



## Three-Dimensional Fluorescence Characteristics of HA-A/A-MCO Sludge Reduction Process

DE-WEI MU, NING ZUO\*, YONG-QIN PENG and XIA LI

Scientific Institute of Chongqing Southwest Port and Waterway Engineering, Chongqing Jiaotong University, Chongqing 400016, P.R. China

\*Corresponding author: Tel: +86 13657647278; E-mail: zuoning\_2424@126.com

(Received: 20 October 2012;

Accepted: 28 June 2013)

AJC-13716

In order to explore methods of improving the removal of phosphorous and nitrogen in sludge reduction technologies, an advanced process combining sludge reduction and the removal of phosphorous and nitrogen was developed, for short, HA-A/A-MCO process (hydrolysis-acidogenesis-anaerobic/anoxic-multistep continuous oxic tank). Under the condition of this process achieving favorable effect of phosphorous and nitrogen removal and sludge reduction. The test results of the process treating campus wastewater showed that when influent COD was 316-407 mg/L, effluent COD was lower than 18 mg/L and COD removal rate exceeded 96 %. Through investigating three-dimensional excitation emission matrix fluorescence characteristics of each tank, the results indicated that each tank of HA-A/A-MCO system was provided with significant degradation to the dissolved organic matter in original sewage.

**Key Words:** Sludge reduction, Phosphorous and nitrogen removal, Three-dimensional excitation emission matrix fluorescence spectrum.

### INTRODUCTION

An advanced process combining excess sludge reduction and phosphorous and nitrogen removal is developed, for short, HA-A/A-MCO process (hydrolysis-acidification-anaerobic/anoxic-multistep continuous oxic tank), which is helpful for improving the removal of phosphorous and nitrogen in sludge reduction technologies<sup>1-3</sup>. HA-A/A-MCO process has better performance of simultaneous sludge reduction and phosphorous and nitrogen removal. This study is aimed to investigate the performance of organic matters removal and three-dimensional characteristics in HA-A/A-MCO process.

### EXPERIMENTAL

**Process:** A-A/A-MCO is an advanced sludge reduction process which is developed by our research group, whose flow path is shown in Fig. 1.

It includes hydrolysis-acidification (HA) tank, anaerobic tank, anoxic tank, multistep continuous oxic tank, secondary sedimentation tank, sidestream sedimentation tank and chemical phosphorous removal tank. And, the virtual volume of hydrolysis-acidification tank, anoxic tank and anaerobic tank is 50, 30 and 30 L, respectively.

Corresponding hydraulic retention time (HRT) is 2.5, 1.5, 1.5 h, respectively. Besides, multistep continuous oxic tank is divided into three areas: the first area is bacterial culture section, whose virtual volume and hydraulic retention time is 15 L, 0.5-0.75 h, respectively. The second area is Protozoa

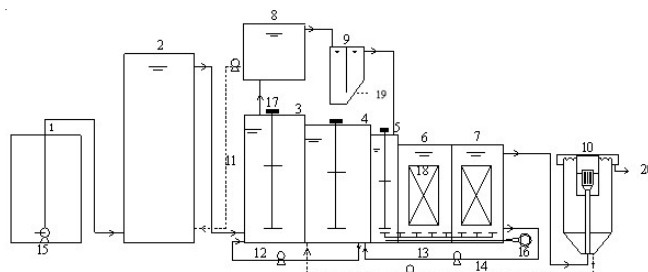


Fig. 1. Flow sketch map of HA-A/A-MCO process. 1. Influent tank; 2. Hydrolysis acidification tank; 3. Anaerobic tank; 4. Anoxic tank; 5, 6, 7. No. 1 Oxic Tank, No.2 Oxic Tank and No.3 Oxic Tank of Multistep Continuous Oxic Tank, respectively; 8. Sidestream Sedimentation Tank; 9. Chemical Phosphorous Removal Tank; 10. Secondary Sedimentation Tank; 11. Phosphorus-release Sludge Return; 12. Denitration Liquor Return; 13. Nitration Liquor Return; 14. Excess Sludge Return; 15. Flow Control Pump; 16. Air Compressor; 17. Stirrer; 18. Filler; 19. High Phosphorus Sludge; 20. Effluent

culture section, whose virtual volume and hydraulic retention time is 30 L, 1.5 h, respectively. The third area is metazoa culture section, whose virtual volume and hydraulic retention time is 40 L, 2 h, respectively. Multistep continuous oxic tank is provided with oxygen by microporous aeration tube at the bottom of the tank. The second area and third area are filled with combined biological filler and the filling ratios are both 40 %. In addition, sidestream sedimentation tank is used to offer anaerobic phosphorus release supernatant to chemical phosphorus removal tank, whose hydraulic retention time is

1 h. Secondary sedimentation tank adopts radial-flow one, whose hydraulic retention time is 1 h.

The influent and a little of anaerobic phosphorus release sludge enter into hydrolysis-acidification tank and dissolved and non-dissolved organic compounds from the influent and anaerobic phosphorus release sludge can be translated into VFA which is prone to biodegraded under the function of hydrolysis-acidification bacteria, meanwhile, sludge quantity is also reduced. Supernatant rich in VFA from hydrolysis-acidification tank along with denitrification return flow of anoxic tank flow into anaerobic tank, in which, phosphorus accumulating bacteria can be intensified and high-concentration phosphorus release flow is obtained through the stimulation of VFA. The proportion of anaerobic phosphorus accumulating sewage entering chemical phosphorus removal tank is equal to 13 % of the influent, where phosphorus can be removed. Phosphorus content of the procreant chemical sludge is higher and phosphorus recycle can be realized. Mixed liquor after anaerobic phosphorus release along with nitrification liquor from multistep continuous oxic tank and return sludge are introduced into anoxic tank, in which, denitrification is realized. The mixed liquor after nitrogen removal along with supernatant from chemical phosphorus removal tank flow into multistep continuous oxic tank, where phosphorus can be absorbed adequately, chemical oxygen demand (COD) and ammonia nitrogen ( $\text{NH}_3\text{-N}$ ) can also be eliminated ulteriorly. In addition, multistep continuous oxic tank increases microbe density and prolongs food chain by controlling appropriate concentration gradient of organic matters, hydraulic retention time, DO and filling ratio of biological filler. Sludge yield can be reduced by using the progressive predator-prey function from metazoan to protozoan to bacteria to organic compounds. Finally, the mixed liquid from multistep continuous oxic tank flows into secondary sedimentation tank, where the effluent is drained out.

When HA-A/A-MCO process operates steadily, influent flow is 20 L/h. DO of each section of multistep continuous oxic tank is 0.5-1.5, 0.5-1.5 and 1.0-1.5 mg/L. Return ratio of excess sludge, nitrification liquor, denitrification liquor and anaerobic phosphorus release sludge is 40, 150, 100 and 2 %, respectively. Sludge retention time (SRT) of the system is 60d, mixed liquor suspended solids (MLSS) is 5100-5800 mg/L and sludge load is 0.18-0.21gCOD/gMLSS.d.

**Experimental water quality:** Experimental wastewater is campus sewage of Chongqing university by adding amyllum, glucose, milk powder,  $\text{NH}_4\text{Cl}$ ,  $\text{KH}_2\text{PO}_4$ . Characteristics of the influent are as follows:  $\rho(\text{COD}) = 316\text{-}407\text{mg/L}$ ;  $\rho(\text{NH}_3\text{-N}) = 30\text{-}40\text{ mg/L}$ ; total nitrogen concentration  $\rho(\text{TN}) = 35\text{-}53\text{ mg/L}$ ;  $\rho(\text{TP}) = 8\text{-}12\text{ mg/L}$ ;  $\text{pH} = 7\text{-}8$ ; temperature is 16-24 °C.

**Detection method:** COD is analyzed by HACH-COD instrument, DO concentration is measured with an YSI oxygen meter, VFA is measured by distillation-titration method and other parameters were analyzed as reported methods<sup>4</sup>.

## RESULTS AND DISCUSSION

**Change of COD concentration:** Fig. 2 shows the information of COD change. When the influent COD = 316-407 mg/L (the mean value is 352 mg/L), the mean concentration

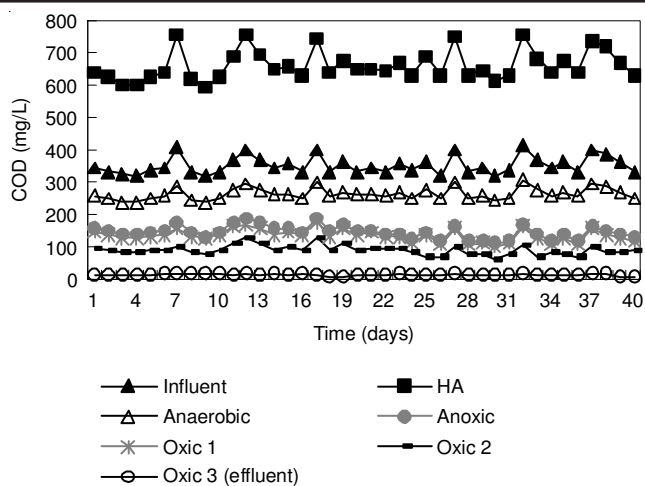


Fig. 2. Removal effect of COD of each tank

can increase to 660 mg/L after hydrolysis. Soon afterwards, the anaerobic effluent mean value is 264 mg/L after anaerobic phosphorus release, the anoxic effluent value is 145 mg/L after denitrification nitrogen removal. The effluent value from each tank of multistep continuous oxic tank is 134, 88 and 13 mg/L, respectively. The COD removal reate of the system is 96 %. And the effluent value can fully meet the demand of First-degree-A standards of GB18918-2002.

**Three-dimensional fluorescence characteristics of effluent water in each process section:** In city sewage organic matter according to the grain size can be divided into particulate organic matter (POM) and dissolved organic matter (DOM) in two categories, including total organic matter dissolved organic matter 30-40 %<sup>5</sup>, is the main object of sewage treatment.

In city sewage composition of dissolved organic matter mainly includes humus, humic acid (HA), fulvic acid (FA), hydrophilic organic acid, amino acid and nucleic acid, surfactant and other organic pollutants. Most of these contaminants molecular structure with conjugated double bonds in aromatic hydrocarbon or carbon based, carboxyl conjugated system<sup>6</sup>, the ultraviolet light irradiation by a specific wavelength excitation will emit fluorescent light at different wavelengths. And three-dimensional fluorescence spectroscopy (3DEEM) can be expressed in the excitation wavelength and emission wavelength (Ex) (Em) at the same time when the change of fluorescence intensity information, can reveal information classification and content of dissolved organic matter in water.

Based on the position of fluorescence peak to indicate in the presence of fluorophore in wastewater and with the letters<sup>7</sup> (Table-1). Use the position of fluorescent peak and intensity change to express the variation of dissolved organic matter with process in HA-A/A-MCO system.

Fig. 3 indicates three-dimensional fluorescence spectroscopy drawing of each process section effluent in the system (hydrolysis tank without phosphorus release sludge reflux) diluted 20 times. Dissolved organic matter fluorescence peak position and fluorescence intensity are shown in Table-2.

It can be seen from Fig. 3 and Table-2 that in the raw water dissolved organic matter mainly includes four kinds-UV-humic acid A (EX/EM:241/406), visible humic acid C (EX/EM:352/430), low excitation wavelength protein (TRP)

Fluorescence peak	$\lambda_{ex}$ (nm)	$\lambda_{em}$ (nm)	Type
S	220-230	320-350	Low excitation wavelength proteinoid (Tryptophan)
T	270-280	320-350	High excitation wavelength Proteinoid (Tryptophan)
A	230-260	380-460	UV-humic acid
C	320-360	400-460	Visible humic acid
D	390	509	Soil fulvic acid
M	455	521	
N	290-310	370-410	Shipping of humic acid
	280	370	Phytoplankton On productivity

Section	UV-Humic acid A		Visible humic acid C	
	EX/EM	$I_A$ (a.u)	EX/EM	$I_C$ (a.u)
Raw water	241/406	299	352/430	1156
Hydrolyzation	247/439	197	340/405	969
Anaerobic	232/436	196	340/405	879
Anoxic	238/418	278	352/400	212
Aerobic 1	—	—	352/400	205
Aerobic 3 (effluent)	—	—	352/400	205
Section	Low excitation wavelength Proteinoid (Tryptophan) S		High excitation wavelength Proteinoid (Tryptophan) T	
	EX/EM	$I_S$ (a.u)	EX/EM	$I_T$ (a.u)
Sewage	223/337	1365	277/337	1027
Hydrolyzation	223/331	1559	277/334	972
Anaerobic	223/331	1069	274/334	713
Anoxic	226/334	1379	274/331	1087
Aerobic 1	226/337	905	271/334	576
Aerobic 3 (effluent)	226/337	828	—	—

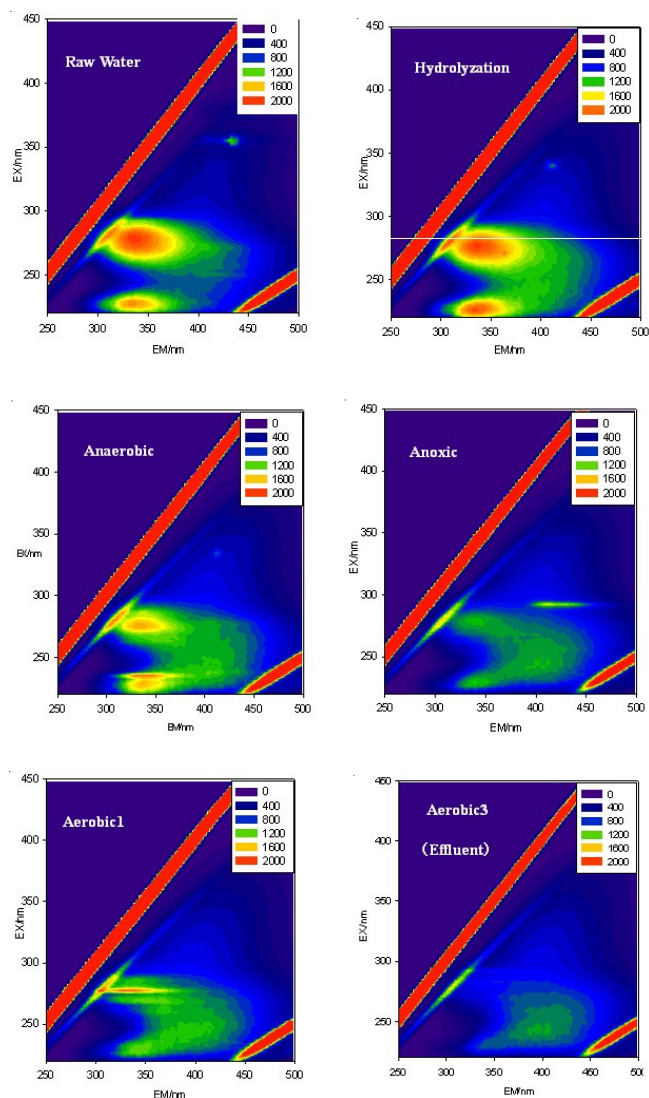


Fig. 3. DEEMs of each tank of HA-A/A-MCO system

S (EX/EM:223/337), high excitation wavelength protein (TRP) T (EX/EM:277/337).

Hydrolytic acidification unit has good removal ability with dissolved organic matter in raw water, especially the removal rate of humic acid (A and C) is most obvious, respectively 39 and 16 %, while the protein (TRP) fluorescence intensity of S

increases 14 %. This is because hydrolytic acidification bacteria in the process of decomposition and transformation of organic matter in raw water, the protein in raw water is degraded and releases fluorescent amino acids (mainly tryptophan).

In anaerobic section in the process of strengthening PAOs phosphorus release, organic matter is used in great quantities. According to the data in Table-3, it also can be seen that anaerobic section continues degradation of dissolved organic matter, in which the low excitation wavelength and high excitation wavelength tryptophan decrease significantly, the fluorescence intensity drops, respectively 31 and 26 %.

In anoxic segment humic acid can be further removed. And the class of tryptophan fluorescence intensity increases, it may be because of denitrifying bacteria using of carbon source for denitrification simultaneous release of a portion of fluorescent tryptophan, at the same time, as a result of multi-stage aeration tank of the metazoan growing zone reflow mixture may contain microbial residues from microfauna predation, it can also make this segment show strong green fluorescence protein.

Aeration tank has obvious removal for UV humic acid and high excitation wavelength tryptophan. In effluent, there is no UV humic acid and high excitation wavelength tryptophan fluorescence peak, only the weaker fluorescence spectral band. At the same time, aeration tank has higher removal effect on the low excitation wavelength tryptophan, the fluorescence intensity decreases 40 %.

In the effluent after treatment by HA-A/A-MCO system, the dissolved organic matter mainly includes two kinds-visible humic acid C (EX/EM:352/400) and low excitation wavelength protein (TRP) S (EX/EM:226/337). The visible humic acid is mainly difficult degradable organics and microbial metabolites and the microorganisms themselves residues exist in water in the form of low excitation wavelength tryptophan.

## Conclusion

The research develops a new sludge reduction of HA-A/A-MCO technology which has the functions of nitrogen and phosphorus removal. When the influent COD is 316-407 mg/L, effluent CODd 18 mg/L, COD average removal rate can be up to 96 %, the effluent organic substrate concentration satisfies the GB18918-2002 level A standard, HA-A/A-MCO process has good decontamination effect.

Through the investigation of three-dimensional fluorescence characteristics in each reaction effluent, it is found that various sections of the system has significant degradation effect on dissolved organic matter in raw water.

## ACKNOWLEDGEMENTS

The authors thanks Chongqing Education Committee Science and Technology Research Projects Project (KJ130420); Fundamental and Advanced Research Projects of Chongqing Science & Technology Commission Project (cstc2013jcyjA20013) for financial support.

## REFERENCES

1. L.T. Pan, J. Wang and Y.B. Shu, *Environ. Pollut. Control*, **30**, 73 (2008) (in Chinese).
2. N. Zuo, F.Y. Ji, X.J. Wan, J. Xi and L. Yang, *Chin. J. Environ. Eng.*, **1**, 105 (2008) (in Chinese).
3. Y.S. Wei, R.T. van Houten, A.R. Borger, D.H. Eikelboom and Y.B. Fan, *Water Res.*, **37**, 4453 (2003).
4. Edit Committee of State Environmental Protection Administration of China, *Test and Analysis Methods of Water and Wastewater*, Beijing: China Environmental Science Press, edn. 4 (2002) (in Chinese).
5. R.X. Hao, K.X. Cao and Y.W. Deng, *J. Instrum. Anal.*, **26**, 789 (2007) (in Chinese).
6. E. Ouyang, X.H. Zhang and W. Wang, *Spectrosc. Spectral Anal.*, **27**, 1373 (2007) (in Chinese).
7. P.Q. Fu, F.C. Wu and C.Q. Liu, *Spectrosc. Spectral Anal.*, **25**, 2024 (2005) (in Chinese).