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Hydrolytic acidification via rumen microorganisms and aerobic MBR to reduce contaminants in pulping midcourse wastewater

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ABSTRACT

Experiments on microbial degradation with hydrolytic acidification–aerobic (membrane bioreactor) MBR process were conducted to treat the pulping midcourse wastewater (PMW) with chemical oxygen demand (COD) concentration of 1,182 mg/L, chromaticity of 327 PCU, and TSS concentration of 153 mg/L. Rumen micro-organisms (RM) were used in the hydrolytic acidification process. The experimental results demonstrated that the hydrolytic–aerobic process could raise the biodegradability of the PMW, the VFA concentration could reach 200 mg/L, and the acidification rate was 24%; the effluent COD could reach 96 mg/L, the chromaticity 80 PCU, and the TSS 15 mg/L. These results suggested that hydrolytic acidification via RM and aerobic MBR could be a promising way for effective disposal of puling midcourse wastewater.

Keywords: Pulping midcourse wastewater; Hydrolytic acidification; Reduce contaminants; Rumen micro-organisms; Aerobic MBR

1. Introduction

Wastewater from pulp and paper mills constitutes a major source of aquatic pollution since it contains high organic substances causing high biochemical oxygen demand (BOD) and chemical oxygen demand (COD), extractives (resin acids), chlorinated organics (measured as adsorbable organic halides), suspended solids, metals, fatty acids, tannins, lignin and its derivatives, etc. [1,2]. The wastewater generated from different production sections, lead to different compositions and quantities of contaminants. The pulping midcourse wastewater (PMW) comes from the process of pulp washing and bleaching [3]. It is a major source of pollution that contains high concentrations of inorganic and organic matters and is highly colored [4]. It was reported that PMW is toxic to aquatic organisms and causes heavily death of fish [5–7]. Therefore, a new approach in wastewater treatment should be developed to face more stringent environmental regulations on the quality of the effluents entering receiving waters.

Many studies have been carried out on the treatment of PMW by biological methods such as, conventional aerobic and anaerobic treatment methods [8–12]. Recently, the traditional processes of "hydrolytic acidification and aerobic contact oxidation" have been extensively applied to wastewater treatment [13–15].

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However, the equipment used for this process not only occupies a large area, but also its effluents are tough to achieve the treatment requirement. Therefore, in the present paper, a new process for PMW treatment is put forward, via. a hydrolytic acidification and immersed MBR system.

The effective degradation of lignocellulosic materials is the key process for these biological treatments. Rumen ecosystem consists mostly of obligate anaerobic micro-organisms such as anaerobic bacteria, fungi, protozoa, methanogenic archaea, and methane-forming bacteria from the genus Methanobrevibacter [16]. The mixed rumen micro-organisms (RM) contain complete enzyme components and high enzyme activities for the degradation of cellulosic materials [17]. The rumen features a dense, active, and stable microbial community that carries out rapid hydrolysis and fermentation of almost all of the biomass components [18]. It shows that they are the primary colonizers of fibrous plant materials in the rumen and are able to degrade lignin-containing plant cell walls [19,20]. The potential application of rumen cultures for anaerobic digestion of lignocellulosic materials has been investigated [21]. The work to search for the optimal operating parameters for a high degradation efficiency and VFA yield has been reported [22,23]. Recently, culture resources and RM were applied to degrade lignocellulosic materials [24,25]. The results showed that RMs are superior over other microbes for the degradation of lignocellulosic materials, which were attributed to higher cellulolytic activities [24].

In this paper, PMW was treated by RM in hydrolytic acidification system. Studies on the application of RM in PMW treatment are rare. Therefore, RM in PMW was investigated with emphasis on the hydrolytic acidification of pollutants in this paper. Meanwhile, stable efficacy was obtained in the present process, and the quality of the effluents completely conformed to the first grade discharge standard of pulp and papermaking industrial pollutants.

2. Materials and methods

2.1. Feed water and rumen bacteria

The wastewater was collected from the midcourse wastewater treatment plant equalization tank of a paper mill in Liaoning, China. The composition of PMW is shown in Table 1.

The rumen fluids were taken from Dalian Bangchuidao Meat-packing Plant. The samples were strained through a fourfold muslin cloth and the vials with rumen fluid were purged with N_2 gas. The strained liquid was centrifuged at low speed (125G) in a Servali SS-1 centrifuge for 5 min, to remove as much as non-bacterial matter as possible [25]. The supernatant liquid was the RM and its characteristics are shown in Table 2.

Table 1
Physical and chemical characteristics of PMW used in this study

Parameters	Values
$SCOD_{Cr}$ (mg/L)	1,182
BOD_5 (mg/L)	398
Chromaticity (PCU)	327
Turbidity (NTU)	26.8
pH	10.36
TSS (mg/L)	153
T.N (mg/L)	1.2
T.P (mg/L)	–

Note: BOD means biological oxygen demand; T.N means total nitrogen; T.P means total phosphorus.

2.2. Experimentals

The test unit made of glass is shown in Fig. 1, it comprised of a hydrolytic acidification bioreactor (5), aerobic bioreactor (9), and a hollow fiber membrane module section in the aerobic reactor. A heater band was twined around the anaerobic reactor and used to heat the anaerobic reactor.

Operation manner of this trial was a continuous and dynamic treatment, and its water flow rate was 0.37 L/h. Influents were pumped into the anaerobic reactor from the influent tank where, the pH was adjusted to 7.0. Wastewater after hydrolytic acidification entered the biological treatment units of MBR with a perforated tube for aeration at the bottom. The module intercepted micro-organisms and several macromolecular substances. Permeated liquids were discharged as the final effluents of the process. The characteristics of the membrane module are shown in Table 3.

2.3. Analytical methods

Determination of COD, BOD, TN, TP, Chromaticity, Turbidity, mixed liquor suspended solids (MLSS),

Table 2
Physical and chemical characteristics of the RM

Parameters	Values
Reducing sugar (g/L)	0.3130
pH	7.2
MLSS (mg/L)	15,083
MLVSS (mg/L)	7,270

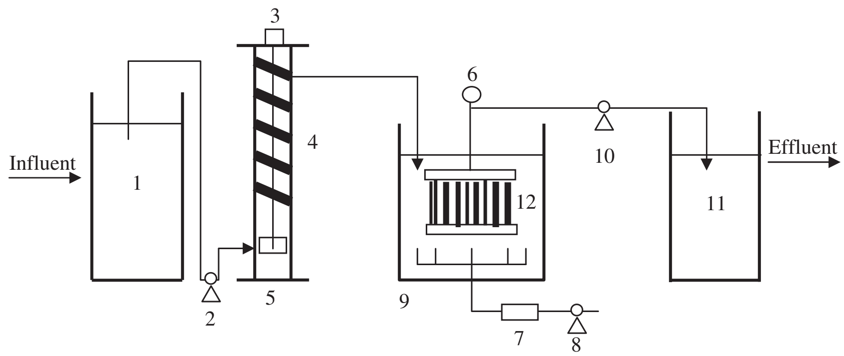

Fig. 1. Flow chart of the test unit: (1), (11) tank, (2), (10) submerged pump, (3) stir, (4) heater band, (5) hydrolytic acidification bioreactor, (6) vaccum meter, (7) flowmeter, (8) air pump, (9) aerobic bioreactor, and (12) hollow fiber membrane module.

Table 3
Characteristics of the membrane module

Parameters	Values
Manufacturer	Mitsubishi
Material	Polyvinylidene
Mean pore size (nm)	20
Filaments length (cm)	40
Filaments OD (mm)	20
Filaments ID (mm)	3
Filter area (m^2)	2.2

and mixed liquor volatile suspended solids (MLVSS) was carried out according to the standard analytical procedures as described in Standard Methods [26]. Determination of reducing sugar was by the DNS method. pH values were determined by a pH meter (Model 20, Denver instruments Ltd.). Liquid samples of 25 mL taken from the hydrolytic acidification bioreactor were centrifuged at 10,000 rpm for 15 min, and the supernatant was passed through a 0.45 μm membrane filter for the analysis of soluble COD (SCOD) and VFA. VFA was determined by gas chromatography (GC-2010, Shimadzu Inc., Japan) equipped with a flame ionization detector and a 30 m × 0.1 μm × 0.53 mm HP–FFAP column. The oven temperature was initially at 70˚C for 3 min, followed by a ramp-up of 20˚C/min for 6 min and held at a final temperature of 180˚C for 3 min. Nitrogen was used as a carrier gas with a flow rate of 1 mL/min.

3. Results and discussion

3.1. The hydrolytic acidification experiment

The RM was used to fill the hydrolytic acidification bioreactor. The influent of the hydrolytic bioreactor

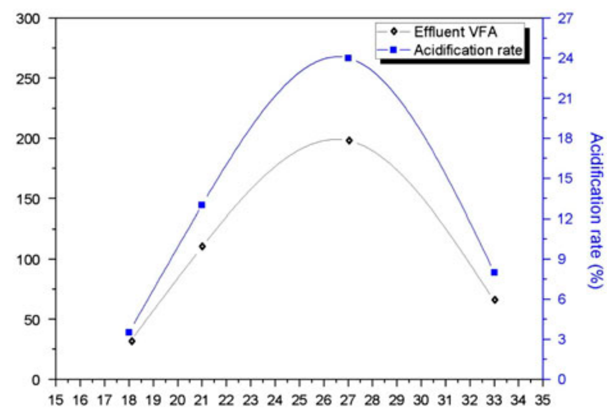

Fig. 2. The VFA concentration and the acidification rate of the influent in the hydrolytic acidification process.

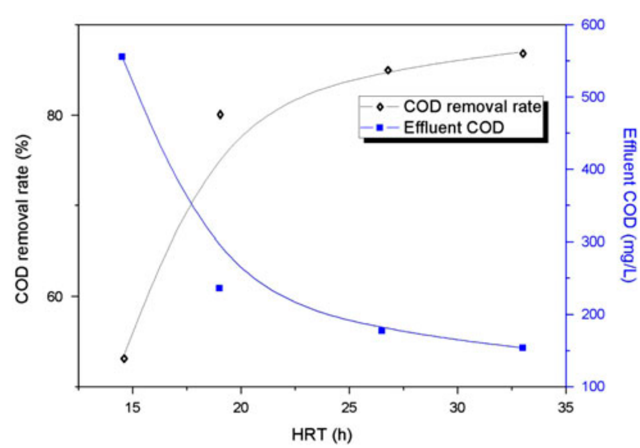

Fig. 3. The COD removal rate of influent in the aerobic process.

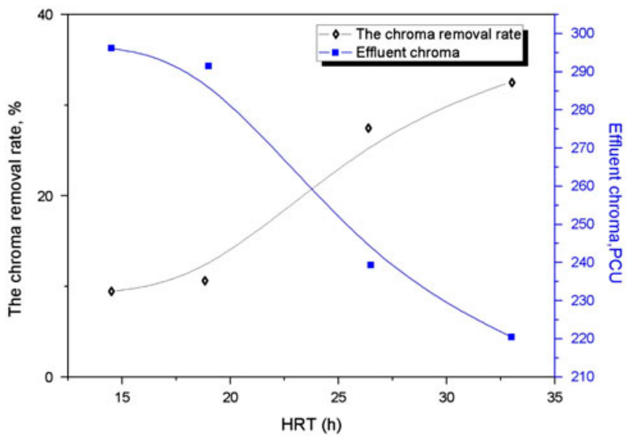

Fig. 4. The chromaticity removal rate of the influent in the aerobic process.

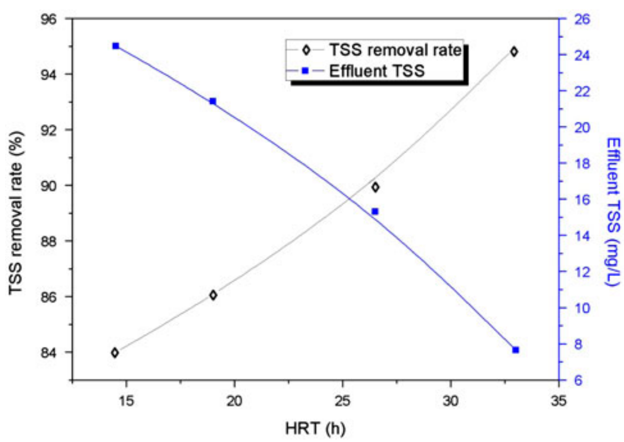

Fig. 5. The TSS removal rate of the influent in the aerobic process.

was upflow. The hydraulic retention times (HRT) were 18, 21, 27, and 33 h. The effluent quality of anaerobic hydrolysis is shown in Fig. 2

Judging from the quality determination of the influent, the nitrogen and phosphorus nutrients were not sufficient, so sufficient nitrogen and phosphorus must be added to all of the influent water used for the biochemical experiments. After a prolonged anaerobic hydrolytic process, the VFA concentration in the wastewater changed evidently. The HRT were 18, 21, 27, and 33 h, respectively, the effluent VFA was about 30 mg/L when the HRT was 18 h and the acidification rate was about 3.5%; the effluent VFA was about 110 mg/L when the HRT was 21 h and the acidification rate was about 13%; the effluent VFA was about 200 mg/L when the HRT was 27 h and the acidification rate was about 24%; the effluent VFA was about 64 mg/L when the HRT was 33 h and the acidification rate was about 8%. The experimental results indicated that the HRT was the main controlling parameter in the anaerobic hydrolytic reaction, and the prolonged HRT of anaerobic hydrolytic reaction was effective to improve the VFA production, but continued prolongation of the HRT led to a decline in the VFA production.

The main organic materials in the PMW were cellulose, hemicellulose, and lignin [27]. The cellulose and hemicellulose were easily utilized by the rumen micro-orgnisms and were converted to VFA, but the lignin was only easy to solubilize [28]. In the present work, the highest acidification rate was about 24%, the low acidification rate suggesting that the soluble lignin in the wastewater couldn't be converted to the VFA, efficiently.

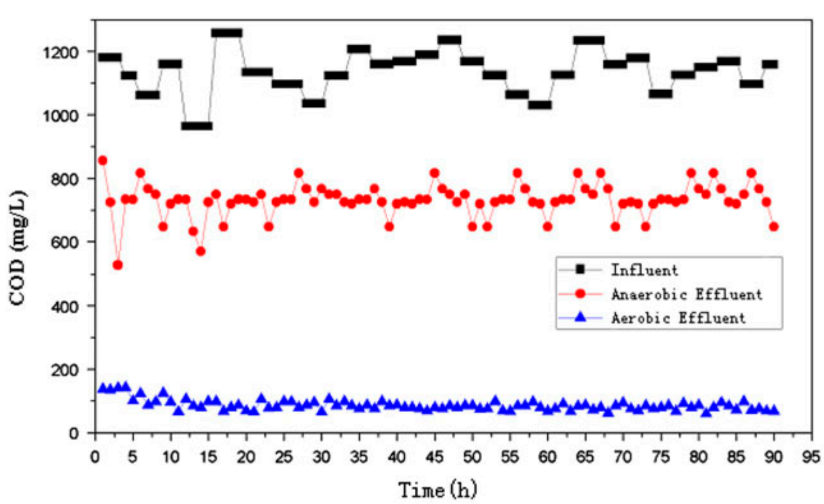

Fig. 6. COD characteristic curve during steady-stage.

3.2. The aerobic MBR experiment of influent

The aerobic experiment was operated in a 12 L bioreactor. The HRT of the aerobic experiment were 14.5, 19, 26.5, and 33 h respectively, and the experimental results are shown in Figs. 3–5.

When treated with aerobic process for four kinds of HRT: 14.5, 19, 26.5, and 33 h, the effluent quality differed greatly, the effluent COD was 563–152 mg/L; the effluent chromaticity was 221–295 PCU, and the removal rate was low. This was mainly because the chromophoric group was difficult to degrade, and this result was in good agreement with the results of Milestone [29]. When the HRT time increased from 14.5 to 33 h, the effluent quality improved, especially the COD removal rate. The TSS in the effluent was low and did not change too much, mainly due to the effects of the filtration of the membrane, which was consistent with the results from Lerner and Zhang's work [30,31].

3.3. The acidification hydrolytic + aerobic MBR experiment

The acidification hydrolytic reactor and aerobic MBR reactors were operated at 27 and 33 h HRT, respectively for 3 months to obtain steady-state performance data. Fig. 6.

During the steady-stage, the COD of the anaerobic hydrolytic effluent was about 720 mg/L, the COD removal rate was about 39%; the COD of the aerobic effluent was about 96 mg/L, the COD removal rate was about 92%.

4. Conclusion

In this paper, the hydrolytic acidification process via RM could transform the big-molecule organics in the pulping midcourse wastewater into the biodegradable small-molecules. After the anaerobic acidification primary treatment, the amount of organic contaminants in wastewater decreased, and it created beneficial conditions for subsequent aerobic treatment.

Using aerobic MBR process to treat the PMW, when the HRT was longer than 33 h, little improvement on the effluent quality was found. After the anaerobic hydrolytic process for 27 h and aerobic process for 33 h to the PMW, the effluent COD fell to 96 mg/L, with the removal rate of about 92%, the effluent chromaticity decreased from 327 to 76, with the removal rate of about 76%, the effluent TSS decreased from 153 to 15, with the removal rate about 90%.

These results suggest that hydrolytic acidification via RM and aerobic MBR could be a promising way for effective disposal of pulping midcourse wastewater.

References

[1] M. Ali, T.R. Sreekrishnan, Aquatic toxicity from pulp and paper mill effluents: A review, Adv. Environ. Res. 5 (2001) 175–196.

[2] S. Lacorte, A. Latorre, D. Barceló, A. Rigol, A. Malmqvist, T. Welander, Organic compound in paper-mill process waters and effluents, Trends Anal. Chem. 22 (2003) 725–737.

[3] M. Mänttäri, K. Viitikko, M. Nyström, Nanofiltration of biologically treated effluents from the pulp and paper industry, J. Membr. Sci. 272 (2006) 152–160.

[4] N. Li, F.L. Yang, W.R. Jin, Anaerobic degradation of pulping midcourse wastewater by rumen microorganisms in batch reactor, Desalin. Water Treat. 53 (2015) 36–40.

[5] K.R. Munkttrick, M.R. Servos, J.H. Carey, G.J. Van Der Kraak, Environmental impact of pulp and paper wastewater: Evidence for a reduction in environmental effects of North American pulp mills since 1992, Water Sci. Technol. 35 (1997) 329–338.

[6] S. Young, D.W. Smith, Effect of pulp mill chemicals on flocculation in river water, Water Sci. Technol. Water Suppl. 1 (2001) 251–258.

[7] T. Rana, S. Gupta, D. Kumar, S. Sharma, M. Rana, V.S. Rathore, B.M.J. Pereira, Toxic effects of pulp and paper-mill effluents on male reproductive organs and some systemic parameters in rats, Environ. Toxicol. Pharm. 18 (2004) 1–7.

[8] R. Skogman, R. Lammi, The efficiency of a biological activated sludge treatment plant with extended system, Water Sci. Technol. 20 (1988) 65–72.

[9] J. Rintala, J.L.S. Martin, G. Lettinga, Thermophilic anaerobic treatment of sulphate rich pulp and paper integrate process water, Water Sci. Technol. 24 (1991) 149–160.

[10] J.A. Rintala, J.A. Puhakka, Anaerobic treatment in pulp and paper-mill waste management: A review, Bioresour. Technol. 47 (1994) 1–18.

[11] H.Q. Yu, G.W. Gu, Treatment of phenolic wastewaters by sequencing batch reactors with aerated and unaerated fills, Waste Manage. 16 (1996) 561–566.

[12] E. Dalentoft, P. Thulin, The use of aerobic selectors in activated sludge systems for treatment of wastewater from the pulp and paper industry, Water Sci. Technol. 35 (1997) 181–188.

[13] X.L. Shi, F.M. Li, H.Y. Hu, Application of hydrolytic acidification-aerobic biological treatment-Fenton process in puling and papermaking wastewater treatment, Water & Wastewater Eng. 38 (2012) 47–51.

[14] Y. Wang, J.Q. Wan, Y.W. Ma, Hydrolytic acidification-aerobic process treatment of the effluent from papermaking with OCC as raw material, China Pulp Pap. 24 (2005) 14–17.

[15] Z.M. Wu, L. Zhang, Treatment of regenerated papermaking wastewater by high-efficiency air floating-hydrolysis-aerobic process, Technol. Water Treat. 35 (2009) 104–106.

[16] T.L. Miller, M.J. Wolin, Inhibition of growth of methane-producing bacteria of the ruminant forestomach by hydroxymethylglutaryl-scoa reductase inhibitors, J. Dairy Sci. 84 (2001) 1445–1448.

[17] Z.H. Hu, G. Wang, H.Q. Yu, Anaerobic degradation of cellulose by rumen microorganisms at various pH values, Biochem. Eng. J. 21 (2004) 59–62.

[18] P.J. Weimer, J.B. Russell, R.E. Muck, Lessons from the cow: What the ruminant animal can teach us about consolidated bioprocessing of cellulosic biomass, Bioresour. Technol. 100 (2009) 5323–5331.
[19] T. Bauchop, Rumen anaerobic fungi of cattle and sheep, Appl. Environ. Microbiol. 38 (1979) 148–158.
[20] D.E. Akin, W.S. Borneman, Role of rumen fungi in fiber degradation, J. Dairy Sci. 73 (1990) 3023–3032.
[21] H.J. Gijzen, K.B. Zwart, F.J.M. Verhagen, G.D. Vogels, Highrate two-phase process for the anaerobic degradation of cellulose, employing rumen microorganisms for an efficient acidogenesis, Biotechnol. Bioeng. 31 (1988) 418–425.
[22] Z.B. Yue, H.Q. Yu, H. Harad, Y.L. Yu, Optimization of anaerobic acidogenesis of an aquatic plant, *Canna indica* L., by rumen cultures, Water Res. 41 (2007) 2361–2370.
[23] Z.H. Hu, G. Wang, H.Q. Yu, Anaerobic degradation of cellulose by rumen microorganisms at various pH values. Biochem. Eng. J. 21 (2004) 59–62.
[24] H.J. Gijzen, P.J.L. Derikx, G.D. Vogels, Application of rumen microorganisms for a high rate anaerobic digestions of papermill sludge, Biol. Wastes 32 (1990) 169–179.
[25] H.J.M. Camp, F.J.M. Verhagen, A.K. Kivaisi, F.E. Windt, H.J. Lubberding, H.J. Gijzen, G.D. Vogels, Effects of lignin on the anaerobic degradation of cellulosic wastes by rumen microor-ganisms, Appl. Microbiol. Biotechnol. 29 (1988) 408–412.
[26] M.A.H. Franson, Physical and aggregate properties, in: Standard methods for the examination of water and wastewater, Port City Publications, Baltimore, MD, 2005, pp. 174–195.
[27] B.Y. Liu, Pollution control of pulp and papermaking industry, China Light Industry Publication, Beijing, 2009.
[28] Z.H. Hu, S.Y. Liu, Z.B. Yue, L.F. Yan, M.T. Yang, H.Q. Yu, Microscale analysis of in vitro anaerobic degradation of lignocellulosic wastes by rumen microorganisms, Environ. Sci. Technol. 42 (2008) 276–281.
[29] C.B. Milestone, T.R. Stuthridge, R.R. Fulthorpe, Role of high molecular mass organics in colour formation during biological treatment of pulp and paper wastewater, Water Sci. Technol. 55 (2007) 191–198.
[30] M. Lerner, N. Stahl, N.I. Galil, Comparative study of MBR and activated sludge in the treatment of paper mill wastewater, Water Sci. Technol. 55 (2007) 23–29.
[31] Y.Z. Zhang, C.M. Ma, F. Ye, Y. Kong, H. Li, The treatment of wastewater of paper mill with integrated membrane process, Desalination 236 (2009) 346–359.