



## Biological pretreatment of tannery wastewater using a full-scale hydrolysis acidification system



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### ABSTRACT

To evaluate the performance of hydrolysis acidification (HA) system on the tannery wastewater treatment in a cold region, the effects of COD, SS, sulphides concentration and the low temperature on tannery wastewater treatment were investigated in a 5000 m<sup>3</sup>/d full-scale HA reactor. The results showed that the removal ratios of COD and SS were in the range of 20%–45% and 65%–82%, respectively. The average BOD/COD of the tannery wastewater was improved from 0.38 to 0.56, and the pH decreased from 8.4 to 7.6 after the HA treatment. The concentration of sludge and COD in the bottom of the HA reactor was significantly higher than those of the top region. The thickness sludge layer shortened the required hydraulic retention time and improved the SS removal efficiency. When the temperature of HA reactor dropped below 8 °C, the COD removal ratio decreased to less than 10%. However, the SS removal ratio was not obviously impacted. The results obtained from this study indicated that the HA system provided an effective biological pre-treatment of the tannery wastewater for organic loading reduction and biodegradability improvement, even in a cold season.

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## 1. Introduction

Tannery wastewater produced from the leather industry is a potential pollution source due to its high concentration of organic matters, nitrogen, suspended solids (SS) and specific pollutants, e.g., sulphides and chromium (Wiemann et al., 1998; Song et al., 2000; Suthanthararajan et al., 2004). An effective treatment process was required to reduce the effects of water pollution from the tannery industry on the environment (Song et al., 2001; Cotman et al., 2004; Calheiros et al., 2007). Sulphides in tannery wastewater were toxic substances for the methanogenic bacteria in anaerobic systems. For wastewater with high organics concentration, aerobic systems had difficulty in achieving the discharge

standard, independently. Furthermore, temperature, pH, COD and SS concentration of the tannery wastewater varied significantly with the tanning procedure. Therefore, a pre-treatment process with anti-shock loading capability was necessary to reduce organic loading for the subsequent aerobic process (Iaconi et al., 2003; Elsheikh, 2009; Mahmoud et al., 2011).

Hydrolysis acidification (HA) has been a widely used bioprocess prior to the anaerobic system (Chen et al., 2007; Ahmed and Mogens, 2008; Leal et al., 2006). The HA process as a biological pre-treatment could not only reduce the organic concentration and improve the biodegradability but also avoid the inhibiting issue of the sulphides on the methanogenic process (Genschow et al., 1996). Moreover, this process was a low-cost process and did not require aeration or temperature control. Therefore, the HA process seemed to be a potential pre-treatment approach for the tannery wastewater prior to the aerobic system. Although the treatment effect of the HA process on slaughterhouse, pharmaceutical and tannery wastewater have been evaluated in the lab-scale reactor at room temperature, the performance of the full-scale HA system on the

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tannery wastewater treatment has not been reported (Cokgor et al., 2008; Masse et al., 2011). The treatment efficiency usually appeared to have a significant difference between the lab-scale reactor and the full-scale system even at the same water quality condition. This could be related to the spatial difference of the hydraulic and mass transfer condition in the full-scale system. Thus, it is more meaningful to assess the treatment effect of the tannery wastewater in the full-scale HA system than that in the lab-scale reactor.

The effect of water quality variation and low temperature on the operational stability of the HA system was an important issue in actual operation. On the one hand, the wastewater characteristics changed significantly with time in practical tannery production, e.g., pH, COD, SS, sulphides and temperature. The variation of these parameters was generally considered to potentially impact the organic removal efficiency in the HA system. The variation of COD, SS, sulphides and pH might impact the stability of the biological ecosystem in the reactor. Thus, the buffering capacity of the HA system to these variations was important in practical application. Moreover, as a pre-treatment process, the effluent quality of the HA reactor was required to be appropriate for the subsequent aerobic process. On the other hand, the low temperature was commonly observed in the water treatment system in cold seasons and the hydrolysis rate of organic matters was closely related to the temperature (Miron et al., 2000). High-temperature hydrolysis of suspended organic matters was studied in the lab-scale and full-scale operation (Phothilangka et al., 2008; Bisceglia et al., 2012). However, the effect of the water quality variation and the low temperature on the full-scale HA system have not been evaluated.

In this study, a 5000 m<sup>3</sup>/d full-scale reactor was used to evaluate the performance of the HA system for practical tannery wastewater treatment. The buffering capacity of the full-scale HA system to the influent variation of COD, SS and sulphides was assessed. The vertical distribution of the sludge and COD concentration was measured in this 8 m high reactor. The influence of low temperature on organics treatment effect was detected. This study provided valuable information for the practical application of the HA system.

## 2. Materials and methods

A full-scale HA system was built in a tannery wastewater treatment plant in northeast China. The tannery wastewater was discharged from Zhaoyuan tannery industrial park. Most of the sulphide and chromium in the wastewater was reduced using catalytic oxidation and chemical precipitation prior to the HA system. The HA reactor was an 8 m high cylinder with a 20 m diameter. Influent of tannery wastewater was pumped to the bottom zone of the HA reactor and evenly distributed by pipes. A portion of the wastewater was pumped from the middle zone to the bottom zone of the HA reactor, and the reflux ratio was 100%. The circulation reflux not only improved the upward-flow velocity of wastewater in this reactor, but also contributed to increase the thickness of the sludge layer. A small amount of oxygen was provided to avoid the anaerobic state in the HA system. A schematic diagram of the full-scale HA system is shown in Fig. 1. The influent flow was 5000 m<sup>3</sup>/d and the hydraulic retention time (HRT) was 12 h. The operating temperature of the HA system changed as the ambient temperature and the inflow wastewater temperature changed.

The quality of the tannery wastewater, discharged from the tannery industrial park, significantly changed during the experiment period. The concentration of COD, BOD and SS in the tannery wastewater was in the range of 900–3800 mg/L, 500–1800 mg/L and 150–390 mg/L, respectively. The concentration of influent ammonia nitrogen, sulfide and total chromium changed in the range of 88–35 mg/L, 160–20 mg/L and 0.25–0.1 mg/L. Moreover, the water temperature in the HA reactor gradually decreased from

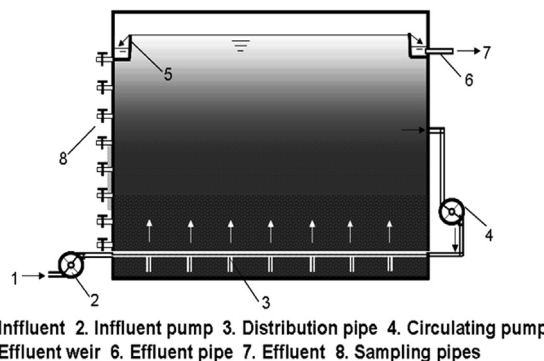


Fig. 1. Schematic diagram of hydrolysis-acidification (HA) system.

25 to 5 °C with the decrease of the ambient temperature. The variation of pH value was in the range of 7.6–8.8 over the testing period. The analysis was conducted in terms of COD, BOD, pH, SS, S<sup>2-</sup>, NH<sub>4</sub>-N, total chromium, pH and MLSS. The analysis of inflow and outflow parameters was conducted according to the standard methods (APHA, 1992). The vertical distribution of the sludge and COD concentration was sampled at each 0.5 m in the vertical direction of the HA reactor.

## 3. Results and discussion

### 3.1. COD and BOD removal

The COD concentration of influent tannery wastewater increased from 900 to 3800 mg/L during the 60-days experiment (Fig. 2a), and the effluent COD concentration synchronously increased from 500 to 2450 mg/L. The correlation between COD and BOD is shown in Fig. 2b. Although the average ratio of BOD and COD increased from 0.37 to 0.56 after the HA treatment, the increased BOD in the effluent was observed to be less than 10% after the bioprocess.

The COD removal ratio of the full-scale HA system ranged from 30 to 40% in the temperature range of 15–25 °C as the influent COD increased from 900 to 3800 mg/L. The COD removal ratio of the HA process was reported to be 28% for the Chinese traditional medicine wastewater and 26.9% for the sweet potato starch wastewater at room temperature (Chen et al., 2012; Tian et al., 2013). These results indicated that the HA process could reduce the organic loading within a limited removal rate but had a high shock-resistance capability for organic loading under the normal temperature condition. However, because the effluent COD of the HA system was much higher than the discharge standard of the tannery wastewater (COD < 150 mg/L) in China, a following treatment step was necessary. In addition, the ratio of BOD and COD was widely used to reflect the biodegradability of the organics in the wastewater. The HA process was supposed to improve the BOD/COD of the wastewater based on the previous study. However, the increased BOD/COD was mainly attributed to the COD removal in this study (Fig. 2b), but was not attributed to the increase of the BOD concentration in the effluent. This is probably because a portion of dissolved organics hydrolysed from the solid organics was mineralized in the system.

### 3.2. SS and sulphide

A high SS removal ratio of the HA system was observed in Fig. 3a. Although the influent SS content varied from 100 to 350 mg/L, the effluent SS content maintained lower than 60 mg/L, and the SS

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