清華大學深圳研究生院
Graduate School at Shenzhen,Tsinghua University

Color and Nitrogen Removal from Synthetic Dye Wastewater in an Integrated Hydrolysis/Acidification and Anoxic/Aerobic Process

Mengqi Gu, Qidong Yin, Aike Liu, Guangxue Wu*
Graduate School at Shenzhen, Tsinghua University
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1. Background

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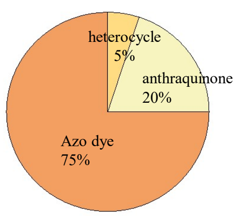
1.1 Dyeing industry and dyeing wastewater

- Production and characteristic of dyeing wastewater



Distribution of dye (Zhao et al., 2018)

Cotton	Wool	Silk	Dacron	Polyester cotton
Direct	Acid	Acid	Disperse	Disperse
Active		Direct	Azo	Reducing
Reducing				
Azo				

Dye used in different industries

Dyeing wastewater

17-20% industry wastewater

COD

Color

NH_4-N

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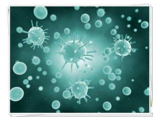
1.2 Technology for color removal

■ Treatment of dyeing wastewater

Treatment
- Physical：Flocculation & Precipitation
- Biological: anaerobic, anoxic, aerobic →
  - Low cost
  - Less environmental affects
  - Low sludge yield
- Chemical：Advanced oxidation

(Chandrakant et al., 2016; Wang et al., 2011)

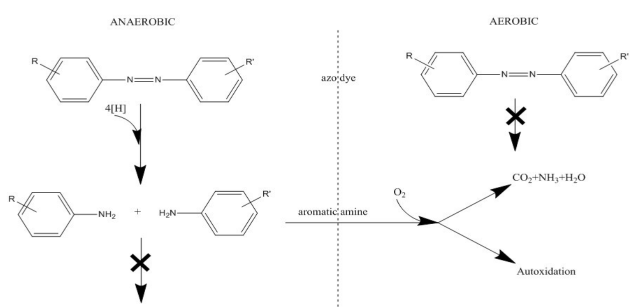


- Dye degradation is based on the function of microorganisms
- Anoxic/aerobic is the most common process for dye degradation
- The color removal efficiency depends on the structure of microbes and the activity of enzymes

1.2 Technology for color removal

■ Biodegradation mechanism for azo dye

- Breaking the azo bond –N=N –
- Aromatic amine compounds generated with 4 electrons for breaking the azo bond in anaerobic process
- The intermediates can be removed by complete mineralization or autoxidation



1.2 Technology for color removal

■ Biological treatment of azo dye

- Biological treatment for azo dye usually needs long HRT, high COD
- Color removal efficiency can not reach 100%

Reactor type	dye	Temperature (℃)	HRT (h)	COD (mg/L)	Color removal(%)	Reference
SBR	DR80	35	48	500-3000	69.1-98.23	Kashif et al., 2015
ABR+ FAS	RR2	35	24	4000	89.5	Naimabadi et al., 2009
SBR	AR14	/	6	1000	85	Franca et al., 2015
SBR	Mixed	27	24	1017	70-80	Tomei et al., 2016
PBB	VBR	/	48	300	99.2	Chen et al., 2016

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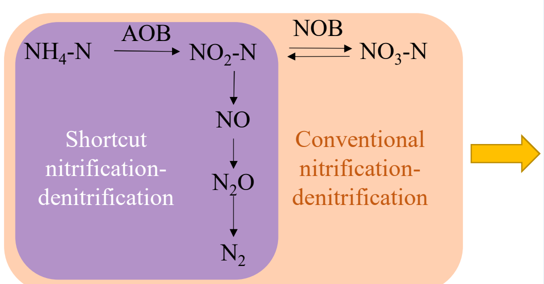
1.3 Enhanced nitrogen removal for dyeing wastewater

■ Biological nitrogen removal

Advantages of shortcut nitrification-denitrification for wastewater



Advantages:

- Saving 25% demand for oxygen
- Saving 40% demand for organic source
- Reducing 63% sludge yield
- Increasing denitrification rate by 1.5-2

(Abeling and Seyfried, 1992; Bernet et al., 2001; Fux et al., 2006; Wang and Yang, 2004)

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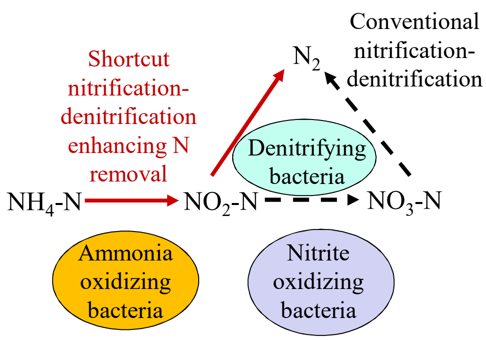
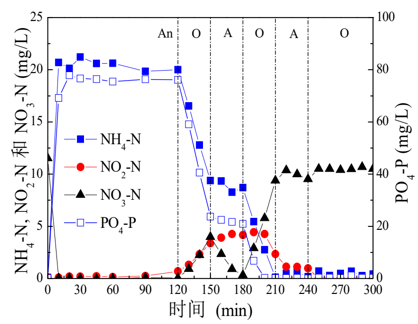
1.3 Enhanced nitrogen removal for dyeing wastewater

■ Enhanced nitrogen removal by multiple AO process

To solve the lack of COD in influent of wastewater, the inhibition of NOB could enhance nitrogen removal through shortcut nitrification-denitrification with multiple AO process





Multiple AO operation mode could control microbial ecology and enhance nitrogen removal

1.4 Requirements and purposes for research

■ Technical requirements of biological treatment

- Color removal：

The lack of researches on the azo dye degradation pathway and the functional microbial community in biological treatment

- Nitrogen removal：

The lack of researches on the nitrogen removal and the application of shortcut nitrification-denitrification in dyeing wastewater treatment

1.4 Requirements and purposes for research

■ Purposes

- The system performance of hydrolysis/acidification and anoxic-aerobic(AO) treatment for azo dye wastewater
- The factors influencing color removal efficiency and the pathway of azo dye in hydrolysis/acidification process
- The factors influencing nitrogen removal in AO process
- The microbial community in the hydrolysis/acidification and AO process

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2. Materials and Methods

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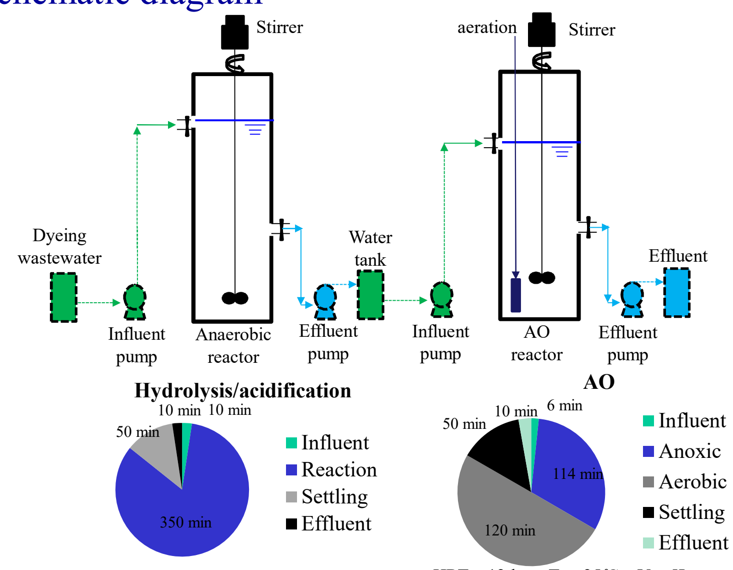
2.1 Experimental setup

■ Schematic diagram



HRT : 12 h T : 25℃ V : 6 L

HRT : 12 h T : 25℃ V : 5L

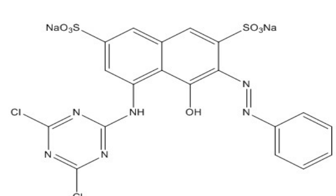
2.1 Experimental setup

■ Components

Components	Concentration (mg/L)	Components	Concentration (mg/L)
NH_4Cl	114.6	$NaHCO_3$	200
Azo dye (RR2)	30	Sodium Acetate	51.28
KH_2PO_4	35.2	Starch	224.93
$MgSO_4 \cdot 7H_2O$	100	Peptone	109.09
$CaCl_2 \cdot 2H_2O$	100	Trace elements	1 mL/L

Mixed carbon source= 1:3:6 COD=400 mg/L

Azo dye
Reactive Red 2



2.2 Method

■ Methods

- COD, NH_4-N, NO_2-N, NO_3-N,MLSS, MLVSS: APHA
- Color: the absorption of azo dye RR2 in 512 nm

  Color removal efficiency (%)=$(A0-A)/A0\times 100$

  A0: absorption of influent A: absorption of effluent
- QTOF detection : Combined Q-TOF MS (Agilent 6560 IM Q-TOF) and LC system (Agilent 1290 Infinity, USA) (LC-IM-QTOF-MS)
- Aniline : LC-MSMS, combined LC system (LC-20AD, Shimadzu, Japan) and mass spectrometer (API 3200, AB Sciex, U.S.)
- Microbial community: 16s rRNA

Condition in mass spectrometer

Curtain Gas	10 psi
Collision Gas	6
IonSpray Voltage	5000 V
Temperature	400 ºC
Ion Source Gas 1	60 psi
Ion Source Gas 2	60 psi

MRM condition for aniline

	Q1/Q3	DP	EP	CEP	CE	CXP
Quantitative Q1/Q3 transition	94.2/77.1	21.0	11.5	12.0	27.0	4.0
Qualitative Q1/Q3 transition	94.2/51.1	21.0	11.5	12.0	45.0	4.0

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3. Results and Discussion

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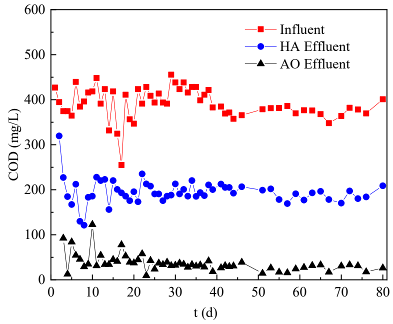
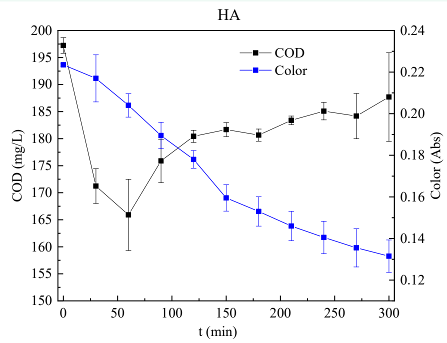
3.1 System performance

■ COD

- Concentration of COD did not change much in the hydrolysis/acidification process
- COD was removed in the denitrification process





	Influent (mg/L)	HA effluent (mg/L)	AO Effluent (mg/L)	Removal efficiency (%)
COD	**381.5±27.7**	**178.1±24.6**	**19.5±9.0**	**94.9**

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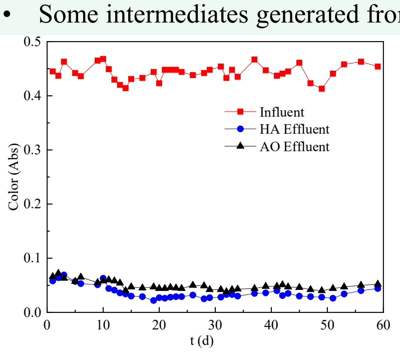
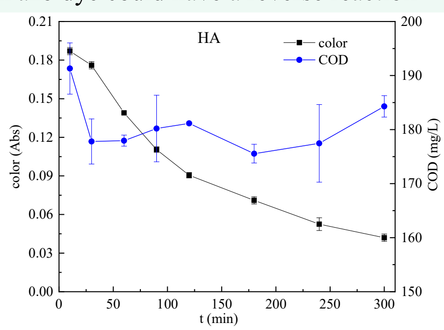
3.1 System performance

■ Color

- Hydrolysis/acidification was the main process for color removal
- AO effluent had higher color
- Some intermediates generated from azo dye could have a reverse reaction





	Influent	HA effluent	AO Effluent	Removal efficiency (%)
Color	**0.442±0.014**	**0.033±0.008**	**0.047±0.005**	**89.4**

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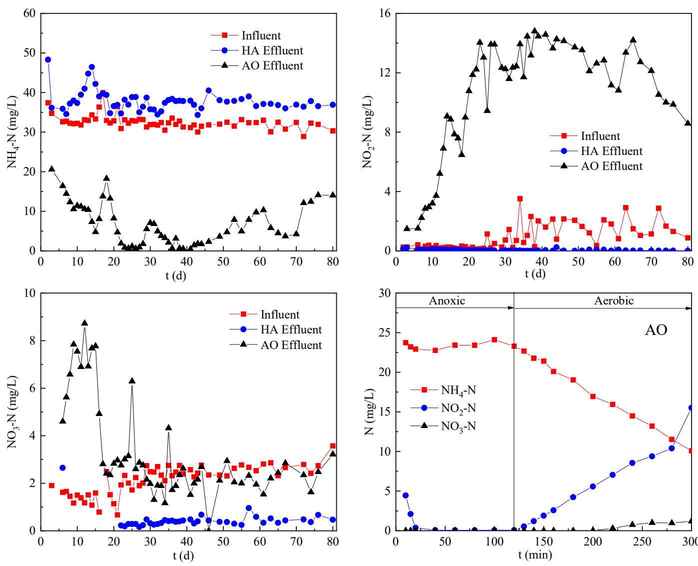
3.1 System performance

- Nitrogen



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3.1 System performance

- Nitrogen

	Influent (mg/L)	HA effluent (mg/L)	AO Effluent (mg/L)	Removal efficiency (%)
NH_4-N	**31.74±1.11**	**37.42±1.39**	**5.23±4.29**	**83.5**
NO_2-N	**1.54±0.84**	**0.03±0.04**	**11.03±3.96**	/
NO_3-N	**2.72±0.49**	**0.48±0.19**	**4.39±5.72**	/

- Nitrite accumulation
- Removal efficiency of total inorganic nitrogen (TIN) : 42.6%

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3.2 Color removal during hydrolysis/acidification

■ Effects of carbon source and temperature on color removal

- Seed sludge: sludge from hydrolysis/acidification reactor under steady condition
- Reaction volume: 500 mL
- Mixing speed: 170 rpm
- Temperature: 25℃ and 35℃
- Influent components: same as the reactor; carbon source (COD= 400 mg/L, Peptone, Starch and mixed carbon source); COD concentration (COD=200, 400, 800 mg/L, mixed carbon source=1:3:6)

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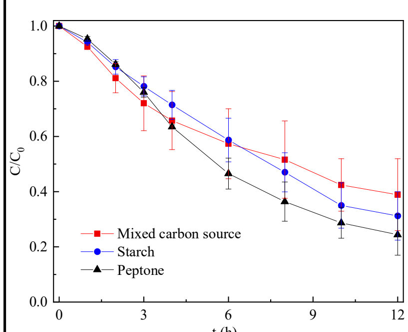
3.2 Color removal during hydrolysis/acidification

■ Effects of carbon source



Carbon source (COD=400 mg/L)	First order kinetics equation	Degradation rate(mg/(L•h))	COD removal efficiency (%)
Mixed carbon source	$y=e^{-0.085x}$	2.55	59.99
Peptone	$y=e^{-0.097x}$	2.91	63.64
Starch	$y=e^{-0.121x}$	3.63	44.01

- Degradation of RR2 was non-specific
- Degradation of RR2 fitted the first order kinetics equation
- When starch was used as carbon source, degradation rate was the fastest, followed by peptone and mixed carbon source

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3.2 Color removal during hydrolysis/acidification

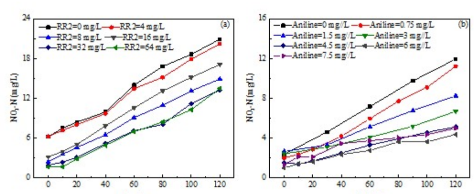
■ Effects of COD concentration and temperature

Temperature	COD (mg/L)	First order kinetics equation	Degradation rate (mg/(L•h))	COD removal efficiency (%)
25℃	800	$y=e^{-0.139x}$	4.17 ↑	57.46
	400	$y=e^{-0.085x}$	2.55	59.99
	200	$y=e^{-0.045x}$	1.35	57.86
35℃	800	$y=e^{-0.245x}$	7.35 ↑	45.05
	400	$y=e^{-0.205x}$	6.15	54.02
	200	$y=e^{-0.149x}$	4.47	26.31

- Degradation rate increased with increasing COD concentrations
- Degradation rate increased apparently with increasing temperature
- Temperature was the main factor affecting the azo dye degradation

3.3 Nitrogen removal during AO

■ Effects of RR2 and aniline on nitrification

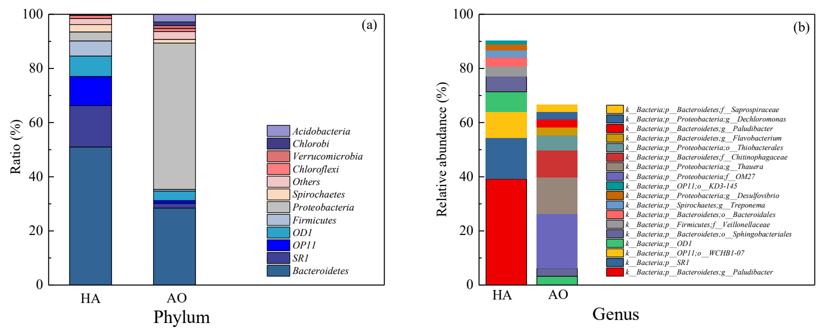


Aniline (mg/L)	NH_4-N	$R_{NH4\text{-}N}$ (mg/(gVSS·h))	NO_3-N	$R_{NO3\text{-}N}$ (mg/(gVSS·h))
0	y = -0.0763x + 27.41	1.38	y = 0.0784x + 3.41	1.42
0.75	y = -0.0852x + 27.03	1.31	y = 0.0978x + 1.88	1.51
1.5	y = -0.0541x + 28.19	0.98	y = 0.0542x + 2.66	0.98
3	y = -0.0507x + 28.66	0.92	y = 0.0415x + 2.37	0.75
4.5	y = -0.0478x + 27.24	0.74	y = 0.0415x + 1.54	0.64
6	y = -0.0345x + 26.71	0.53	y = 0.0345x + 1.39	0.53
7.5	y = -0.0371x + 28.65	0.57	y = 0.0356x + 2.18	0.55

- RR2 had no obvious effects on nitrification process
- Aniline could inhibit nitrification process
- When aniline reached 6 mg/L, nitrification was inhibited

3.4 Microbial community

■ Hydrolysis/acidification and AO



- **The dominant bacteria in hydrolysis/acidification: *Paludibacter*, *SR1*, *OP11* and *OD1***
- ***Desulfovibrio* (relative abundance: 2.23%) was mainly responsible for azo dye degradation (Xie et al., 2018)**
- **The dominant bacteria in AO: *Myxococcales*, *Thauera*, *Chitinophagaceae*, *Thiobacterales*, *OD1* and *Flavobacterium***
- ***Thauera* was a typical shortcut denitrifying bacteria (Fernandes et al., 2018)**

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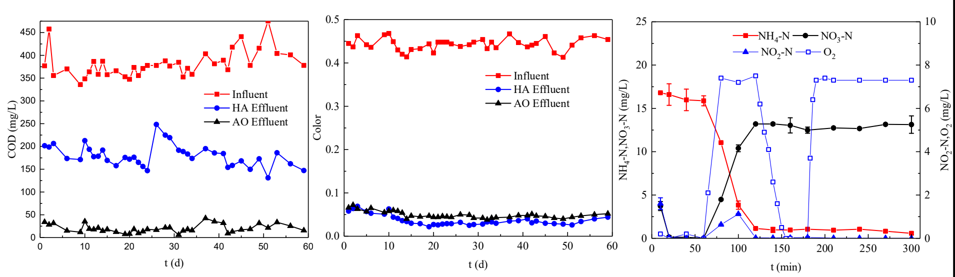
3.5 Hydrolysis/acidification-multiple AO process

■ System performance



	Influent (mg/L)	HA Effluent (mg/L)	AO Effluent (mg/L)	Removal efficiency (%)
COD	381.5±27.7	178.1±24.6	19.5±9.0	94.9
Color	0.442±0.014	0.033±0.008	0.047±0.005	89.4
NH_4-N	22.53±1.87	29.23±2.58	0.53±0.18	97.64
NO_2-N	1.79±0.94	0.01±0.00	0.02±0.01	98.89
NO_3-N	3.47±1.20	0.56±0.18	13.75±1.14	/

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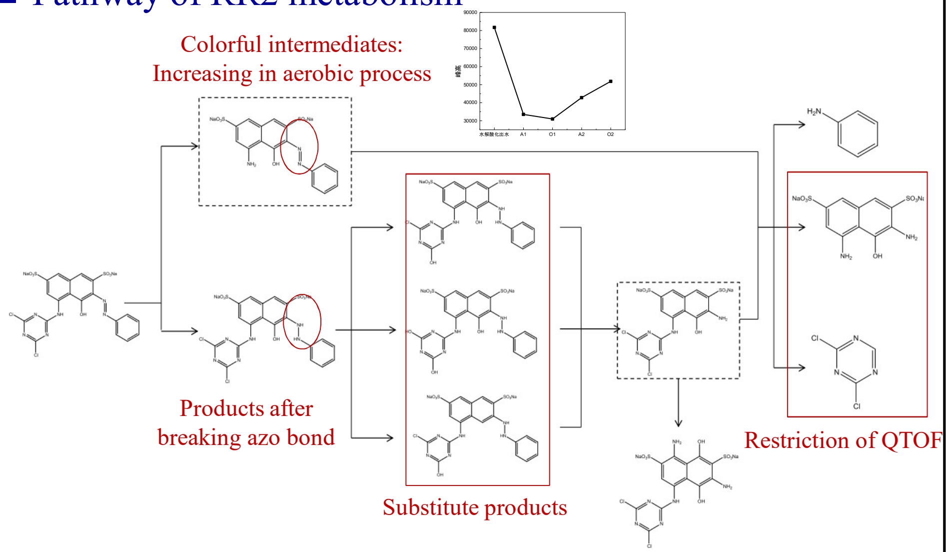
3.5 Hydrolysis/acidification-multiple AO process

■ Pathway of RR2 metabolism



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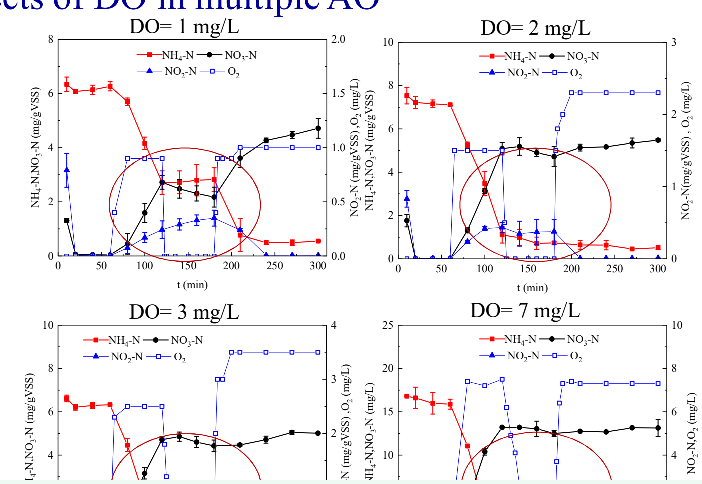
3.5 Hydrolysis/acidification-multiple AO process

■ Effects of DO in multiple AO



- Low DO could increase TIN removal efficiency
- Low DO could accumulate nitrite, inhibit activity of NOB

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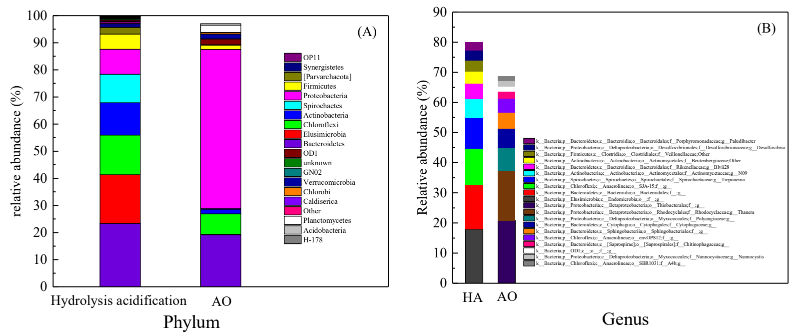
3.5 Hydrolysis/acidification-multiple AO process

■ Microbial community



- **The dominant bacteria in hydrolysis/acidification: *Elusimicrobia, Bacteroidetes , Chloroflexi***
- **The dominant bacteria in AO: *Thauera, Sphingobacteriales* (denitrifying bacteria) and *Nitrospira, Nitrosomonadaceae* (nitrifying bacteria)**

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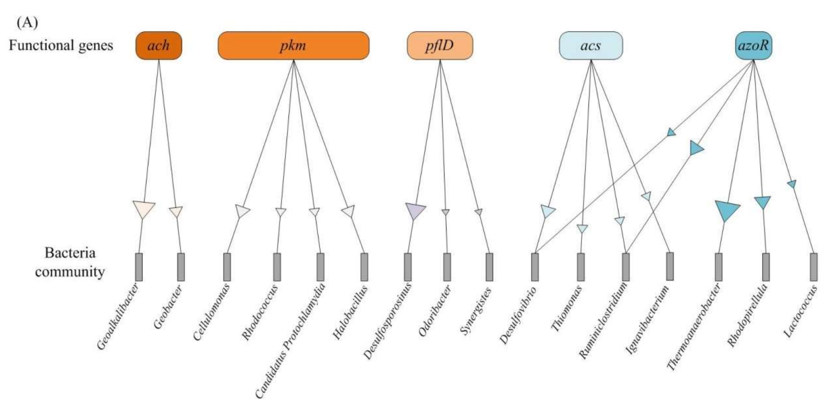
3.5 Hydrolysis/acidification-multiple AO process

■ Functional genes in hydrolysis/acidification



Desulfovibrio aminophilus, *Thermoanaerobacter*, *Lactococcus raffinolactis*, *Ruminiclostridium* and *Rhodopirellula* contained azoreductase, indicating that they had potential to degrade azo dye

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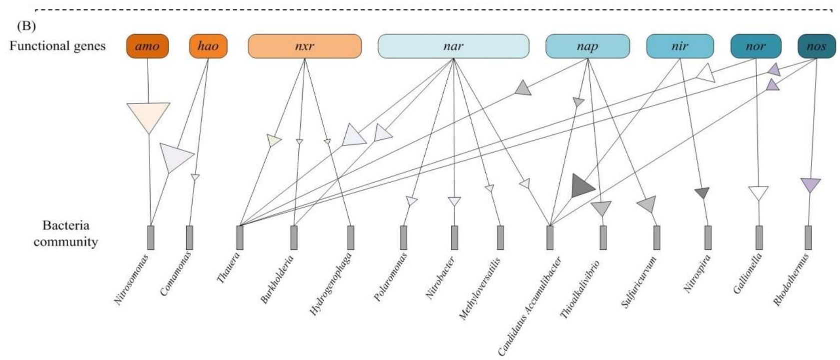
3.5 Hydrolysis/acidification-multiple AO process

- Functional genes in nitrogen metabolism



- Nitrification: *Nitrosomonas, Nitrosospira, Comamonas, Thauera*
- Denitrifictaion: *Thauera, Candidatus Accumulibacter*

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4. Conclusion

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4. Conclusion

- Hydrolysis/acidification-AO and hydrolysis/acidification-multiple AO process could treat dyeing wastewater efficiently
- The main factors affecting color removal were carbon source, COD concentration and temperature
- The main factors affecting nitrogen removal were azo dye, intermediates and DO
- The dominant bacteria for azo dye degradation were *Desulfovibrio aminophilus, Thermoanaerobacter, Lactococcus raffinolactis, Ruminiclostridium* and *Rhodopirellula*

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Thank you for your kind attention!

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