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Anaerobic–aerobic treatment of purified terephthalic acid (PTA) effluent; a techno-economic alternative to two-stage aerobic process

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Abstract

This paper addresses the treatment of purified terephthalic acid (PTA) effluent using anaerobic and aerobic processes. Laboratory studies were carried out on flow proportionate composite wastewater generated from the manufacturing of PTA. An activated sludge process (ASP—two stage and single stage) and an upflow anaerobic fixed film fixed bed reactor (AFFFBR) were used, individually and in combination. The performance of a full-scale ETP under existing operating conditions was also studied. Full scale ETP studies revealed that the treatment of PTA effluent using a two-stage ASP alone does not meet treated effluent quality within the prescribed Indian Standards. The biomass produced in the two stage ASP was very viscous and fluffy and the sludge volume index (SVI) was very high (200–450 ml/g). However, pretreatment of PTA effluent using an upflow AFFFBR ensured substantial reduction in BOD (63%) and COD (62%) with recovery of biogas at 1.8–1.96 l/l effluent treated at a volumetric loading rate (VLR) 4–5 kg COD/m^3 d. The methane content in the biogas varied between 55% and 60%. The pretreated effluent from the upflow AFFFBR was then treated through a single stage ASP. The biomass produced in the ASP after anaerobic treatment had very good settlability (SVI: 75–90 ml/g) as compared to the two stage ASP and the treated effluent quality with respect to BOD, COD and SS was within the prescribed Indian Standards. The alternative treatment process comprising an upflow AFFFBR and a single stage ASP ensured net power saving of 257 kW and in addition generated 442 kW of power through the AFFFBR.

Keywords: PTA effluent; Activated sludge process; Anaerobic reactor; Wastewater treatment; Resource recovery

1. Introduction

The applicability of purified terephthalic acid (PTA) in every day life does not need any introduction. PTA is used in the manufacturing of audio films, polyester fibers, moulded resins and polyethylene terephthalate (PET) bottles (Kleerebezem and Lettinga, 2000). Macarie et al. (1992) have discussed the production of PTA in various countries and stated its usages in manufacturing products and by-products. In this study, a full-scale effluent treatment plant (ETP) treating PTA effluent has been upgraded, following field investigations and extensive laboratory R&D studies. The study was aimed at treatment of PTA effluent with a goal of resource recovery and improving the treated effluent quality to meet the prescribed Indian Standards.

2. Description of PTA manufacturing process

The manufacturing process of PTA comprises the following three major stages:

- Manufacturing of crude terephthalic acid (CTA).
- Purification of CTA to PTA.
- Recovery and regeneration of CTA oxidation catalyst.

In the CTA stage, para-xylene is oxidized by air in the presence of cobalt and manganese as the catalysts, and acetic acid as the solvent, at 200 °C and 15 kg/cm^2 G

Abbreviations: ASP, activated sludge process; AFFFBR, anaerobic fixed film fixed bed reactor; PTA, purified terephthalic acid; CTA, crude terephthalic acid; TA, terephthalic acid; UASB, upflow anaerobic sludge blanket; ETP, effluent treatment plant

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Nomenclature

bCOD	biodegradable chemical oxygen demand (mg/l)
BOD_5	five-day bio-chemical oxygen demand (mg/l)
COD	chemical oxygen demand (mg/l)
DO	dissolved oxygen (mg/l)
HRT	hydraulic retention time (d)
k_d	decay coefficient (d^{-1})
MLSS	mixed liquor suspended solids (mg/l)
SRT	sludge retention time (d)
SS	suspended solids (mg/l)
SVI	sludge volume index (ml/g)
TDS	total dissolved solids (mg/l)
UBOD	ultimate BOD (mg/l)
VLR	volumetric loading rate (kg COD/m^3 d)
Y	yield coefficient (g VSS per g BOD)
Y_H	synthesis yield coefficient, g VSS per g COD used
f_d	fraction of cell mass remaining as cell debris (g/g)

pressure in the reactor. The off-gases are led into an off gas turbine from where it is vented. The CTA thus produced is crystallized and filtered to separate CTA from the solvent and catalysts. Thereafter, CTA is dried and sent for purification. This stage involves an acetic acid distillation process, where the byproduct water is formed and removed. The CTA is purified to obtain PTA by dissolving it in pure water and converting the intermediate products (4-carboxyl benzaldehyde) to para-toluic acid, at a around 85 kg/cm^2 G and at a temperature of over 290 °C, in the presence of a lead catalyst in a hydrogen atmosphere. The para-toluic acid thus formed is recycled into the process for further oxidation to produce PTA. The PTA is subsequently crystallized, dried and packed in container bags. The catalyst is recovered and regenerated. The oxidation of para-xylene and purification of CTA is shown in Fig. 1.

3. Wastewater generation

The major sources of wastewater generation are the catalyst recovery section, cleaning and washing water, PTA scrubbing water, and distillate acid water. The wastewater generation varies from 3 to 10 m^3 per tonne of PTA produced and is equivalent to 5–20 kg COD/m^3 (Kleerebezem et al., 1997). The total quantity of process wastewater generated is 3540 m^3/d. The PTA scrubbing section generates the maximum quantity of wastewater, followed by distillate acid water, catalyst recovery and cleaning water. A breakup of the wastewater generation and its characteristics for major parameters are shown in Fig. 2.

4. Treatment of PTA effluent

Traditionally, PTA wastewaters were treated using the activated sludge process (ASP) (Lau, 1978). Advantages of aerobic treatment are high purification efficiency (>90%), high process stability and rapid biodegradability of all compounds. However, in recent years anaerobic treatment has been preferred to conventional aerobic activated sludge treatment processes. The reasons for this are

(A) the aerobic process is highly energy intensive,
(B) it produces a large volume of sludge and hence incurs heavy expenditure on sludge handling and management,
(C) it requires highly skilled operation and process control,
(D) external addition of nutrients is essential, which further increases the O&M cost,
(E) it requires overall costly technical specifications, and
(F) the settleabilty of solids produced in ASP is very poor.

Aerobically treated PTA effluent has the specific problem of poor settling as determined in an operational full-scale plant in Eastern India. A similar problem has also been reported in the literature (Brugnaro and Polo, 1985). The poor settling characteristics of the mixed liquor suspended solids (MLSS) was the major problem in achieving treated effluent quality within the prescribed Indian Standards. Kleerebezem et al. (1997) classified compounds that are anaerobically easily degradable (benzoate and acetate) and compounds whose anaerobic biodegradability is unclear (terephthalate and *p*-toluate). Acetate is the main precursor of methane in anaerobic bioreactors and can be converted directly into methane and bicarbonate by methanogenic organisms. Macarie et al. (1992) presented a comparative study of anaerobic treatment using upflow anaerobic sludge blanket (UASB; U and T) and tubular fixed film (Down flow) processes for treatment of PTA effluent. They concluded that primary sedimentation of PTA raw wastewater, followed by anaerobic treatment using a down flow fixed film reactor gives 84% reduction in chemical oxygen demand (COD) at a hydraulic retention time (HRT) of 3.4 days. Kleerebezem and Lettinga (2000) presented an optimized concept for start up and operation of a two-stage anaerobic bioreactor system. They suggested a gradual transition between initial operations in parallel to operation in series. Sheng-shung et al. (1997) demonstrated that a UASB reactor can achieve up to 62% reduction in COD at a volumetric loading rate (VLR) 2.93 kg COD/m^3 d. Young et al. (2000) studied two-stage anaerobic treatment consisting of Hybrid and Contact processes for treatment of PTA effluent and found that COD reductions with Hybrid and Contact processes were 80–93% and 70–85%, respectively. The maximum removal capacity of anaerobic pretreatment (UASB Process) for PTA effluent, when fed with terephthalate as the sole carbon source, was found to be 3.9 kg COD/m^3 d at a VLR 4.4 kg COD/m^3 d and HRT 24 h (Kleerebezem et al., 1997). Noyola et al. (2000) upgraded a petrochemical