-orifice oscillatory baffled column (MOBC) [22] scaled up from single-orifice OBC technology, allowing mixing and hydrodynamic flow conditions produced at laboratory scale to be easily mimicked at pilot and industrial-scale [16]. This study provides proof-of-concept data related to the performance of a continuous 10-L scale MOBC ozonation reactor in the presence of small fluid oscillations. The increased performance of the MOBC ozonation reactor was benchmarked against a BC design, by monitoring the degradation of *p*-hydroxybenzoic acid (*p*-HBA) model water contaminant and total organic carbon (TOC) conversion and their removal efficiencies. The MOBC provides a novel approach to the intensification of water and wastewater treatment with ozone and other gaseous oxidants.

2. Materials and methods

2.1. Reagents

Chemicals were used as received without further purification. *p*-HBA (>99%) was from Sigma–Aldrich (UK). NaOH and H₂SO₄ for pH adjustment were Fluka (UK). For HPLC analysis, methanol

(HPLC gradient grade) was sourced from Fisher Scientific (UK). Ozone was generated from high-purity oxygen (99.999%, BOC gases, UK) in an OZOMAX, 8Vtt (OZOMAX, Canada), which delivered ozone doses of up to 23 g O₃/m³. The ultra-high purity water used in all experiments and analytical analysis was sourced from a Millipore Elix 35 water purification system (i.e. type 2 analytical-grade water).

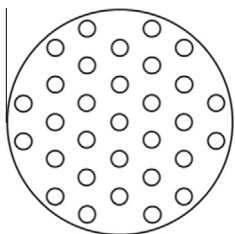
2.2. Experimental setup

Continuous flow ozonation experiments were performed in a vertical glass column (diameter 0.150 m, height 0.540 m) having a maximum operating volume of 9.6 L. In the MOBC configuration (Fig. 1) the column was equipped with a set of acrylic baffles, based on a previous optimisation study with CO₂ dissolution [16]. Table 1 summarises the design of the baffles.

Experiments were carried out by continuously injecting ozone, at a concentration of 23 g O₃/m³ and at different gas flow rates (2.1–4.7 L/min), to a stream of alkaline water (pH 10 ± 0.1, unbuffered) to decompose O₃ to ·OH favouring a gas–liquid reaction in the fast kinetic regime (Hatta number higher than 0.3), spiked with 50 mg/L of *p*-HBA flowing at a constant flow rate of 4.0 L/min (mean hydraulic time 2.25 min). The gas flow rate fed to the reactors was varied with the use of a mass flow controller (Cole Parmer, 0.05–5 L/min) diverting excess ozone from the ozonator to a thermal destroyer. The pH was monitored throughout the experiments

Table 1
Geometry of baffles used in the MOBC.

| Baffle design | |
|---------------------------------------|---------|
| Average number of orifices per baffle | 31 |
| Orifice diameter, mm | 10.5 |
| Equivalent hydraulic diameter, mm | 26.9 |
| Baffle open area, % | 15 |
| Baffle spacing, mm | 40 |
| Construction material | Acrylic |



* The definition of the equivalent hydraulic diameter is reported in [16].

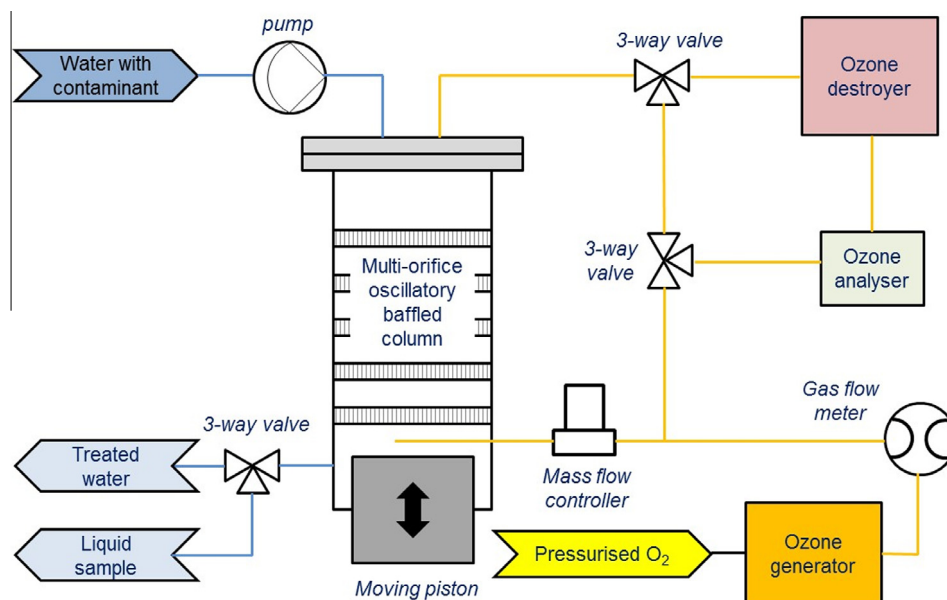


Fig. 1. Configuration of the pilot-plant multi-orifice oscillatory baffled column used in the ozonation experiments.

using a Thermo Orion 420 pH meter. The concentrations of *p*-HBA and total organic carbon (TOC) were followed by sampling the effluent from the MOBC. Sinusoidal fluid pulsations in the MOBC were imposed using a 125 mm diameter piston attached to the bottom of the column driven by a servo-hydraulic system [16], capable of delivering fluid oscillations of 0–10 Hz frequency (f) and 0–10 mm centre-to-peak amplitude (x_0). The results presented are for $f = 2$ Hz and $x_0 = 10$ mm, corresponding to a modified oscillatory Reynolds number of $Re'_o = 20,220$ and modified Strouhal number of $St' = 0.2$ as shown elsewhere [16].

The liquid reactor outlet at the bottom of the column and the reactor inlet at the top section of the column, were driven by two peristaltic pumps (Masterflex 77200-62, Cole-Parmer, USA) operated at the same flow rates, that maintained constant flow through the reactor, avoiding water accumulation in the column. The volume of liquid in both BC and MOBC was kept to 9 L. The experimental gas hold-up at $f = 2$ Hz and $x_0 = 10$ mm in the MOBC was 20%. The gas inlet stream enriched with ozone entered via a perforated tube sparger placed at the column bottom, and the outlet gas stream was directly connected from the top of the column to a thermal ozone destroyer and an ozone analyser. The ozone concentration, at the inlet and outlet gas streams, was continuously monitored with an Ozomat GM-BWA analyser (Anseros, Germany). For ozone measurements in the water phase, AccuVac[®] Ampules (Hach, ozone LR, 0.004–0.25 mg/L; ozone MR, 0.005–0.75 mg/L) were immersed in an aqueous sample and analysed with a Hach Odyssey at 600 nm. Analysis was based on the indigo method [23,24]. All experiments were carried out at atmospheric pressure and room temperature (20 °C). Experiments were repeated multiple times at the same conditions to assure results reproducibility. In the BC reactor configuration the same experiments were carried out in the absence of both baffles and fluid oscillations. The ozone consumption was calculated by the difference of the molar flow rate of ozone at the reactors inlet and outlet.

2.3. Analytical methods

Samples collected at appropriate time intervals were bubbled with nitrogen for 5 min to removal any trace of residual ozone, filtered through a 0.22 μ m cut-off, 33 mm diameter sterile Millex[®] syringe driven filter (Millipore) and injected into a high performance liquid chromatograph (HPLC, Agilent 1100 series) comprising a diode array detector, a mobile phase degassing unit and an autosampler. The optimised operating conditions were: Gemini C18 (250 \times 4.6 mm, 5 μ m) column supplied by Phenomenex, mobile phase constituted by a mixture water/methanol/acetic acid (88/10/2), flow rate 1 mL/min, column temperature 20 °C and UV detector $\lambda = 254$ nm [25,26]. Calibration of the HPLC chromatographic peaks against standards of *p*-HBA resulted in a linear response in the range of concentrations investigated. The organic matter in the samples was characterised in a TOC (Shimadzu TOC-VCPH).

3. Results and discussion

Fig. 2 shows the influence of ozone flowrate on the degradation and mineralisation of *p*-HBA under “continuous flow” operation for both BC and MOBC. The oxidation of *p*-HBA in both MOBC and BC increased with an increase in the ozone-rich gas flow rate from 2.1 to 4.7 L/min, suggesting that the oxidation of *p*-HBA was controlled by the rate of ozone supplied to the reactors. Under this operational regime, the reaction between ozone and *p*-HBA occurred at the gas–liquid interface, under the fast or moderately fast gas–liquid kinetic regime (Hatta number higher than 0.3) [25] therefore we recorded no dissolved ozone in the aqueous phase during the

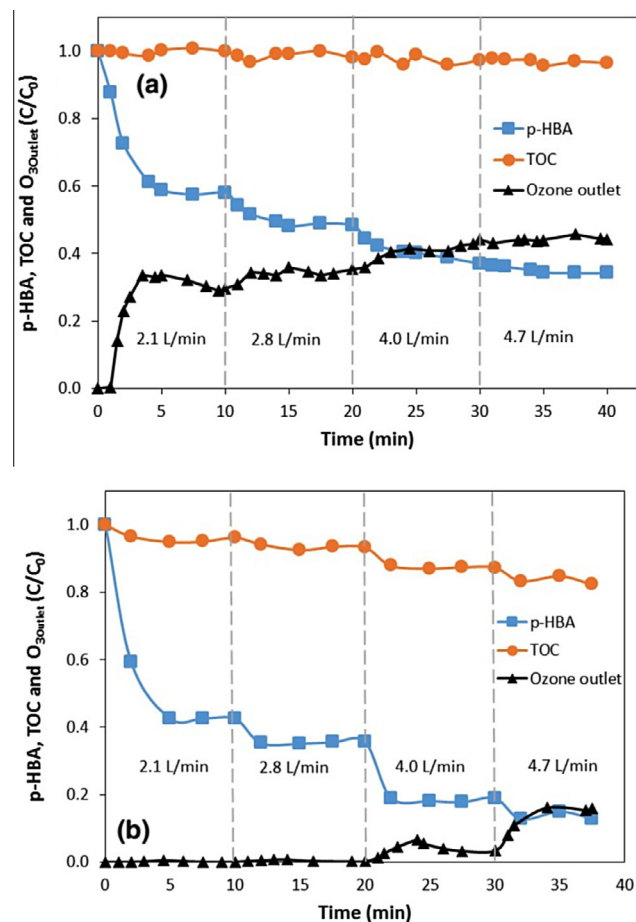


Fig. 2. Influence of ozone gas flowrate on the degradation and mineralisation of *p*-HBA under continuous flow operation (a) BC and (b) MOBC. [*p*-HBA]₀ = 50 mg/L, [TOC]₀ = 32 mg/L, [O₃]₀ = 23 g/m³. In the MOBC the fluid was oscillated with $f = 2$ Hz and $x_0 = 10$ mm.

experiments. The superior performance of the MOBC in comparison to the BC in the oxidation of *p*-HBA, results from using small fluid pulsations and orifice baffles, which gives a significant increase in gas–liquid mass transfer rates [14–16,18–20]. More significantly, the analysis of the composition of inlet and outlet gas streams revealed full, 100% utilisation of ozone in the MOBC and only to 60–65% maximum ozone utilisation in the BC, revealing that the MOBC was significantly more efficient in utilising the ozone injected in the reactor.

Many ozonation systems are wasteful of either oxidant or space and are inherently inefficient. The oxidation of water contaminants usually benefits from higher rates of ozone supply, however, in practice this is not always possible in conventional, industrial scale, ozonation contactors (e.g. bubble columns), since an increasing fraction of the ozone supplied usually escapes unreacted at higher gas flow rates. Other ozonation systems utilising ozone injection through a Venturi tube, a static mixer or other injector systems have very short contact times between the gas and the contaminants, and in consequence they require very bulky downstream holding tanks in which the reaction between the dissolved ozone and the water contaminants is carried out in the slow kinetic regime over a long residence time.

The MOBC presented here is uniquely capable to fully utilise the ozone supplied to the system, as demonstrated from the undetectable ozone concentration in the outlet gas stream (Fig. 2b) and the absence of dissolved ozone, and this mainly results from

two physical phenomena. Firstly, the gas phase in the MOBC is efficiently dispersed into a large number of very small bubbles (in the range of few hundreds of microns, measured by a high speed CCD camera following the methodology in [16]) by the shear produced by the fluid oscillations and orifice baffles, which provided extremely large interfacial area resulting in enhanced mass transfer rates [16]. The visual appearance of the ozone gas–water liquid system in the reactor resembled a whitish milky solution, which became fully transparent in the absence of oscillations. Secondly, the strong eddy vortices formed between the baffles in the MOBC were capable of trapping the microbubbles within the liquid (see Graphical Abstract), meaning extended gas–liquid contacting times in the column (large gas hold-up, $\sim 20\%$ at $f = 2$ Hz and $x_0 = 10$ mm in the MOBC compared to typically 3% in the BC [18,21]) and therefore an increased rate of ozone utilisation [27].

The *p*-HBA mineralisation (i.e. reduction in TOC), was 3–8-fold higher in the MOBC compared to a BC, with a maximum of 18% TOC removal in the MOBC at the highest gas flow rate tested (Fig. 2). TOC reduction remained undetectable in the BC at all gas flow rates tested. Typically, mineralisation of contaminants with ozone is a slow process due to the multistep reaction sequence, however, the results in Fig. 2 demonstrate that the MOBC was capable of not just oxidising *p*-HBA but also its intermediates (e.g. quinones and carboxylic acids [28]), yielding significantly higher levels of carbon mineralisation in comparison to the BC. It can be hypothesised that full mineralisation of *p*-HBA should be possible for extended contacting time in the MOBC.

Fig. 3 shows the rates of degradation and mineralisation of *p*-HBA in both BC and MOBC, as a function of O_3 supplied (molar

flowrate of O_3 fed to the reactor) or consumed (molar flowrate of O_3 fed to the reactor minus the molar flowrate of O_3 at reactor gas outlet) after reaching steady-state conditions in the reactors (note that both reactors were operated in continuous flow). Fig. 3 (a) shows that the rate of degradation of *p*-HBA per mole of ozone consumed was equal in both BC and MOBC reactors. This suggests that the reaction stoichiometry was independent of reactor type and that within the observed degree of conversion of *p*-HBA, the ozone demand remained the same in the two reactors. The slope of the best fitting line drawn through the data points yields the inverse of the stoichiometric ratio of the reaction of *p*-HBA with ozone. The stoichiometric ratio determined from our continuous flow experiments in the MOBC and BC at pH 10 was 2.44, which approached the value of 2.0 (pH invariant in the range 2–9) reported in a batch reactor [25]. The discrepancy due to the start-up delay in the batch reactor to reach a constant gas hold-up.

In terms of the ozone supplied to each reactor, the MOBC was on average 20% more efficient than the BC (Fig. 3c) in the rate of *p*-HBA degradation, but more significant differences between the two reactors were observed in the rate of *p*-HBA mineralisation. Fig. 3(b) shows that the rate of TOC removal per mole of ozone consumed in the MOBC was 75% higher than in the BC, which was evaluated by the ratio of the slopes of the fitting lines. The pH of the water fed to the reactor decreased from 10 to 8 in the BC and to just below 7 in the MOBC, further confirming a higher degree of mineralisation of *p*-HBA to carboxylic acids in the MOBC. Limitations of the rate of ozone consumption by the reaction in the BC reactor were quickly reached due to gas by-passing, large bubble size and much smaller gas holdup (approximately 3% [19,22]).

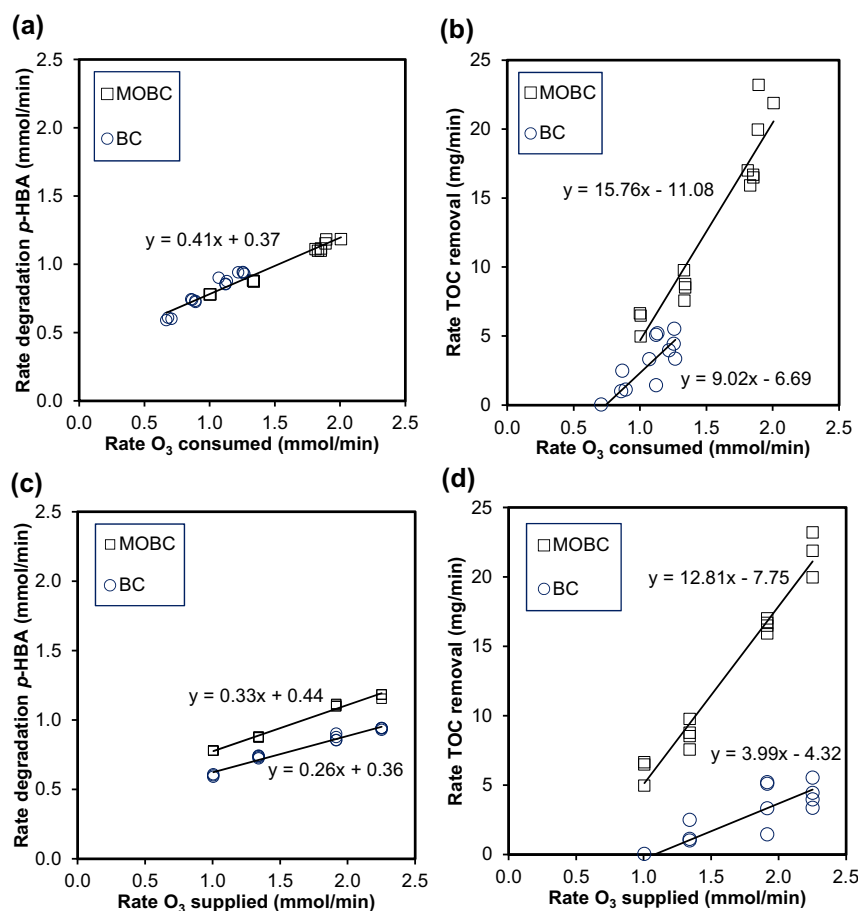


Fig. 3. Rates of degradation and mineralisation of *p*-HBA as a function of O_3 supplied or utilised after reaching steady state conditions. The continuous line represent a linear fitting of the experimental data.

In contrast the MOBC reached significantly higher rates of TOC removal. More significantly, Fig. 3(d) shows that at equal rate of ozone supplied to each reactor, the rate of TOC removal in the MOBC was 4.5–5.0-fold higher than in the BC. The ozone supplied to the MOBC was effectively used in the oxidation of the contaminants and intermediates with zero or very little waste at very high flow rate (Fig. 3) whilst the BC was ineffective in utilising all the ozone supplied.

The results herein presented suggest the MOBC is uniquely capable of keeping consistent gas utilisation efficiencies independent of the rate of ozone injected into the column, therefore reducing the need of further holding gas–liquid equipment. This represents a significant step forward in the intensification of ozonation processes, particularly in water treatment. Conventionally, ozone utilisation efficiencies sharply reduce as the ozone dosage or rate of ozone injection is increased [2,13,29]. Therefore ozonation systems, which are primarily based on adaptation of reactors for ozone disinfection, are normally operated at reduced ozone dosages, which naturally leads to large equipment volume, high consumption rate of gas (air or oxygen) and extended contacting times for effective removal of higher concentrations of water contaminants.

The MOBC technology approach presented here disrupts conventional ozonation design systems for water treatment and allows significantly higher rates of ozone utilisation and process intensification, in a highly compact device. Overall, it is estimated the MOBC achieves a significant reduction in reactor volume to achieve the same rate of ozone mass transfer obtained in conventional ozonation reactors. The power dissipation required for providing the oscillation of the fluid can be evaluated from established OBCs correlations in literature [19] and amounts to less than 1 kW/m³ water treated in the MOBC, which would represent an insignificant cost compared to the significant savings due to more effective use of the ozone supplied.

4. Conclusions

This study presents a novel approach for the intensification of ozonation of water and wastewater using a highly efficient and compact multi-orifice oscillatory baffled column ozonation contactor. The MOBC technology approach disrupts conventional ozonation design systems for water treatment and allows significantly higher rates of ozone utilisation and process intensification, in a highly compact device. MOBC achieves a significant reduction in reactor volume to achieve the same rate of ozone mass transfer obtained in conventional ozonation reactors. The increased performance of the MOBC ozonation reactor benchmarked against a bubble column design, resulted in 20% increase on the rate of *p*-HBA degradation, 75% increase in the rate of mineralisation of *p*-HBA per mole of ozone consumed, and 4.5–5.0-fold increase in the rate of mineralisation of *p*-HBA per mole of ozone supplied. Ozonation and ozone-driven treatment processes can be applied to wastewater treatment in the MOBC with lower costs, reduced hydraulic time and less ozone consumption, which can be translated to a smaller carbon footprint.

Acknowledgements

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