# Effect of Influent Ratio on Anaerobic Treatment of Coal Gasification Wastewater

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**Abstract.** The synactic effect of anammox coupling with heterotrophic denitrification process was investigated in an anaerobic reactor with an influent at the temperature of 35℃, pH of 7.0, hydraulic detention time (HRT) of 30 h. The nitrate and nitrite solution with different ratio (R=0-100%) to raw waste water was introduced into the influent with ammonia of 70-120 mg/L, COD concentration of 800-1200 mg/L before entering the anaerobic reactor to investigate the removal of nitrogen and organics. The experimental results show that in the influent ratio is 75%, the removal of ammonia, nitrite, total nitrogen (TN) and COD can reach 55.71%, 63.65%, 64.56% and 80%, respectively, under the condition of ammonia nitrogen, nitrite nitrogen influent concentration of 75.43mg/L99.87mg/La TN load of 233.82 mg /(L·d). The results show that the optimum dilution can not only dilute the raw waste water but also achieve co-effect of anammox and anaerobic denitrification by dosing appropriate nitrate and nitrate.

## 1 Introduction

Anaerobic ammonium oxidation process(ANAMMOX) is a promising biological nitrogen removal technology [1][2]. Compared with the traditional biological denitrification technology, it has the advantages of low oxygen demand, low operating cost, no additional carbon source, less sludge production and so on [3][4]. The process uses nitrite as electron acceptor under anaerobic or anoxic conditions, and the ammonia is converted to the biological processes of nitrogen [5]. Due to the anaerobic ammonia oxidizing bacteria is autotrophic, the activity of anammox bacteria will be inhibited under the condition of high concentration of organic carbon source and seriously affected on the removal effect of nitrogen [6]. Coal gasification wastewater [7][8][9] is a kind of typical organic wastewater which is hard to be degraded by high ammonia and phenol concentration, causing difficulties in achieving anaerobic ammonium oxidation. So it is very important to study the coupling of anaerobic ammonium oxidation and denitrification to achieve the simultaneous removal of nitrogen and organics. Large quantities of organic compounds (such as glucose) will seriously affected the ANAMMOX process although small amount organics have slight effect on ammonium oxidation [10]. The activated sludge could show a high denitrification activity while the anaerobic ammonium oxidation activity is inhibited. Some studies shown that the coupling of anaerobic ammonium oxidation and denitrification in the presence of phenol is also feasible [11]. Although there is competition of the same substrate of nitrite between the two processes, the presence of the denitrification bacteria can remove the inhibition effect of organic compounds on anaerobic ammonium oxidizing bacteria. The denitrification bacteria exist in the anoxic conditions can consume a small amount of $O_2$ introduced into the water and decrease the effect of $O_2$ on the anaerobic ammonium oxidizing bacteria. At the same time, the $CO_2$ produced by denitrification can provide inorganic carbon source for anaerobic bacteria. The nitrate produced by the anaerobic ammonium oxidation reaction can provide the substrate for denitrification. All the processes can achieve the goal of simultaneous denitrification and carbon removal in competition.

The study on the performance of anaerobic ammonium oxidation and denitrification has been rarely reported under the condition of high concentration organic carbon source. The coal gasification wastewater is a typical high ammonia wastewater containing phenol. The simulated coal gasification wastewater was used to study the effect of anaerobic ammonium oxidation coupled with the heterotrophic denitrification in anaerobic reactor. Because of the high concentration of ammonia nitrogen and COD concentration in the raw water, the nitrite content is very small, nitrite was introduced into the anaerobic stage to achieve the ammonia oxidation. Also the nitrate was introduced to investigate the possibility of anaerobic denitrification. The artificial water with nitrite and nitrate concentration was introduced into the anaerobic reactor according to the ratio of R in order to study the effect of nitrogen removal in anaerobic phase.

## 2 Materials and methods

### *2.1 Experimental apparatus*

The effective volume of anaerobic reactor was 2.5L with the height of 40cm and the diameter of 10cm. The creeping pump is used to control flow rate. The reactor was operated at about 35ºC in a water bath and covered with black cloth to avoid light. The HRT was 30h. The influent pH was controlled by the NaOH and the HCl around 7.

### *2.2 Simulated wastewater*

Artificial water was used in the experiment and influent composition of anaerobic reactor were composed by: glucose 230-250mg/L, volatile phenol 150-250mg/L, ammonia nitrogen 100-200mg/L, thiocyanat 20-50mg/L, sulfide 20-50mg/L, pyridine compounds 20-40mg/L, Furan compounds 20-40mg/L, benzpyrole compounds 20-30mg/L, Benzene compounds 100-150mg/L, $KH2PO_4$ 27mg/L, $CaCl_2 \cdot 2H_2O$ 180mg/L, $MgSO_4 \cdot 7H_2O$ 300mg/L, $NaHCO_3$ 0.5g/L. Trace element concentration liquid I and trace element I I concentration 1ml/L [12].

### *2.3 Measurement*

Water quality parameters were tested according to The Standard Methods for Water and Wastewater Quality Monitoring (Fourth Edition). The COD, $NH_4^+$-N $NO_2^-$-N $NO_3$-N TN and total phenol and volatile phenol were determined by fast closed catalytic digestion method, Nessler's Reagent spectrophotometric method, N-(1-naphthyl) ethylenediamine dihydrochloride spectrophotometric method, UV spectrophotometry, alkaline potassium sulfate oxidation UV spectrophotometry; 4-aminoantipyrine direct spectrophotometric method, UV spectrophotometry, respectively. All charts and data were analyzed and processed with the Origin 8.5 software.

### *2.4 Experimental procedure*

The anaerobic reactor has been operated for six months. The optimum operating conditions were determined by orthogonal experiments. Volatile phenols, total phenols and COD influent concentrations were 200~240mg/L, 390~420mg/L and 1400~1600mg/L, respectively. The removal rates were 48.35%, 51.37% and 51.63%., respectively. In order to reduce the inhibitory effect of high concentration organic compounds on the anaerobic ammonium oxidation under the best anaerobic environment, another influent containing nitrite nitrogen and nitrate nitrogen was introduced into the anaerobic reactor to dilute the influent anaerobic water and provide nitrite the same time， achieving the coupling of anaerobic ammonium oxidation, denitrification and heterotrophic anaerobic bacteria and simultaneous removal of organic matter and nitrogen. The influent dilution ratio R is the influent including the nitrite and nitrate to the simulated influent flow. Nitrite and nitrate in artificial water were supplied by $NaNO_2$ and $NaNO_3$. Both influents were made by tap water and imported by peristalsis pump into the anaerobic reactor bottom.

The ammonia nitrogen concentration was kept at 130~150mg/L in raw water. Then designed different influent dilution ratio R were taken 25%, 50%, 75%, 100%. The influent and outlet concentrations of ammonia, volatile phenol, and the dilution in the total reactor under different ratio of R were analyzed.The anaerobic reactor was operated continuously for about 10 days under each different ratio of R. For the convenience of data processing, the ammonia, volatile phenol, total phenol, COD concentration were caculated by dilute concentration after the artificial water distribution influent in the anaerobic reactor. The $NO_2^-$-N/ $NH_4^+$-N mass concentration ratio was controlled at 1:1.32.

## 3 Result and discussion

### *3.1 Effect of R on nitrogen removal*

The influent water and effluent water quality was shown in Fig. 1 for 1~11d, 12~19d, 20~29d, 30~40d corresponding to the influent ratio of R were 25%, 50%, 75%, 100%, respectively, including the $NH_4^+$-N, $NO_2^-$-N, $NO_3^-$-N, TN concentration and the removal tendency.

Figure 1 shows that at the ratio of 25%, 50%, $NH_4^+$-N, $NO_2^-$-N, TN of the effluent were not stable except $NO_3^-$-N. At the ratio of 75%, 100% , $NH_4^+$-N, $NO_2^-$-N, $NO_3^-$-N, TN of the effluent water were relatively stable. $NO_2^-$-N, TN of the effluent concentration is the lowest at the ratio of 75%, while the concentration of ammonia nitrogen is only 3mg/L higher than that at the ratio of 100%.

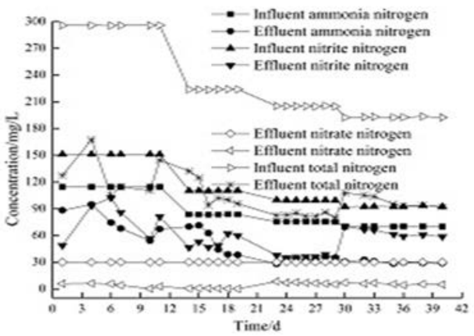


Fig. 1 content change curve of influent and effluent $NH_4^+$-N, $NO_2^-$-N, $NO_3^-$-N, TN

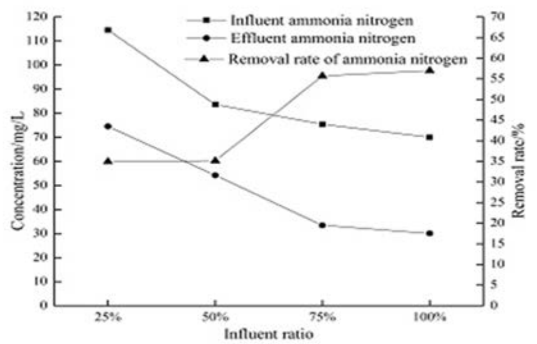


Fig. 2 influent ratio on $NH_4^+$-N removal

With the increase in the proportion of water, ammonia nitrogen removal rate showed an upward trend in Fig. 2. When the ratio increased from 50% to 75%, the removal rate increased nearly 20% to the maximum value. The removal of ammonia nitrogen is also the largest at the *R* of 75%. Fig. 3 also shows a maximum removal of nitrite at the influent ratio of 75%. When the influent ratio is 25%~75%, the removal rate is linear dependent on *R*. When the influent ratio increased from 75% to 100%, the removal rate appeared to be greatly reduced from 63.65% to 31.58%.

Fig.3 and 4 shows some difference between effects of R on nitrite and nitrate. When the influent concentration of nitrate was about 30mg/L and the influent ratio was 50%, the average removal rate was the highest up to 98.97%. In the contrast, the removal rate of nitrate was the lowest when the ratio of nitrate was 75%, and the average removal rate was 77.52%. The total nitrogen removal was similar with nitrite, when the removal rate could reach a maximum value of 64.56% at *R*=75%. When the influent ratio is 100%, the removal rate of TN was the lowest with an average value of 48.76%.

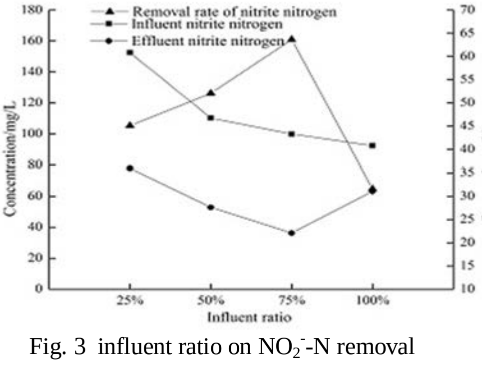


Fig. 3 influent ratio on $NO_2^-$-N removal

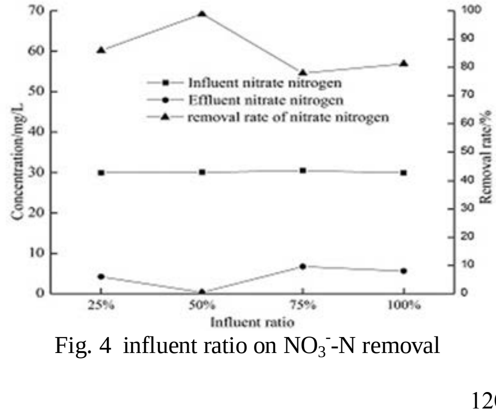


Fig. 4 influent ratio on $NO_3^-$-N removal

### *3.2 the effect of different influent ratio of R on nitrogen removal*

$NH_4^+$-N, $NO_2^-$-N are the substrate for the anaerobic ammonium oxidation reaction and $NO_2^-$-N, $NO_3^-$-N are the substrate for denitrification. The $NH_4^+$-N was chosen as a reference to measure the proportion of anaerobic ammonium oxidation reactions in the coupling. Fig. 6 shows that when the influent ratio was 25%, ammonia removed was 40.02mg/L, the nitrite and nitrate removed were 74.65mg/L and 25.79mg/L, respectively. Nitrite reduced by ANAMMOX should be 52.83mg/L which could be calculated theoretically by ammonia oxidized. Accordingly the formation of nitrate was10.41mg/L. Totally 21.82mg/L nitrite was removed through denitrification. So the total nitrogen involved in denitrification was 58.02mg/L, which accounted for 33.99% of the total nitrogen removal rate. Among them, the denitrification of nitrite as electron acceptor accounted for 12.78% of the total nitrogen removal, and the contribution of anaerobic ammonium oxidation to total nitrogen removal rate was 66.01%. When R=50%, 75%, contributions of nitrogen removal could be calculated as above, which was shown in Fig. 6.

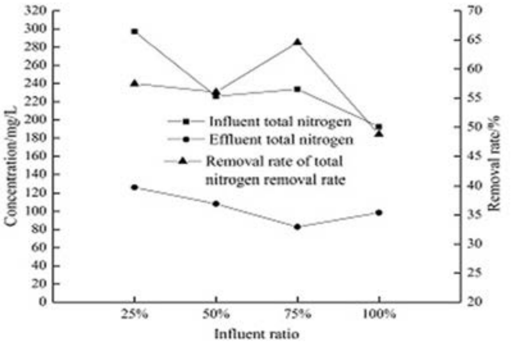


Fig. 5 influent ratio on TN removal

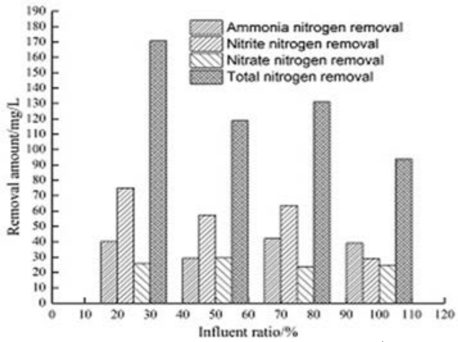


Fig. 6 influent ratio on removal amount of $NH_4^+$-N, $NO_2^-$-N, $NO_3^-$-N, TN

When the water inlet ratio is 100%, the nitrogen removal condition is different from above. The removed $NH_4^+$-N was 39.9mg/L, and the effluent concentration of $NO_2^-$-N, $NO_3^-$-N were 63.22mg/L, 5.62mg/L, respectively The amount of nitrite consumed in the anaerobic ammonium oxidation reaction was caculated by consumption of ammonia as 52.67mg/L, less than that of the influent concentration of 92.4mg/L. Accumulation of nitrite occured at this influent ratio, which was caused by partial denitrification of nitrate. The total amount of the nitrate in the effluent and the nitrite consumed by anaerobic ammonium oxidation were 115.89mg/L, while that of the influent is 92.4mg/L. The production of nitrite from the denitrification was 23.49mg/L. The nitrate in anaerobic ammonium oxidation was 10.16mg/L, and that in the influent was 30mg/L. The total amount of actual nitrate nitrogen was 40.16 mg/L, while the effluent nitrate nitrogen was 5.62 mg/L. So the nitrate nitrogen in the process of complete denitrification was 11.05mg/L, which accounted for 11.78% in the total nitrogen removal. Nitrogen removed by anaerobic ammonium oxidation accounted for 88.22% of the total nitrogen removal. The final calculation results were shown in Table 1.

Table 1 calculation results of anaerobic ammonium oxidation and denitrification on nitrogen removal (mg/L)

| Influent ratio R | Consume | Theory $NO_2^-$-N | Produce $NO_3^-$-N | Total $NO_3^{-}$-N | denitrificationNO$_x^-$-N |
|---|---|---|---|---|---|
| 25% | 40.02 | 52.83 | 10.41 | 36.20 | 58.02 |
| 50% | 29.37 | 42.33 | 7.55 | 37.01 | 52.08 |
| 75% | 43.02 | 55.47 | 10.93 | 34.19 | 42.29 |
| 100% | 39.90 | 52.67 | 10.16 | 35.44 | 11.05 |

### *3.3 Effect of R on organics removal*

The concentrations of volatile phenols, total phenols, COD in the influent and effluent were shown in Fig. 7. When the ratio of volatile phenols and total phenols increased from 25% to 50%, the volatile phenols removal was not improved, and the removed COD was also reduced by about 80mg/L. This might be caused by adding nitrate and nitrite solution in the early stage, causing the changes in the influent ORP. Increased ORP had negative effect on anaerobic bacteria, causing decrease of phenol removal. When the influent ratio increased from 50% to 75%, the removal efficiency increased significantly, for exampe, the removal of COD increased about 30mg/L, 50mg/L compared with the influent ratio of 25% and 50%, respectively. This was due to the introduction of nitrate and nitrite in the period of about 20 days, some anaerobic bacteria adapted to the conditions of the raw water. Or the bacteria population got adapted to the influent, causing recovery of the activity and phenol removal. With increased influent ratio, the removal improvement was not obvious. The concentration of volatile phenol in effluent was still at about 20 mg/L, and the removal rate of total phenol concentration was not significantly increased either. On the contrary, removal rate of COD decreased with the increased *R*.

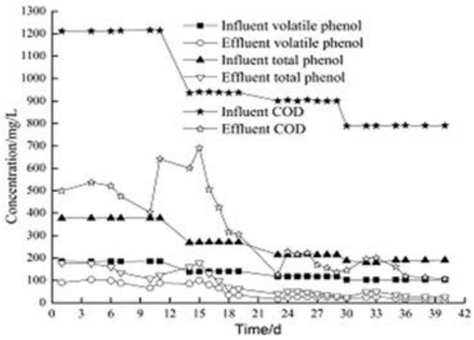


Fig.7 content change curve of influent and effluent phenol, COD

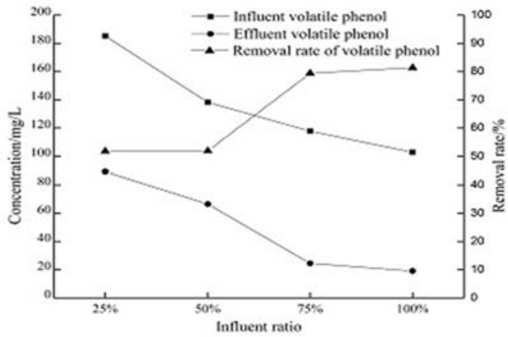


Fig.8 influent ratio on volatiel phenol removal

From the Fig. 8 and 9, we could see that the removal of volatile phenol and total phenol with the increased influent ratio was almost the same. The removal efficiency of organic matters was the best between 75% and 100%. COD removal could reach the maximum of 721.29 mg/L when R=75%.

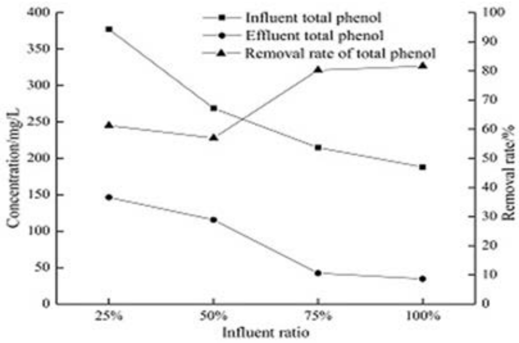


Fig.9 influent ratio on total phenol removal

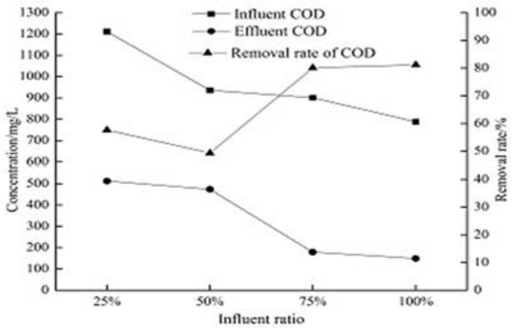


Fig.10 influent ratio on COD removal

From the theoretical equation of denitrification reaction, the decomposition of 1mg organic matter (COD) requires 0.58mg $NO_3^-$-N and 0.35mg $NO_2^-$-N. The amount of COD consumed can be calculated by analyzing nitrogen removed, which was shown in Table 2.

Table 2 COD removed in denitrification ( mg/L )

| Influent ratio R | Consumed $NO_2^-$-N | Consumed $NO_3^-$-N | $NO_2^-$-N Consumed COD | $NO_3^-$-N Consumed COD | $NO_x^-$-N Consumed COD |
|---|---|---|---|---|---|
| 25% | 21.82 | 36.20 | 37.62 | 103.43 | 139.63 |
| 50% | 15.07 | 37.01 | 25.98 | 105.74 | 131.72 |
| 75% | 8.10 | 34.19 | 13.97 | 97.69 | 111.66 |
| 100% | 0 | 11.05 | 0 | 58.35 | 58.35 |

The enitrification showed a downward trend with the increase of influent ratio in the Table 2. This is because the denitrification bacteria are heterotrophic bacteria, which use organic matter as the carbon source for growth and reproduction. With the increase of influent ratio, the concentration of organic matter gradually decreased, which led to the decrease of the activity of the denitrification bacteria. Although the removal rate of COD was reduced by denitrification, the removal rate of phenolic compounds and COD was positively correlated with the influent ratio in the figure 11. This means in the anaerobic reactor, in addition to the presence of heterotrophic denitrification bacteria and anaerobic ammonium oxidizing bacteria, there are other heterotrophic anaerobic bacteria. This was similar to the results of the EGSB reactor studied by Qi Xuliang [13], and the coupling of the anaerobic reactor investigated by Zu Bo[14]. The activity of heterotrophic anaerobic bacteria might increase with the increase of influent ratio. It seemed that denitrifying bacteria mainly used phenolic compounds as organic substrate by analyzing influent phenol concentration and denitrifying removal of COD. In most cases, the presence of phenolic compounds inhibits the activity of anaerobic ammonium oxidizing bacteria, but the inhibition could be relieved by domestication, forming strong resistance to phenol of the anaerobic ammonium oxidizing bacteria [15].

### *3.4 Discussion of R on anaerobic section effects*

From the Fig. 2~5 and Fig. 7~10, it can be seen that the removal rate was decreased and the other indicators of the removal rate of the basic and influent ratio was positively correlated and when the ratio increased from 75% to 100% except the total nitrogen and nitrite nitrogen increased, and the removal rate did not increase obviously. The favorite influent ratio was 75% accroding to the experiments. When the influent ratio was 75%, the ratio of C/N was 4.21, and the removal rate of COD and ammonia nitrogen was the largest among ratios tested, which showed it is favoriable for COD and ammonia nitrogen remvoal in the lower C/N, which was beneficial to the coupling of anaerobic ammonium oxidation and denitrification. The results of this study were in acordance with that of Ran Chunqiu[16], that is, the removal of total nitrogen is the result of the coupling action of anaerobic ammonium oxidation and denitrification.

## 4 Conclusions

The following conclusion s can be drawn from the experiments:

(1) The coupling of anaerobic ammonium oxidation, heterotrophic denitrification and heterotrophic anaerobic process can be achieved using simulated coal gasification wastewater at the temperature of 35 C, the influent pH value around 7.0, HRT of the 30h, COD concentration of 800~1200mg/L. The results of TN removal is combined action of heterotrophic denitrification and anaerobic ammonium oxidation, and the removal of COD was the results of the cooperation and competition between heterotrophic denitrification and heterotrophic anaerobic bacteria.

(2) There are cooperation and competition in anaerobic ammonium oxidation, heterotrophic denitrification and anaerobic bacteria coupled anaerobic system. The influent ratio can change the synergy and competition effect among the three. Under the influent ratio of 75%, the coupling effect of heterotrophic denitrification and anaerobic ammonium oxidation was the best, and the removal rate of TN was 64.56%. The coupling effect of heterotrophic denitrification bacteria and heterotrophic anaerobic bacteria is also good as well, the COD removal rate is 80.1% and COD removal rate was only 1.38% lower than that at R of 100%.

(3) At the influent ratio was 75%, the removal of nitrogen by denitrification accounts for 32.39% of TN removal rate and the removal of nitrogen by anaerobic ammonium oxidation accounts for 67.72% of TN removal, when the consumption of $NH_4^+$-N and $NO_2^-$-N are 42.02mg/L, 63.57mg/L, respectively. That is, consumption ration of $NH_4^+$-N/$NO_2^-$-N is 1.51. The amount of COD consumed by denitrification was 111.66mg/L, which accounted for 15.48% of the total amount of COD removal. The contribution rate of heterotrophic anaerobic bacteria to COD removal was 84.52%, among them, the heterotrophic denitrification bacteria are mainly phenol denitrification bacteria.

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