Removal of antibiotics by coagulation and granular activated carbon filtration

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Abstract

Treatment of seven tetracycline classes of antibiotic (TAs) from raw waters (synthetic and river) was evaluated using coagulation and granular activated carbon (GAC) filtration in this study. Both coagulation and GAC filtration were effective for removal of TAs, and the removal efficiency depended on the type of TAs. GAC filtration was relatively more effective for removal of tetracycline (TC), doxycycline-hyclate (DXC), and chlortetracycline-HCl (CTC), which were difficult to remove by coagulation. It was speculated that TAs would be removed through the charge neutralization and sweep coagulation when poly-aluminum chloride (PACl) was added into the raw waters. The charge neutralization of zwitterionic or negative TAs by cationic Al (III) species drove removal of TAs from the synthetic water. When sufficient alkalinity was available (river water), aluminum hydroxide precipitates were formed. TAs could be removed by being enmeshed into or adsorbed onto the precipitates when PACl was added to the river water.
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1. Introduction

Many kinds of medicine are used in the farming of livestock and fish. These include antibiotics, hormone drugs, insecticides, nutrition promoters, antiseptics, and anesthetics. Among these, antibiotics are usually employed to prevent a disease rather than to cure a disease. According to Jung [1], the Korean industry of livestock farming used 1541 tons of antibiotics in 2003. More than half of these amounts were added into the livestock feed to prevent a disease and to promote growth.

Tetracycline, sulfonamide, and penicillin class of antibiotics were the most commonly used in the livestock farming. TAs were used the most and sulfonamide class of antibiotics was the second and the penicillin class of antibiotics was the third. Chlortetracycline, which was discovered from *streptomyces aureofaciens* in 1948, was known first. Then, other TAs followed. Oxytetracycline was discovered in 1950, tetracycline in 1952, dimethylchlorotetracycline in 1957, and doxycycline and minocycline in 1960s [2]. TAs are bacteriostatic. They interfere with bacterial protein synthesis. Broad spectrum of microbes including gram – positive and gram – negative bacteria, anaerobic bacteria, and protozoa such as rickettsiae, mycoplasma, amoeba are sensitive to TAs [2]. Subsequently, the extensive use of these antibiotics could result in an increase in bacterial resistance to these antibiotics [3–5]. Their potential threat to human health has also been warned [6–8].

According to Choi et al. [9], TAs were detected up to $0.37\,\mu g/L$ in the Korean river water. Since a risk of TAs appearing in raw water exists, removal of these antibiotics during drinking water treatment and wastewater treatment has recently been a popular subject for researchers [10–15]. However, most of these studies involved advanced processes such as oxidation and adsorption, despite most drinking water treatment plants rely on conventional processes such as coagulation, flocculation, sedimentation, and filtration. There was a few study available to evaluate the performances of conventional process in removal of pharmaceutical products and endocrine disrupting chemicals. Therefore, treatment of TAs by conventional treatment process was examined in this study. Considering that aluminum could cause the release of TA through complex formation [16], alu-

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minum coagulation was selected as conventional process in this study. Treatment of TAs by GAC adsorption was also examined.

2. Experimental

2.1. Reagents and standards

Seven TAs (Sigma, U.S.A.) were selected in this study. They are oxytetracycline-HCl (OTC), minocycline-HCl (MNC), DXC, meclocycline-sulfosalicylate (MCC), CTC, democlocycline-HCl (DMC), and TC. These antibiotics were used in salt forms in order to increase their solubility in water, except TC. To help their solubility, TAs were dissolved in methanol and then diluted by distilled water. Simatone (Dr. Ehrnestorfer GmbH, Germany) was used as an internal standard at 0.1 µg/L. Fig. 1 shows chemical structures of these TAs. According to Fig. 1, these TAs are present in ionic forms at neutral pH. Detailed information about characteristics of these materials can be found elsewhere [17–18].

2.2. Solid-phase extraction (SPE) and liquid chromatography/mass spectrometric detector (LC/MSD) analytical method

The Spark Holland on-line equipment was used for SPE. The analytes were extracted using the Prospekt^{TM} Oasis HLB cartridges (10 mm × 2 mm, Waters, U.S.A.). These cartridges were preconditioned with 1 mL of methyl alcohol, 1 mL of 0.5N HCl, and 1 mL of deionized water. After sampling, 0.2 mL of 5% Na$_2$EDTA was added to 50 mL of the filtered water for the extraction preparation. After the EDTA addition, the sample pH was adjusted to less than 3.0 by adding 40% sulfuric acid. The water sample of 10 mL was then passed through the cartridges at the flow rate of 2 mL/min. The cartridges were connected to the LC/MSD on-line, so that all antibiotics in the water sample could be passed to LC/MSD without any loss. Such connection enabled the analysis of the antibiotics at very low concentration despite the extracted sample volume being small. Detailed information about this analytical method can be found elsewhere [8]. The Agilent 1100 LC/MSD (Agilent, U.S.A.) was used with the diode array detector. The ultraviolet wavelength was 360 nm. The separation column was the Atlantis dC18$^{®}$ (2.1 mm × 50 mm, C$_{18}$ column) with a pore size of 3 µm (Waters, U.S.A.).

2.3. Coagulation experiments

Two raw waters (synthetic water and river water) were used for the coagulation experiments. The synthetic water was prepared by adding kaolin to distilled water so that its turbidity became 10 NTU. Initial TAs concentrations of these waters were set to 100 µg/L. The pH of the synthetic water was 6.0. The river water was used to evaluate organic interference on coagulation efficiency. Its average characteristics are as follows; pH 8.1, alkalinity of 65 mg/L as CaCO$_3$, DOC of 3.12 mg/L, and turbidity of 15.3 NTU. A main difference between these raw waters was organic content and alkalinity. There was no organic

Table 1
Physical characteristics of activated carbons used in this study

Species		Coal (calgon F400)	Coconut (samchully)
Apparent density	(g/cm^3)	0.40	0.47
Specific surface area	(m^2/g)	1100	1230
Total pore volume	(cc/g)	0.548	0.495
Mean pore radius	(Å)	23	18
Effective size	(mm)	0.94	0.95

content and alkalinity for the synthetic water, while they were present in the river water. Since the difference in pH (6 and 8) and turbidity (10 and 15.3 NTU) between these raw waters was considered insignificant for coagulation efficiency, their adjustment was not given. While the raw water of 1 liter was mixed at 120 rpm, PACl was added as coagulant at dosages of 5~60 mg/L. After 5 min of mixing, supernatant was filtered through a filter paper of 0.45 µm (Sartorius, Germany). The filtrate was then measured for its TAs concentrations.

2.4. Adsorption experiments

GAC filter column was used for the adsorption experiments. The column was 50 mm in its inside-diameter and 2000 mm in its length. Two columns were filled with two different carbons. They were different in base material; coal-based carbon (Calgon F-400, U.S.A.) and coconut-based carbon (Samchully, Korea). Their pore volume and specific surface area, which were measured by the Autosorb-1 MP (Quantachrome, U.S.A.), are summarized in Table 1. Raw water was fed into the column at the flow rate of 200 mL/min. The carbon depth was 1000 mm so that an empty bed contact time (EBCT) became 10 min.

The pilot plant effluent was used as raw water for the adsorption experiments. The pilot plant treats the river water, which was used for the coagulation experiments. The pilot plant consists of pre-ozonation, coagulation, flocculation, sedimentation, filtration, intermediate-ozonation, and GAC filtration. An average DOC concentration of the pilot plant effluent was 0.8 mg/L. TAs were spiked to the effluent so that their initial concentration became 10 µg/L before the adsorption experiments. Since coagulation is an upstream process during water treatment and adsorption a downstream process, lower initial concentration was used for the adsorption experiments (10 µg/L) than the coagulation experiments (100 µg/L). The DOC concentration was measured using the TOC analyzer (Sievers 820, U.S.A.).

3. Results and discussion

3.1. TA removal by coagulation

Table 2 shows that coagulation was effective for removal of TAs. According to Table 2, PACl addition of 5 mg/L was able to remove 21~54% of TAs from the synthetic water. The removal efficiency depended on the type of TAs. Coagulation could remove approximately 50% of OTC, MNC, MCC, DMC, and TC, but the removal efficiency decreased to approximately 20% for DXC and CTC. It is not clear why the coagulation

performance was different with the type of TAs. As shown in Fig. 1, all of these TAs possessed similar chemical structures. The removal efficiency improved with increasing dosage from 5 to 60 mg/L. The best efficiency was obtained at addition of 40 mg/L (40~94%). The best removal efficiency was obtained at a dosage of 30 mg/L for DXC.

The solution pH was important for removal of TAs. As shown in Fig. 1, TAs contain three functional groups of tricarbonyl, dimethylamine, and β-diketone, which contribute to dissociation of TAs. Their dissociation constants are $pK_{a,1}$ of 3~4, $pK_{a,2}$ of 7~8, and $pK_{a,3}$ of 9~10 [17]. Therefore, most TAs are positively charged below pH 3.0 and zwitterionic or negatively charged
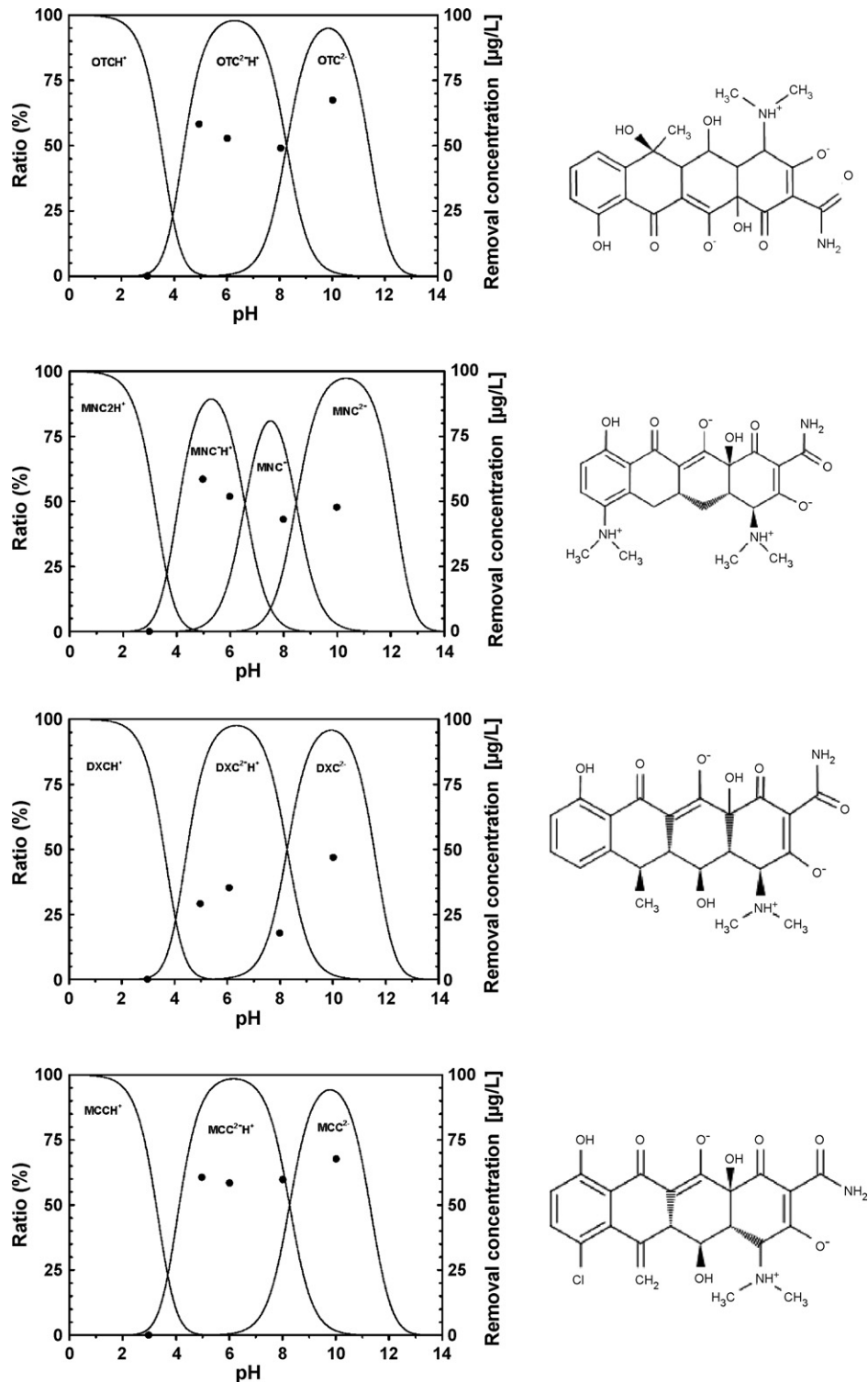

Fig. 1. Chemical structures of the TAs used in this study together with their removal efficiency by addition of poly-aluminum chloride (PACl) 10 mg/L at pHs 3, 5, 6, 8, and 10.
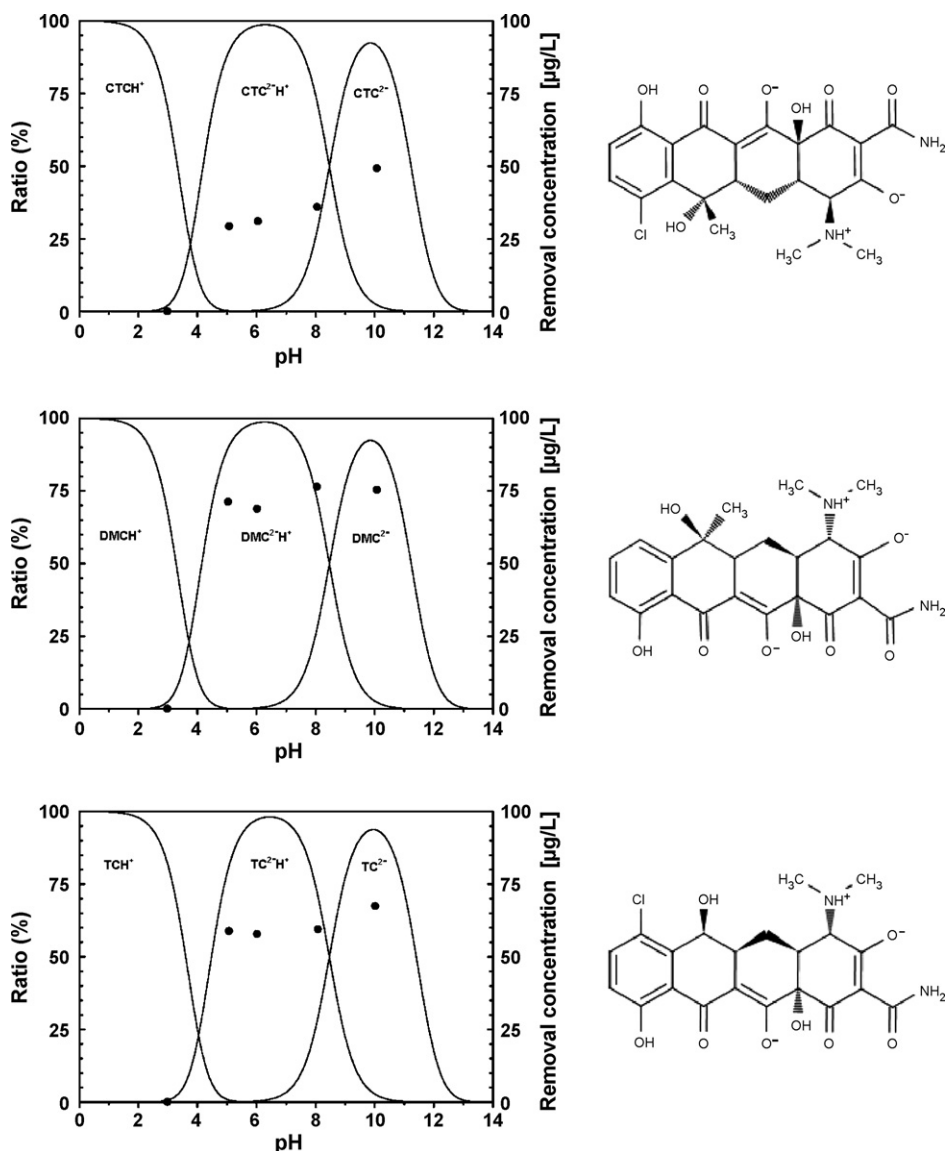
Fig. 1. (*Continued*).

above pH 3.0. They are in zwitterionic forms at pH 5.0∼6.0, which was the range observed during the coagulation experiments of the synthetic water. PACl addition of 40 mg/L lowered the solution pH from 6.0 to 5.0. It seemed that the charge neutralization drove the TA removal when PACl was added to the synthetic water. Since the synthetic water was prepared without alkalinity, aluminum hydroxide precipitates could not form. Instead, aluminum hydrolysis species with positive charge were used to neutralize zwitterionic or negative surface charge of TAs. The resulting products were then separated from water by filtration. Re-stabilization occurred upon overdose, which confirmed the charge neutralization. When the PACl dosage exceeded 40 mg/L, the removal efficiency deteriorated due to re-stabilization.

The coagulation efficiency decreased when dissolved organic was present in the raw water. Table 2 shows that the coagulation efficiency deteriorated when PACl was added into the river water. Competition could cause a decrease in the coagula-

tion efficiency. The river water contained considerable amount of dissolved organics, which required separate coagulant consumption. When dissolved organic was absent, all of aluminum added could be used to react with TAs. However, since negatively charged dissolved organics could also react with positively charged aluminum hydrolysis species, less coagulant became available for removal of TAs when PACl was added to the river water. Subsequently, the coagulation efficiency deteriorated for the river water. Coagulation removed 44∼67% of incoming TAs from the river water at the optimum condition.

According to the coagulation diagram [19], the pH of about 6.8∼8.3 and alum dosage of about 20∼50 mg/L belongs to the optimum sweep coagulation region. During the coagulation experiments of the river water, PACl addition of 60 mg/L decreased the solution pH from 8.1 to 7.4. The Al_2O_3 content of PACl is 10%, while that of alum is 7%. Therefore, 20∼50 mg/L of alum equals to 3.4∼8.5 mg/L as Al_2O_3, and 60 mg/L of PACl equals to 6.0 mg/L as Al_2O_3. Subsequently, coagulation at the

Table 2
Results of PACl coagulation for TAs removal from both the synthetic and the river water (unit: %)

		PACl dose (mg/L)						
TA	Raw water	5	10	20	30	40	50	60
OTC	Synthetic water	53	57	74	78	87	80	75
	River water	–	19	33	34	37	45	47
MNC	Synthetic water	50	58	72	73	72	64	63
	River water	–	59	60	63	62	66	66
DXC	Synthetic water	24	23	42	50	40	36	38
	River water	–	22	32	37	30	42	39
MCC	Synthetic water	44	42	50	56	80	80	79
	River water	–	40	51	53	49	58	57
CTC	Synthetic water	21	22	33	43	43	41	42
	River water	–	38	47	49	49	55	55
DMC	Synthetic water	54	53	71	71	94	93	92
	River water	–	33	49	54	54	62	65
TC	Synthetic water	50	50	73	75	85	80	76
	River water	–	27	38	40	41	48	49

PACl dosage of 60 mg/L and at the pH 7.4 corresponds to the optimum sweep coagulation region. Aluminum hydroxide precipitates could form under this condition. TAs would then be removed by being enmeshed into or adsorbed onto these precipitates.

There was a substantial difference in the removal efficiencies of TAs from the synthetic water depending on the type. However, their removal efficiencies became relatively constant regardless of the type when TAs were removed from the river water. This could be explained by different coagulation mechanisms. As mentioned earlier, the charge neutralization drove removal of TAs from the synthetic water. On the other hand, sweep coagulation could be responsible for removal of TAs from the river water. During the charge neutralization, the hydrolysis products of PACl carrying positive charge were adsorbed onto the TAs surface. Subsequently, the energy required for the particle contact was minimized. The destabilization would be affected by the TA characteristics such as molecular structure and surface charge. Depending on the characteristics, some TAs would be more inclined for the destabilization and others would not. On the other hand, the effect of TA type would not be important during sweep coagulation of the river water because TAs would be enmeshed into the precipitate or adsorbed onto the precipitate.

3.2. TA removal by adsorption

According to Fig. 2, GAC filtration was effective for removal of TAs. The performance of GAC filtration was generally better than that of coagulation. GAC filtration with coal-based carbon could remove more than 68% of incoming TAs. Among two carbons, coal-based carbon was slightly better in removal of TAs than coconut-based carbon, but the difference could not be confirmed statistically. Pore volume could cause the difference. Coal-based carbon possessed larger pore volume than coconut-based carbon, as shown in Table 1. According to Choi et al. [20], pore volume is the most important factor for adsorption.
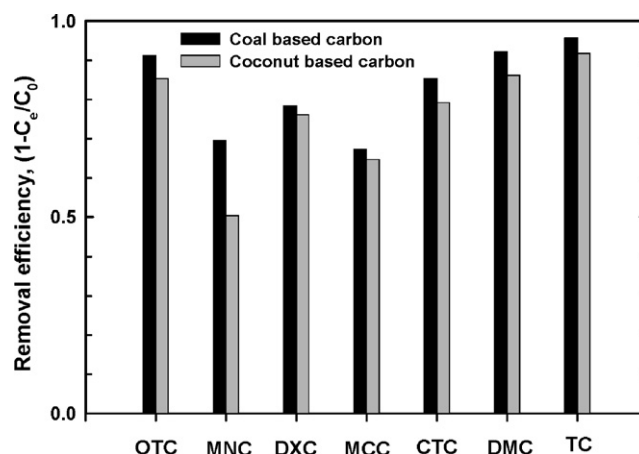

Fig. 2. The performance of the pilot GAC filters for removal of TAs at EBCT of 10 min.

Larger pore volume resulted in better adsorption. Coconut-based carbon had relatively large volume of micro-pore, while coal-based carbon had large volume of meso-pore. Like coagulation, the performance of GAC filtration was different with the type of TAs. OTC, DMC, and TC were easy to remove by the GAC filter (>90% with coal-based carbon), while MNC and MCC were difficult to remove (<70% with coal-based carbon). Fortunately, GAC filtration was effective for removal of TC, DXC, and CTC, which were difficult to remove by coagulation.

4. Conclusions

Treatment of seven TAs from raw waters (synthetic and river) was evaluated using coagulation and GAC filtration in this study. PACl was used as coagulants, and GAC filter was used for adsorption. According to this study, coagulation was effective for removal of TAs, and addition of PACl could remove 43~94% of TAs at the optimum conditions from the synthetic water. The removal efficiency depended on the type of TAs. When TAs were

removed from the synthetic water, coagulation was the least effective for DXC and CTC. The removal efficiencies slightly deteriorated (44∼67%) in the river water due to organic interference. Unlike the synthetic water, the difference in removal efficiencies of TAs was insignificant in the river water.

It was postulated that TAs would be removed through the charge neutralization and sweep coagulation when PACl was added into the raw waters. The charge neutralization of zwitterionic or negative TAs by cationic aluminum hydrolysis species drove removal of TAs when PACl was added to the synthetic water. The destabilization products from the charge neutralization were then removed by filtration. When sufficient alkalinity was available (river water), aluminum hydroxide precipitates formed. Subsequently, TAs could be removed by being enmeshed into or adsorbed onto aluminum hydroxide precipitates when PACl was added to the river water.

GAC filtration was generally more effective for removal of TAs than coagulation. When coal-based carbon was employed, GAC filtration could remove more than 68% of incoming TAs. The type of TAs affected the removal efficiency of GAC filtration. OTC, DMC, and TC were easy to remove by GAC filtration (>90%), while MNC and MCC were difficult to remove (<70%). Since GAC filtration was effective for removal of TC, DXC, and CTC, which were difficult to remove by coagulation, coupling of coagulation with GAC filtration would improve removal of TAs.

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