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Abstract Title: OZONE, O3 PLUS AOP: AN OPTIMIZED TREATMENT LINE FOR COD & TOC REMOVAL. WANHUA, FROM LAB TESTS TO FULL SCALE PLANT

Abstract: KEYWORDS

COD & TOC removal, AOP O3 O3/H2O2, Ozonation, Reverse osmosis concentrate, Denitrification, Coagulation, process design

An industrial project for the treatment of Wan Hua (Yantai) Reverse Osmosis concentrate is introduced in this presentation. It is including background of the project, trials at laboratory, demonstration trials on site, optimization and process design.

BACKGROUND

Wan Hua group is a famous state owned chemical company with 2015 revenue of 20 Billion RMB (2.54 Billion Euro). In WanHua YanTai Park, 108 effluents are collected and treated in YanTai Wanhua's waste water treatment unit. As Wan Hua is consuming 1/3 of total water of Yantai city, water recovery is critical due to water scarcity in the area so they have implemented a reverse osmosis process (RO). Up to now, concentrate effluent from RO has been treated by external municipal waste water treatment, but due to lack of biodegradability this will soon not be possible anymore and Wanhua needs to find an alternative solution that is why an internal treatment is foreseen.

SPECIFICATIONS

The RO concentrate flow rate is ~ 500 m3/h and 1000 m3/h respectively for phase 1 and 2. This matrix contain: COD around, TOC ~100 mg/L, TN ~100 mg/L. According to specifications GB 31571-2015 (main parameters COD <50 mg/L, TOC < 20 mg/L, TN<40 mg/L) treated effluent can be discharged to the sea.

TRIALS AT LAB

Firstly, trials on RO concentrate were conducted in Solvay Shanghai Laboratory focusing on TN, COD and TOC removal.

1) Denitrification (TN removal)

Figure 1 : Denitrification reactor Figure 2 : Performances of denitrification

With COD inlet 270 mg/L and TN 100 mg/L, by adding ethanol as carbon source (COD/TN=5.0), it is possible to remove TN down to 11 mg/L (Specification < 40 mg/L). COD after this step is around 244 mg/l.

2) Coagulation+O3/H2O2 (COD and TOC removal)

Figure 3 : Jar tests for coagulation trials Figure 4 : O3/H2O2 laboratory equipment in Solvay

After coagulation trials at different pH, TOC decreased from 65 to 39 mg/L at pH ~9.5 (TOC removal efficiency ~40%). For O3/H2O2 treatment, COD decreased from 120-140 mg/L to below 40 mg/L and TOC to below 20 mg/l. O3 transferred regarding to the amount of COD removed is around 4 to 4.2 g/g.

DEMONSTRATION TRIALS ON SITE

To further validate laboratory trials results, 2-3 weeks demonstration pilot trials in continuous were conducted in WanHua site.

Figure 5 : Continuous coagulation pilot Figure 6 : O3/H2O2 pilot

Inlet TOC was 60-120 mg/L and after coagulation, outlet TOC was ~35-45 mg/L which confirmed removal efficiency 40-50%. After O3/H2O2 treatment, TOC was finally decreased to below 20 mg/L with O3 transfer versus removed COD of 4.5 g/g.

OPTIMIZATION BY SUEZ

In order to optimized O3 consumption and overall operational costs, Oxyblue technology was proposed by Suez. The objective is to realize a first step of ozonation which increase biodegradability, followed by a biological step which remove the COD, transformed in BOD, at lower costs: A final AOP treatment completes the process. For ozone pretreatment, with O3 transfer dosage 0.15 g/L, 45 % of COD can be removed and B/C can be increased from 0.03 to 0.26. In that case O3 transfer versus COD removed is only 2.5 since molecules are easier to oxydize at the beginning.

Figure 7 : O3 laboratory equipment in Suez Figure 8 : Increase of biodegradability after O3 trials

TECHNICAL PROPOSAL AND BIDDING

Based on laboratory and demonstration pilot trials results, a global process including coagulation, pretreatment by O3, denitrification and biological treatment, O3/H2O2 was defined as the most efficient and cheapest solution to achieve the target. This process was proposed to the client and quoted. Finally, Solvay/Suez alliance won the bidding for both phase 1 and 2 (design flow rate 1000 m3/h, O3 capacity 425 kg/h, H2O2 244 t/y).