Removal of Levoﬂoxacin from aqueous solution by Magnesium-impregnated Biochar: batch and column experiments

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ABSTRACT
Adsorption of levoﬂoxacin (LEV) onto four types of magnesium (Mg)-impregnated biochars, fabricated via thermal pyrolysis of wood chips pretreated with MgSO_4 was investigated. The Mg-impregnated biochars were characterized with various tools and techniques. Batch sorption experiments were conducted to determine the sorption kinetics and isotherms of LEV onto the Mg-impregnated biochars. The pseudo-second order kinetic model described the adsorption kinetic data better than the pseudo-first order kinetic model and the Elovich equation. Due to multi-mechanisms, the Freundlich model described the experimental isotherms better than the Langmuir model. The Langmuir maximum adsorption capacities of the Mg-impregnated biochars to LEV ranged from 7.38 to 25.2 mg g⁻¹. In the fixed-bed column experiment, higher bed height and lower flow rate led to greater LEV removal. Findings from this work indicate that Mg-impregnated biochars can be used as an alternative adsorbent to effectively remove LEV from aqueous solutions.

1. Introduction
Antibiotic has been widely used (annual consumption of 100,000–200,000 tons) in human medicine, veterinary, and aquaculture [1–3]. Fluoroquinolones (FQs) are the third largest group of antibiotics accounting for 17% of the antibiotic market [4]. With the character of resistance to degradation, more than 70% of unmetabolized FQs have been generally excreted, and the half-lives of FQs may be 10.6 days in surface water [5,6]. A number of studies indicate that FQs and their residuals in the environment have adverse ecological impacts [7–9]. The occurrence and impact of FQs in surface water, soil and groundwater systems have been recognized as one of the emerging environmental issues [6]. Levoﬂoxacin (LEV) is one of the most widely used FQ antibiotic [10–12], which has been detected in the aqueous environment [13,14]. With the potential risks, developing the efficient techniques to remove LEV from aqueous solutions have received increasing concern in recent years.

Several approaches including chemical and biological degradation [14–18], sonochemical decomposition [19], and adsorption [20,21] have been adopted to treat LEV contamination. Adsorption has been recognized as a highly effective and promising treatment method to remove LEV from aqueous solutions with its relatively low cost and easy operation. As a novel adsorbent, biochar has been widely used to treat various aqueous contaminants including antibiotics [22–24]. Yi et al. [25] found that pristine wood biochar produced at 300°C and 600°C can adsorb LEV from aqueous solutions. However, the LEV adsorption capacity of the two wood biochars are relatively low, with the maximum Langmuir adsorption capacities of only 4.59 mg g⁻¹ and 7.72 mg g⁻¹ [25].

Recent studies have demonstrated that pretreatment of biomasses with metal chemicals (e.g. iron salts, and aluminum chlorides, magnesium chlorides,) may generate metal oxides on the biochar particles, and can effectively improve the biochar’s adsorption capacities [26–28]. Compared to other metal chemicals, magnesium (Mg) salts and its oxides were usually regarded as the lower-cost, easier-acquirable and more environmentally friendly modifier. Furthermore, it has been demonstrated that Mg pretreated biochars have obviously adsorption capacities to common aqueous pollutants such as phosphate and nitrate [28–31], implying the potential adsorption ability of Mg pretreated biochar on levoﬂoxacin. However, fewer previous studies has examined the adsorption of antibiotics, particularly LEV onto Mg-impregnated biochars. Furthermore, most of previous studies on LEV adsorption were performed in batch operation to measure the effectiveness of the sorbents, while the continuous adsorption is often desired in industrial application due to the flexibility of fixed-bed column systems and low operational cost [32].
In this work, four kinds of Mg-impregnated biochars were derived from wood chips under different pretreatment and pyrolysis conditions. Characterizations of Mg-impregnated biochars were conducted using scanning electron microscopy coupled with energy dispersive X-ray fluorescence spectroscopy (SEM-EDX), Fourier transform infrared spectroscopy (FTIR), elemental analyzer (EA), inductively-coupled plasma emission spectroscopy (ICP-OES), surface area analyzer (BET) and thermo-gravimetric analyzer (TG-DTG). Both batch and fixed bed column experiments were carried out to examine adsorption ability of the biochars and to determine their feasibilities in industrial application. The adsorption mechanisms of Mg-impregnated biochar to LEV were determined based on findings from characterization and adsorption experiments. The main objectives of this work are to: 1) develop a simple and feasible method to prepare Mg-impregnated biochars for LEV removal 2) determine the physiochemical properties of the Mg-impregnated biochars; 3) evaluate the adsorption ability of the Mg-impregnated biochars under batch and continuous flow conditions; and 4) explore the adsorption mechanisms.

2. Materials and methods

2.1. Reagents

Levofloxacin (>98.5%) was obtained from Dalian Meilun Biology Technology, Ltd (China). Levofloxacin is the levo isomer of the racemate ofloxacin and often used as the hemihydrate. Levofloxacin has two acidity coefficients (pKa) of 6.02 and 8.15 separately [25]. Chemical structure and properties of LEV are reported in Fig. S1 (Supporting information). Stock solutions of LEV were prepared in DI water at a concentration of 1000 mg L\(^{-1}\) and stored at 4°C in darkness prior to use. MgSO\(_4\)·7H\(_2\)O and acetonitrile (HPLC grade) were purchased from Shanghai Aladdin Biological Technology Company, Ltd (China) and Tedia Company, Inc. (China), respectively. All the other analytic grade chemicals were obtained locally. Pine wood chip was collected from Fujian province, China.

2.2. Preparation of Mg-impregnated biochar

The wood chips were washed with deionized (DI) water to remove the impurities, dried in an oven at 80°C for 24 h and then were ground to powder in a disintegrator. To pretreat the feedstock, the dried powder (20 g) was immersed in 500 mL MgSO\(_4\) solutions (0.25 M and 0.5 M, respectively) with magnetic stirring at the constant temperature (30 ± 2°C) for 60 h. After the treatment, the wood chip powder was vacuum-filtered, oven-dried at 90°C for 12 h, and muffle-pyrolyzed at 300°C for 4 h or 600°C for 30 min followed the procedures of Ding et al. [33]. After cooling down to room temperature (~25°C), the resultant biochars were collected and rinsed with DI water several times to remove impurities. The samples were dried and then sieved through a 100-mesh sieve to obtain a uniform size. The obtained Mg-impregnated biochars from 0.25 M (the quality rate of Mg to biomass was 15%) and 0.5 M (the quality rate of Mg to biomass was 30%) MgSO\(_4\) treated biomass pyrolyzed at 300°C were labeled as WCM315 and WCM330, respectively; and those at 600°C were labeled as WCM615 and WCM630, respectively. The untreated biochar pyrolyzed at 300°C and 600°C were labeled as WC300 and WC600 separately, which was detailed in our previous study [25].

2.3. Characterization of Mg-impregnated biochar

The contents of non-metallic elements such as C, H and N of the biochar samples were determined using an elemental analyzer (EA, Vario MICRO, Elementar). Surface area analyzer (BET, ASAP20, Micromeritics, Ltd., U.S.A) were used to measure the specific surface areas using the N\(_2\) adsorption methods. The content of main mineral elements (Mg, Ca, Al, and K) of the biochars were analyzed using an inductively coupled plasma emission spectroscopy (ICP-OES, Optima 5300, PerkinElmer, U.S.A) at afterashing the samples at the temperature of 550°C and dissolved with 7% hydrochloric acid (w/w). Thermo-gravimetry was conducted to compare the pyrolysis behaviors of the Mg-impregnated biochars using a thermo-gravimetric analyzer (TG-DTG, Pyris 1 DSC, PerkinElmer, Ltd., U.S.A) at a heating rate of 10°C min\(^{-1}\) from 30°C to 700°C in a nitrogen environment. The surface morphology and surface elemental distributions of the samples were examined by scanning electron microscope coupled with energy dispersive X-ray fluorescence spectroscopy (SEM-EDX, S-3400N II, Hitachi, Ltd., Japan) FTIR spectra of the samples were recorded on a NEXUS870 FTIR (U.S.A) in the range 4000–400 cm\(^{-1}\) with a resolution of 0.2 cm\(^{-1}\).

2.4. Batch experiments

Batch sorption experiments were carried out in 50 mL polyethylene centrifuge tubes at the temperature of 30°C. Sorption kinetics were performed with the mixtures of 0.05 g Mg-impregnated biochar and 25 mL LEV solutions with initial LEV concentrations of 100 mg L\(^{-1}\) for WCM315 and WCM615 and 150 mg L\(^{-1}\) for WCM330 and WCM630. The tubes were shaken at 125 rpm and withdrawn at different intervals (0, 5, 10, 15, 30, 45, 60, 90, 120, 180, 240, 360, 480 and 600 min). The samples were then immediately filtered through 0.45 μm pore size nylon membranes to determine the aqueous concentrations of LEV using a high-performance liquid
chromatography (HPLC, Agilent 1200, Agilent Technologies, Co., California, U.S.A) with the method developed in a previous study [25]. Sorption isotherms were determined by filling the tubes with the mixtures of 0.05 g of the Mg-impregnated biochar and 25 mL of LEV solution ranging from 15 to 150 mg L\(^{-1}\) (0, 15, 20, 25, 30, 40, 50, 75, 100, 125 and 150 mg L\(^{-1}\)) for WCM315, WCM330, and WCM615 and from 25 to 200 mg L\(^{-1}\) (0, 25, 30, 40, 50, 75, 100, 125, 150, 175 and 200 mg L\(^{-1}\)) for WCM630. The tubes were shaken at 125 rpm for 24 h. The samples were filtered through 0.45 μm pore size nylon membranes to determine the aqueous equilibrium concentrations. The LEV removal rates were calculated based on the difference between their initial and final concentrations. The batch experiments were carried out in triplicate.

2.5. Fixed-bed column experiment

Fixed-bed column experiments were conducted with acrylic columns (inside diameter 1.5 cm and 5 cm height). Stainless steel membranes with 30 μm pores were used to seal the inlet and outlet of the column to hold the quartz sand and distribute the flow. About half of the column was first wet-packed with 0.11–0.15 mm quartz sand (acid-cleaned following the procedure of Tian et al. [34]). WCM630 of different amounts was then wet-packed into column as the interlayer. Stainless steel membranes were used to separate the sand and biochar layers, preventing their mixing. Finally, the rest of the column was filled with the sand using the same wet-packing method.

The columns were first flushed with DI water (pH 5.6) overnight to precondition the filters and remove potential impurities. The fixed-bed column experiment was then initiated by switching the influent to the LEV solution (5 mg L\(^{-1}\)). A peristaltic pump (BT100–1F, Longer Pump, China) was used at the inlet of the column to maintain an upward velocity. To determine the influence of flow rate, 0.2 and 0.5 mL min\(^{-1}\) were tested with 0.27 g of biochar as the interlayer. To determine the effect of bed height, 3 different amounts of biochar (i.e. 0.27, 0.57, and 0.85 g, corresponding to 0.5, 1.0, and 1.5 cm, respectively) were tested in the column with a flow rate of 0.5 mL min\(^{-1}\). Sand columns without biochar were also included as experimental controls. Effluent samples were collected from the top of the column discretely with a fraction collector (BS–100A, Puyang Scientific Instrument Research Institute, China). After filtration, the LEV concentration of samples was determined using the HPLC. All the column treatments were tested in duplicate.

2.6. Mathematical models

In addition to the commonly used pseudo-first-order and pseudo-second-order models, the Elovich model was also used to simulate batch sorption kinetics. The equations are represented as follows:

\[
\log(q_e - q_t) = \log q_e - K_1/(2.303 t), \text{ first order} \tag{2.1}
\]

\[
\frac{1}{q_t} = \frac{1}{K_2 q_{\text{max}} - q_e} - \frac{t}{q_{\text{er}}}, \text{ second order} \tag{2.2}
\]

\[
q_t = \ln(ab)/b + \text{Int}/b, \text{ Elovich} \tag{2.3}
\]

Where \(q_t\) and \(q_e\) are the amount of LEV sorbed at time \(t\) and at equilibrium, respectively (mg g\(^{-1}\)), and \(K_1, K_2\) are the first-order, second-order apparent adsorption rate constants (h\(^{-1}\) and g mg\(^{-1}\) h\(^{-1}\)), respectively. Also, \(a\) is the initial adsorption rate (mg g\(^{-1}\) min\(^{-1}\)) and \(b\) is the desorption constant (g mg\(^{-1}\)).

Two isotherm equations were applied to simulate the LEV adsorption onto the biochar:

\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}} K_f} + \frac{C_e}{q_{\text{max}}}, \text{ Langmuir} \tag{2.4}
\]

\[
\ln q_e = \ln K_f + (1/n) \ln C_e, \text{ Freundlich} \tag{2.5}
\]

Where \(K_f\) and \(K_f\) represent the Langmuir bonding term related to interaction energies (L mg\(^{-1}\)) and the Freundlich affinity coefficient (mg\(^{1/n}\) L\(^n\) g\(^{-1}\)), respectively, \(q_{\text{max}}\) denotes the Langmuir maximum capacity (mg g\(^{-1}\)), \(C_e\) is the equilibrium solution concentration mg L\(^{-1}\) of the sorbate, and \(n\) is the Freundlich linearity constant.

The intra-particle diffusion model has been applied by several researchers to predict the role of diffusion, and it is depicted by the following equation:

\[
q_t = K_{\text{dif}} t^{0.5} + C_i \tag{2.6}
\]

Where \(q_t\) is the amount of LEV sorbed at time \(t\), \(K_{\text{dif}}\) represents the intraparticle diffusion coefficient (mg g\(^{-1}\) min\(^{-0.5}\)), and \(C_i\) is a constant reflecting the initial or external adsorption rate.

3. Results and discussion

3.1 Physicochemical properties

The element composition, ash content, and surface area of Mg-impregnated biochars are listed in Table 1. The Mg contents of WCM315, WCM330, WCM615 and WCM630 were 0.63%, 1.37%, 8.65% and 12.5%, respectively, indicating that Mg is loaded in the biochar matrix. Previous studies have shown that pretreatment with Mg salts may increase Mg oxides in biochars [28]. Higher ash contents of the Mg-impregnated biochar likely resulted from the formation of new Mg-impregnated minerals [35]. The BET surface area for WCM315 and WCM330 were 2.70 and 2.65 mg\(^2\) g\(^{-1}\) separately, and for WCM615 and WCM630 were 266 and 225 mg\(^2\) g\(^{-1}\). These suggest that Mg-impregnated biochars pyrolyzed at high temperature may
have much larger surface area than that pyrolyzed at low temperature, which was consistent with previous studies [36].

TGA showed that the pyrolysis behaviors of four kinds of Mg-impregnated biochars were not distinguished significantly during initial 350°C (Fig. S2, Supporting information), with the mass loss below 90%. At the temperature range of above 500°C, the order of weight loss ratios was WCM615 > WCM630 > WCM330 > WCM315, reflecting the different thermal stability.

The morphology and elemental distribution of the Mg-impregnated biochar were characterized by using SEM-EDX (Fig. S3-S6, Supporting information). C, S and O on the engineered biochar surfaces and distinct peaks of Mg was also observed in the EDX spectra (Fig. S7, Supporting information), which is consistent with elemental analysis and confirms the existence of Mg-impregnated particles. The SEM and EDX mapping analysis of Mg-impregnated biochars also showed that Mg elements had been successfully loaded on the biochar. According to the previous studies, it was speculated that the Mg-compounds on the treated biochar may contain MgSO₄, MgO, Mg(OH)₂ and other Mg chemicals [28,37,38]. However, the EDX mapping analysis showed large blocky Mg particles in WCM615 and WCM630 but not in WCM315 and WCM330, suggesting that the biochars may be impregnated with different Mg compounds.

The FTIR result showed the presence of -OH (3000–3690 cm⁻¹) on Mg-impregnated biochars (Figure 1). In particular, compared with the pristine biochar tested in our previous study [25], extra -OH was generated on Mg-impregnated biochar pyrolyzed at 600°C, which may increase the adsorption ability of biochars to LEV. Previous studies also indicated that different from the original biochar, -OH (bonded) was generated on the Mg-impregnated biochar pyrolyzed at 600°C [37]. The FTIR peaks with high intensity of WCM615 and WCM630 at about 3700 cm⁻¹ can be attributed to the A₂u(OH) lattice vibration of Mg(OH)₂ [39,40]. A series of bands recorded in the 400–800 cm⁻¹ region can be ascribed to the Mg–O and O–Mg–O [41], suggesting the presence of Mg oxyhydroxides.

### 3.2 Batch sorption

The adsorption of LEV onto Mg-impregnated biochar were relatively fast in the initial 90 min (Figure 2(a)), accounting for 78.3%, 81.8%, 92.4% and 94.2% of sorption capacity of WCM315, WCM330, WCM615 and WCM630, respectively. Thereafter the adsorption proceeded at a slower rate until equilibrium, suggesting the potential involvement of two or more distinct sorption mechanisms, such as non-specific and specific sorption [42]. The rapid sorption phase may be ascribed to the rapid occupation of easily accessible external surface sorption sites, likely via physical adsorption [43]. The slow sorption phase may be attributed to specific (chemo-) and irreversible adsorption [35]. The LEV adsorption rates of WCM615 and WCM630 were slightly higher than those of WCM315 and WCM330 (Table 2). The surface areas of WCM615 and WCM630 were about 100 times higher than those WCM315 and WCM330, suggesting that WCM615 and WCM630 may have more adsorption sites [44–46].

| Biochar | BET surface area (m² g⁻¹) | Ash (wt%) | C  | H  | N  | O* | Mg  | Ca+Al+K | O/C | H/C |
|--------|--------------------------|-----------|----|----|----|----|-----|--------|-----|-----|
| WCM315 | 2.70                     | 3.03      | 64.9 | 4.53 | -  | 27.6 | 0.63 | 0.070  | 0.425 | 0.070 |
| WCM330 | 2.65                     | 5.34      | 63.9 | 4.46 | -  | 26.3 | 1.37 | 0.120  | 0.412 | 0.070 |
| WCM615 | 266                      | 34.4      | 52.0 | 2.49 | -  | 11.0 | 8.65 | 0.150  | 0.212 | 0.048 |
| WCM630 | 225                      | 45.6      | 38.4 | 2.05 | 0.01 | 13.9 | 12.5 | 0.300  | 0.363 | 0.053 |

*Oxygen contents were determined by weight difference assuming that the total weight of the samples was made up of the tested elements only.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Fourier transform infrared spectroscopy (FTIR) of biochars before (a) and after LEV sorption (b).
The pseudo-first-order kinetic model, pseudo-second-order kinetic model, and Elovich equation were used to describe the kinetics data and to explore the adsorption mechanisms [47]. The $R^2$ values (>0.997) acquired for the pseudo-second order kinetic model were higher than those of the other models for all the biochars (Table 2), suggesting that LEV adsorption onto the modified biochar could be controlled by chemisorption [36]. The $R^2$ values of the Elovich model exceeding 0.911 for all the biochars also suggested the importance of chemisorption to LEV adsorption onto four kinds of Mg-impregnated biochars [48]. The intra-particle diffusion model was applied to further explore the adsorption mechanism. It can be seen from Figure 3 that there is a liner relationship between $q_t$ and $t^{1/2}$ for all the data, indicating the importance of intraparticle diffusion to the adsorption process [47].

Sorption isotherms (Figure 2(b)) illustrated that LEV adsorption capacity of Mg-impregnated biochar were much higher than that of the pristine wood chip biochar [25]. The Langmuir maximum capacities of WCM315, WCM330, WCM615 and WCM630 to LEV were 7.38 mg g$^{-1}$, 20.4 mg g$^{-1}$, 14.8 mg g$^{-1}$ and 25.2 mg g$^{-1}$, respectively. While the pristine biochars have the Langmuir maximum capacities of 4.59 mg g$^{-1}$ and 7.72 mg g$^{-1}$ for WC300 and WC600, respectively [25]. Freundlich models reproduced the data better than Langmuir models (Figure 2(b)) with $R^2$ of four kinds of Mg-impregnated biochar exceeding 0.953. The $R_L$ ($R_L = 1/(1 + K_L C_0)$) of the Langmuir model were all between 0–1. The empirical parameter $1/n$ of the Freundlich model were all lower than 0.228 (Table 3), suggesting the affinity between LEV and biochar and the adsorption sites of all the biochars are favorable for the LEV [49]. The Langmuir maximum capacity of WCM630 (25.2 mg g$^{-1}$) was much higher than those of the other three Mg-impregnated biochars. The $K_L$ and $K_F$ of WCM630 were both the highest, confirming that WCM630 was the most effective one. The maximum LEV adsorption capacities of the Mg-impregnated biochars are similar or greater than previously reported values of other adsorbents (Table S1, Supporting information).

Yi et al. [25] showed that multiple mechanisms including pore-filling, π-π interaction, and hydrophobic interaction control the adsorption of LEV onto biochar. In addition to these mechanism, electrostatic attractions may play an important role in controlling the adsorption of LEV onto the four Mg-impregnated biochars. Under the tested conditions (pH=7), LEV were dominated by zwitterionic and thus can interact with the Mg minerals on biochar surface through electrostatic interactions [47]. The polarity index [O + N]/C of the functional groups of the four Mg-impregnated biochars were above 0.2, which has
been reported as electron-rich-π-donors [50]. LEV contains a benzene ring in its molecular structure and has been proposed as π-electron-acceptor due to the strong electron withdrawing ability of the fluorine group [51]. It can be speculated that π-π interaction may be an important machine on LEV adsorption onto biochar. Furthermore, the FTIR result showed the appearance and disappearance of peaks after adsorption of LEV (Figure. 1), indicating interactions between LEV and surface functional groups may also contribute to the adsorption process. FTIR spectra of Mg-impregnated biochars before and after adsorption of LEV showed the following differences: 1) the peaks of WCM615 and WCM630 in region around 1100–1200 cm⁻¹ disappeared after sorption, suggesting the involvement of phenolic -OH (~1200 cm⁻¹) and C-O-C (~1100 cm⁻¹) [52]; 2) some peaks (~935, 717, 600 cm⁻¹) of WCM615 disappeared after adsorption of LEV, suggesting the involvement of aromatic CH [53]; and 3) the intensive of peaks in WCM315 and WCM330 between 3378 and 3693 cm⁻¹ increased after adsorption of LEV, suggesting the involvement of -OH [54]. For another, Mg-pretreated biomass usually endow more positive charge on the biochar surface, which may also increase the adsorption of levofloxacin on biochar [36,37].

### 3.3 Column experiment

Above all, it could be indicated that Mg-impregnated biochar had high adsorption ability on LEV, implying its potential as adsorbent in fixed-bed filter to remove LEV from flow. WCM630 with the highest adsorption capacity was chosen as the adsorbent to build the fixed-bed filter in column study. Bed depth and influent flow rate are two important operation factors influencing adsorption performance of a fixed-bed filter. Figures. 4 and 5 display the breakthrough curves of LEV under different conditions with the fixed-bed parameters. The effect of flow rate on adsorption of LEV is shown in Figure. 4. Increasing flow rate made the breakthrough curves of LEV steeper with shorter breakthrough time. As the bed depth was 0.5cm, flow rate was increased from 0.2 to 0.5 mL min⁻¹, the breakthrough time decreased from 400 to 150 min. This behavior is probably due to the insufficient contact time of LEV with the biochar in column at a high flow rate [55]. The effect of the bed depth (0.5 cm, 1 cm and 1.5 cm) on LEV removal was studied with the flow velocity maintained as 0.5 mL min⁻¹ (Figure. 5). Increasing bed depth also increased breakthrough and exhaustion time due to the increase of the sorbents. The slope of the LEV breakthrough curve decreased with increasing bed depth, reflecting a broadened mass transfer zone [56,57].

### 4. Conclusions

This work developed a feasible and easy operational method to produce Mg-impregnated biochars. EA, ICP-OES, SEM-EDX, TG, and FTIR analyses showed that Mg pretreatment increased Mg crystalline minerals and functional groups on biochar surface. As a result, the Mg-impregnated biochar had strong sorption ability to LEV (WCM630 Langmuir maximum sorption capacity of 25.2 mg g⁻¹). Fixed-bed columns experiment...
demonstrated that Mg-impregnated biochar also effectively removed LEV in continuous aqueous flow. In comparison with other commercial sorbents such as activated carbon, biochar has lower cost and can be obtained from a variety of biomass feedstocks including waste biomass. Taking LEV adsorption capacity and the preparation costs into account, the Mg-impregnated biochar thus can be an excellent sorbent for the treatment of aqueous antibiotics.

Disclosure statement

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