



## Enhanced primary treatment of low-concentration municipal wastewater by means of bio-flocculant Pullulan\*

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**Abstract:** Jar tests were conducted to investigate the performance of enhanced primary treatment processes for low-concentration municipal wastewater from South China by using composite flocculant combined with bio-flocculants Pullulan and poly-aluminum-chloride (PAC). The optimum dosage for composite flocculant and conditions for flocculation were determined. The experimental results indicated that composite flocculant had high efficiency for removing over 95% of turbidity, over 58% of COD<sub>Cr</sub> (chemical oxygen demand determined with potassium dichromate), over 91% of TP (total phosphate), and over 15% of NH<sub>3</sub>-N. Moreover, it could improve sludge settling and dehydration properties, and decrease the treatment cost.

**Key words:** Bio-flocculant, Pullulan, Enhanced primary treatment

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### INTRODUCTION

The concentration of municipal wastewater in South China is generally on the low side, so that the influent concentration is lower than the designed value in most two-stage wastewater treatment plants. Not only does it bring inconvenience to the operation management, but it also results in a huge waste of funds and resources (Shao, 1999). In fact, under some conditions, wastewater of intermediate and low concentration that goes through only primary treatment or enhanced primary treatment can meet the requirements of the discharge standard (State Environmental Protection Administration of China, 2002). Thus, a low-investment and low-energy-consumption technique devised for enhanced primary treatment of municipal wastewater is of much far-reaching practical significance to municipal wastewater treatment in South China.

Compared to traditional chemical flocculant,

Pullulan is an extracellular water-soluble microbial polysaccharide produced by strains of *Aureobasidium Pullulans*. With merits like innocuity, edibility, bio-degradability and non-pollution, it would become an excellent flocculant in wastewater treatment (Kang and Tang, 1996). Nowadays, the product developed by Kang Jianxiong of Huzhong University of Science and Technology (China) is comparable to the similar Japanese products in the market in terms of performance but at lower price. Meanwhile, other types of bioflocculants were also developed and their flocculation characters were studied in wastewater treatment field (Zhu *et al.*, 2004; Lu *et al.*, 2005; Fujita *et al.*, 2000; Gutzeit *et al.*, 2005; Boltz *et al.*, 2006). In view of the absence and the good prospect of enhanced primary treatment of municipal wastewater by means of bio-flocculant, experiments were carried out in this work through enhanced primary treatment of low-concentration municipal wastewater typical in South China (the influent from Wuhan Wastewater Treatment Plant), adopting composite flocculant combined with bio-flocculant Pullulan and poly-aluminum-chloride (PAC).

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## TEST CONDITIONS

### Wastewater samples

The raw wastewater was taken from the influent of Wuhan Wastewater Treatment Plant, with its quality shown as in Table 1.

**Table 1** Quality of raw wastewater

Parameter	Value	Parameter	Value
COD <sub>Cr</sub> (mg/L)	6~140	SS (mg/L)	60~100
BOD <sub>5</sub> (mg/L)	30~80	Turbidity (NTU)	24~96
NH <sub>3</sub> -N (mg/L)	7~11	pH	7.0~7.3
TP (mg/L)	15~29		

Note: COD<sub>Cr</sub>: Chemical oxygen demand determined with potassium dichromate; BOD<sub>5</sub>: Bio-chemical oxygen demand determined at 5 d; TP: Total phosphate; SS: Suspended solid

### Parameters and analytical methods

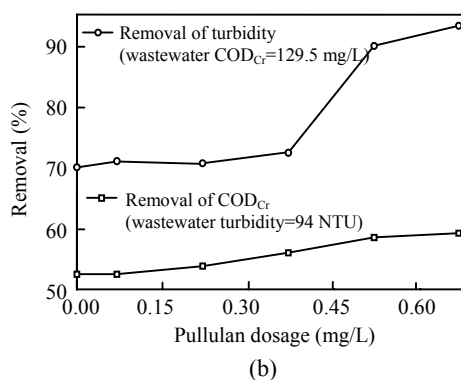
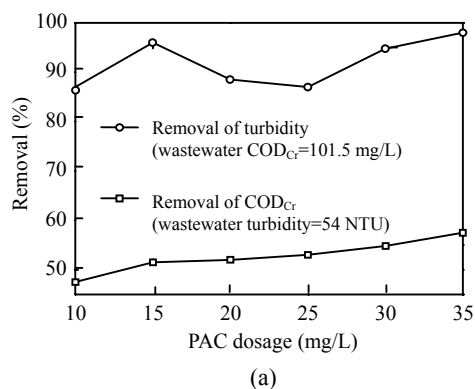
Turbidity was analyzed with 2100P photoelectric turbidity meter (Hach, USA), suspended solid (SS) with filtration method (State Environmental Protection Administration of China, 2002), NH<sub>3</sub>-N with Nessler's reagent colorimetric method (GB18918-2002), TP with ascorbimetry (GB18918-2002), BOD<sub>5</sub> with dilution and inoculation (GB18918-2002), water content of sludge with water determination index (GB18918-2002), COD<sub>Cr</sub> with potassium dichromate method (GB18918-2002), jar test with DBJ-621 variable speed stirrer (China). The dehydration test method: The sludge sample was taken out through vacuum filtration using a vacuum pump and Buchner funnel and the mud cake was not picked for test until it was completely dehydrated.

## RESULTS AND DISCUSSION

### Determination of optimum composite proportion

By means of jar tests, the optimum PAC dosage was determined first. Then while the PAC dosage was maintained, the optimum Pullulan dosage in the composite flocculant was decided. Conditions applied during the process were: rapid mixing stirring at velocity of 200 r/min; slow-speed reaction stirring velocity of 60 r/min; rapid mixing stirring time, 1 min; slow-speed reaction stirring time, 10 min. The composite ingredients and adding order were: Pullulan was added first and then stirred rapidly at

200 r/min for 1 min before PAC was added. Test results are shown in Fig.1.



**Fig.1** Results of optimum PAC (a) and Pullulan (b) dosage test

According to the varying trend of the removal of COD<sub>Cr</sub> along with increased PAC dosage (Fig.1a), the maximum PAC dosage was set at 15 mg/L.

While maintaining the PAC dosage at 15 mg/L, the removal efficiency of COD<sub>Cr</sub> increased with increasing of Pullulan dosage (Fig.1b). Once the Pullulan dosage reached 0.52 mg/L, the flocculent effect was remarkably improved, efficiency of removing turbidity and COD<sub>Cr</sub> increased 20% and 5.5% respectively compared to that without Pullulan. When Pullulan dosage exceeded 0.6 mg/L, the efficiency of removing turbidity and COD<sub>Cr</sub> did not remarkable rise along with the increase of Pullulan dosage. So the optimum Pullulan dosage was set at 0.6 mg/L.

To sum up, by using composite flocculant with the optimum Pullulan dosage and PAC dosage, the efficiency of removing turbidity and COD<sub>Cr</sub> is comparative to that when only more PAC was added

(30~40 mg/L). Therefore, the optimum composite proportion was determined to be 0.6 mg/L Pullulan+15 mg/L PAC.

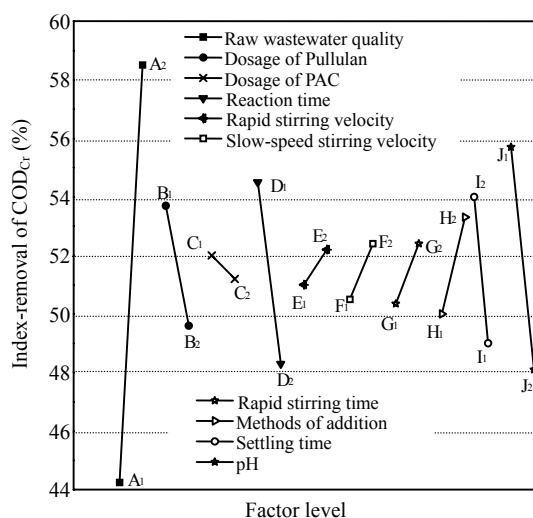
**Tests of influencing factors on performance of composite flocculant**

First, the single-factor method was used to examine the effects of adding methods of flocculant, pH, stirring methods, settling time, temperature, etc. on the flocculent efficiency. Then the single-factor level was optimized through orthogonal tests. Orthogonal test factor levels are given in Table 2, and the relationship between factors and indexes are illustrated in Fig.2.

**Table 2 Orthogonal test factor level**

Factor	Mark	Level 1	Level 2
Influent quality	A	A <sub>1</sub>	A <sub>2</sub>
Pullulan dosage (mg/L)	B	0.5	0.6
PAC dosage (mg/L)	C	10	15
Reaction time (min)	D	10	15
Rapid mixing stirring speed (r/min)	E	200	250
Slow-speed mixing stirring speed (r/min)	F	40	60
Rapid mixing stirring time (min)	G	0.5	1.0
Methods of addition	H	Pullulan first	Simultaneously
Settling time (min)	I	30	45
pH	J	7.0	8.5

Note: COD<sub>Cr</sub> concentrations of A<sub>1</sub> and A<sub>2</sub> water samples were 77.42 mg/L (A<sub>1</sub>) and 81.11 mg/L (A<sub>2</sub>) respectively



**Fig.2 Relationship between factors and indexes in optimum flocculent condition optimization test**

According to Fig.2, it can be concluded through range analysis. Factors can be put ordered according to the extent of the effects on flocculent efficiency: raw wastewater quality>pH>reaction time>settling time>Pullulan dosage>method of addition>rapid mixing stirring time>slow-speed mixing stirring velocity>rapid mixing stirring velocity>PAC dosage. The most significant factors impacting flocculent effect were raw wastewater quality and pH.

According to the low concentration (COD<sub>Cr</sub> being 80 mg/L) and quality fluctuation of the raw wastewater, the optimum PAC level was maintained at 15 mg/L. Moreover, the optimum flocculent condition of composite flocculant is determined as follows:

(1) The optimum pH was neutral for municipal wastewater, pH need not be adjusted; flocculent effect does not have a lot to do with temperature; the optimum composite proportion was 0.6 mg/L Pullulan+15 mg/L PAC.

(2) The optimized flocculent conditions were: Pullulan and PAC were added simultaneously into water samples. Then the mixture was stirred at 250 r/min for 1 min and reduced to 60 r/min for 10 min. The corresponding *G* (velocity gradient) value was 23 s<sup>-1</sup>, *GT* (camp numbers: velocity gradient by the time taken for flocculation) was 1.4×10<sup>4</sup>, and the optimum settling time was 30 min.

**Effects of raw wastewater quality on flocculent**

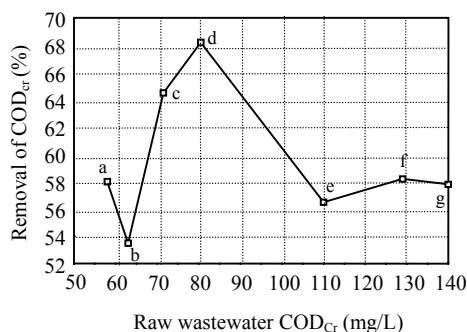
Under the optimum composite and flocculent conditions, the effects of the changes in COD<sub>Cr</sub> of the raw wastewater on flocculation are shown in Fig.3.

It can be found in Fig.3 that composite flocculant has rather strong adaptability to the change of municipal wastewater quality. As the raw wastewater COD<sub>Cr</sub> value varied from 58 mg/L to 140 mg/L, the COD<sub>Cr</sub> removal efficiency remained at 52%, regardless of a certain range of fluctuation. And the average effluent quality is better than the First Level Standard of National Integrated Wastewater Discharge (State Environmental Protection Administration of China, 2002).

**Nitrogen and phosphorus removal efficiency of composite flocculant**

According to the best composite proportion and flocculent conditions, jar tests were carried out for the

determination of  $\text{NH}_3\text{-N}$  and TP of supernatant, etc. The results are shown in Table 3.



**Fig.3 Tests of the influence of raw wastewater quality on flocculent**

Dosage: 0.6 mg/L Pullulan+15 mg/L PAC

**Table 3 Test results of nitrogen and phosphorus removal efficiency of the composite flocculant**

Parameter	$\text{NH}_3\text{-N}$	TP
Influent concentration (mg/L)	10.70	29.28
Effluent concentration (mg/L)	9.08	2.73
Removal efficiency (%)	15.06	90.70

Table 3 indicates that the composite flocculant had remarkably high removal efficiency of phosphorus under the optimum flocculent conditions, with the TP and  $\text{NH}_3\text{-N}$  removal efficiencies being at 91% and 15% respectively.

### Tests of characteristics of composite flocculant settled sludge

For characterization, a graduated cylinder was used to collect settled sludge, and to observe and record the size of sludge at different times. Then vacuum filtration test was carried out on sludge that has settled for 30 min on sludge specific resistance determinator. In the end, water determinator and analytical balance were used to determine the water content of the sludge sediment before and after the vacuum filtration. The results are shown in Tables 4 and 5.

**Table 4 Test results of composite flocculant settled sludge quantity**

Settling time (min)	Sludge volume (ml)	Volume ratio of sludge quantity to wastewater (%)
0	40~50	5.00~6.25
15	30~35	3.750~4.375
30	20~25	2.500~3.125
60	15~18	1.875~2.250

**Table 5 Test results of water content of composite flocculant settled sludge**

Sludge sample	Water content (%)
Settled sludge	99.4~99.5
Sludge before vacuum filtration	99.1~99.3
Sludge after vacuum filtration	75.13~76.10

According to Table 4, the flocculent settling did not yield much sludge, which was 5%~6% of the volume of the wastewater approximately. Furthermore, the settled sludge thickened readily by gravity, so it took only 30~60 min for the sludge volume to be reduced to 1/3 of the initial volume without any flocculant being added, which showed the high thickening efficiency.

Table 5 shows that the settled sludge had a rather high water content of 99.4%, mainly due to the low concentration of suspended solids in the wastewater. Before and after the vacuum filtration, the water content of sludge decreased about 24%, and that of the mud cake reduced to about 75%. To some extent, it implied that the dehydration performance of settled sludge was better than that of the normal "aluminum sludge". According to related researches (Russell and George, 1986), the "aluminum sludge" produced by flocculant like alum, was difficult to dehydrate during vacuum dehydration, with the water content of the dehydrated mud cake generally being 80%~90%.

### CONCLUSION

(1) Under the optimum flocculent conditions, composite flocculant enhanced primary treatment with high efficiency. In most cases, the discharged water quality was better than the national first-level standard for integrated wastewater discharge. Sludge settled and dehydrated readily with low sludge production.

(2) Due to low concentration of municipal wastewater in South China, this process not only had better disposal efficiency than the normal two-stage wastewater treatment process, but also had advantages such as low investment and treatment costs and good ability to resist the shock of loading rate. Therefore, it can be considered as an efficient wastewater treatment technology.

(3) Replacing bio-flocculant with inorganic

floculant improves the chemical characteristics of sludge, resulting in harmless and diverse treatment and disposal of sludge.

## References

- Boltz, J.P., La, M., Enrique, J., Madrigal, J.A., 2006. The role of bioflocculation on suspended solids and particulate COD removal in the trickling filter process. *Journal of Environmental Engineering*, **132**(5):506-513. [doi:10.1061/(ASCE)0733-9372(2006)132:5(506)]
- Fujita, M., Ike, M., Tachibana, S., Kitada, G., Kim, S.M., Inoue, Z., 2000. Characterization of a bioflocculant produced by *Citrobacter* sp. TKF04 from acetic and propionic acids. *Journal of Bioscience and Bioengineering*, **89**(1):40-46. [doi:10.1016/S1389-1723(00)88048-2]
- Gutzeit, G., Lorch, D., Weber, A., Engeis, M., Neis, U., 2005. Bioflocculent algal-bacterial biomass improves low-cost wastewater treatment. *Water Science and Technology*, **52**(12):9-18.
- Kang, J.X., Tang, Y.Z., 1996. Research on Aureobasidium Pullulans flocculant. *Applicable Technological Market*, **12**:3-5 (in Chinese).
- Lu, W.Y., Zhang, T., Zhang, D.Y., Li, C.H., Wen, J.P., Du, L.X., 2005. A novel bioflocculant produced by *Enterobacter aerogenes* and this use in defecating the trona suspension. *Biochemical Engineering Journal*, **27**(1):1-7. [doi:10.1016/j.bej.2005.04.026]
- Russell, L.C., George, M.W., 1986. Handbook of Advanced Wastewater Treatment. Translated by Zhang, Z.H., China Construction Industry Press, Beijing, p.281-284 (in Chinese).
- Shao, L.G., 1999. Operation of urban WTP in South China. *Water and Wastewater Engineering*, **25**(2):11-13 (in Chinese).
- State Environmental Protection Administration of China, 2002. Discharge Standard of Pollution for Municipal Wastewater Treatment Plant (GB18918-2002). China Environmental Science Press, Beijing, p.5-11 (in Chinese).
- Zhu, Y.B., Feng, M., Yang, J.X., Ma, F., Wu, B., Li, S.G., Huang, J.L., 2004. Screening of complex bioflocculant producing bacterium and their flocculating mechanism. *Journal of Harbin Institute of Technology*, **36**(6):759-762 (in Chinese).



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