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Sulfide removal in wastewater from petrochemical industries by autotrophic denitrification

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Abstract

An alternative flowchart for the biological removal of hydrogen sulfide from oil-refining wastewater is presented; autotrophic denitrification in a multi-stage treatment plant was utilized. A pilot-scale plant was fed with a mixture of the following constituents: (a) original wastewater from an oil refining industry (b), the effluent of the existing nitrification-stage treatment plant and (c) sulfide in the form of Na_2S. Anoxic sulfide to sulfate oxidation, with nitrate as a terminal electron acceptor, proved very successful, as incoming concentrations of 110 mg S^{2-}/L were totally converted to SO_4^{2-}. At complete denitrification, the concentration of S^{2-} in the reactor effluent was less than 0.1 mg/L. Fluctuating S^{2-} concentration in the feed could be tolerated without any problems, as the accumulated sulfide in the effluent of the denitrification stage is oxidized aerobically in a subsequent activated-sludge treatment stage. This alternative new treatment scheme was further introduced at the refinery's wastewater processing plant. Thus, complete H_2S removal is now accomplished by the combination of the proposed biological method and the existing stripping with CO_2. As a result, stripping, and thus its cost, is reduced by 70%.

Keywords: Autotrophic denitrification; Hydrogen sulfide; Nitrogen; Oil-refining industry; Petrochemical wastewater

1. Introduction

Wastewater, generated by the catalytic hydrocracking and refining of various crude-oil fractions, contains, in addition to hydrocarbons, large amounts of nitrogen and sulfur, in the form of ammonia (NH_3) and hydrogen sulfide (H_2S), respectively.

Hydrogen sulfide is a toxic and corrosive gas that causes environmental and economic problems in a variety of sectors such as sewage, oil fields, petrochemical industry, etc. Among other strategies to control and remove sulfide is the use of nitrate, which has proved very effective, as previous researchers have shown (Jenneman et al., 1999; Mathioudakis et al., 2005; Telang et al., 1997).

The DEA Wesseling Works in Germany is a refining and petrochemical complex with an annual crude-oil throughput of 6×10^6 tons, an industry that is a direct discharger into the Rhine River. A modern five-stage wastewater treatment plant (Fig. 1), which is based on the Bayer tower-biology principle (Zlokarnik, 1985), treats an average of 5700 m^3 of wastewater daily, that corresponds to 4.8 tons of biochemical oxygen demand (BOD) per day (800 mg BOD_5/L).

The wastewater consists mainly of two separate streams: (a) the so-called C/N (carbon and nitrogen)-containing stream (130 m^3/h), which is characterized by a low concentration of organic content (400 mg BOD/L),

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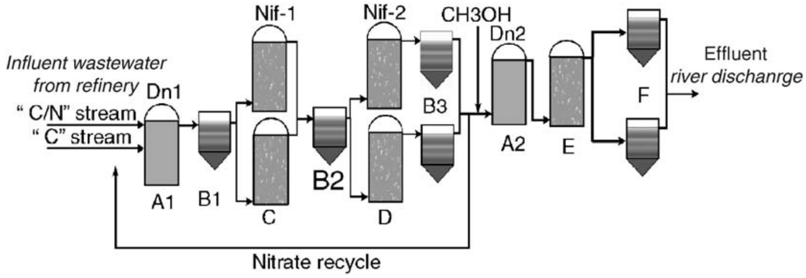

Fig. 1. Schematic diagram of the DEA Wesseling wastewater plant: (a) denitrification (Dn1); (b) intermediate clarification (B); (c) activated-sludge treatment with partial nitrification (Nif-1); (d) nitrification (Nif-2); (e) activated-sludge treatment (E); (f) final clarification (F).

while ammonia concentration averages 280 mg/L, and (b) the C (carbon)-containing stream (40 m^3/h) that is characterized by a higher concentration of organic compounds (BOD: 2000 mg/L). The remaining hydraulic flow contains sulfide water and some other–not further characterized mud-water with a negligible flow.

Separable oils are removed by phase separation in a coupled upstream physical purification stage. Stripping with CO_2 (2000 m^3/h) permits the H_2S level of the wastewater to be lowered to a maximum of 10 ppm, normally less than 2 ppm. This sulfide-water, with a reduced sulfide concentration, enters the wastewater treatment plant along with the C/N-containing stream. The stripped hydrogen sulfide is then converted to elemental sulfur by the Claus process. Ammonia, with an initial concentration of 1500 mg/L, is removed by steam stripping, lowering its concentration to a level of 195–365 mg/L (280 mg/L).

The wastewater treatment plant (Fig. 1) consists of five biological stages (A1, C, D, A2, E) that operate at 28–30 °C. The first of the above stages is a denitrification one (A1), in which about 40% of the BOD_5 from the raw wastewater is degraded by anoxic respiration utilizing a nitrate-containing recycle stream from the last nitrification stage (Nif-2). The remaining BOD degradation and nitrification is carried out in two stages. In the first one (Nif-1) aerobic degradation of the remaining BOD_5 and partial nitrification of the ammonium nitrogen (50–85%) occurs, whereas complete nitrification takes place in the second nitrification stage (Nif-2). The nitrate is converted to molecular nitrogen in the second denitrification stage (A2) with methanol (2700 kg/d) added as a carbon source. The activated-sludge treatment phase (E) serves as protection against a possible BOD_5 breakthrough.

Denitrifying bacteria can grow on a wide range of substrates; however, many of these are too expensive to be economically usable for wastewater treatment. Thus, in addition to methanol, acetate and sulfur been have also used; the latter relies on *Thiobacillus (T) denitrificans* and related bacteria (Batchelor and Lawrence, 1978; Claus and Kutzner, 1985). Alternatively, hydrogen sulfide in the biogas, generated by sulfate-reducing bacteria simultaneously with methane formation from methanogenic bacteria, has been applied as an electron donor in an autotrophic post-denitrification step (Darbi and Viraraghavan, 2003; Davidova et al., 2001; Kleerebezem and Mendez, 2001; Robertson and Kuenen, 1983; Telang et al., 1997). Denitrification, with sulfide as an electron donor, is an autotrophic process characterized by significant low biomass yields when compared to heterotrophic denitrification.

A number of colorless sulfur bacteria are capable of anaerobic growth, if nitrate or nitrite serves as an electron acceptor. The group includes several obligate autotrophes, such as *T. denitrificans* and *Thiomicrospira* (*Tms.*) *denitrificans* (Batchelor and Lawrence, 1978; Claus and Kutzner, 1985; Timmer–ten Hoor, 1975). During competition studies with the denitrifying obligate chemolitotrophes *T. denitrificans* and *Tms. denitrificans* (Timmer-ten Hoor, 1977), it was found that, although their maximum growth specific rates in pure culture were similar, in anaerobic environments *Tms. denitrificans* dominated. However, if oxygen was not vigorously excluded from the chemostate, *T. denitrificans* gained the advantage. *Tms. denitrificans* has constitutive denitrifying enzymes, whereas *T. denitrificans* will only induce production of such enzymes under anaerobiosis in the presence of nitrate (Timmer-ten Hoor, 1975). This probably explains the ability of *Tms. denitrificans* to establish itself in anaerobic cultures. However, in wastewater treatment systems, the autotrophic denitrifiers have to compete also with the heterotrophic species for nitrate, which is the common terminal electron acceptor. From the thermodynamic point of view, the change of the reaction free energy under standard conditions ($\Delta G_R^{o\prime}$) for the sulfide–nitrate couple, having a value of -740 kJ/mol H_2S, represents no principal bottleneck for its application (Fig. 2); the values of $\Delta G_R^{o\prime}$ have been calculated according to the thermodynamic data reported by Decker et al. (1975). Nevertheless, since in practice, the concentration of