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Project Summary

Innovative Destruction of Complex Industrial Wastes—Auto Oxidation of Tannery Beamhouse Wastewater

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This project was intended to obtain data on the effectiveness of a novel destruction technique for treating potentially toxic pollutants from a wide range of manufacturing sources. The particular waste used for evaluation was a tannery unhairing effluent. The novel technique examined was an auto-oxidation process.

Tannery unhairing waste was treated in a pilot plant scale auto-oxidation unit designed and built by Technical Associates for Industry, Inc., Red Bank, New Jersey 07701. This waste is highly alkaline with a pH generally higher than 11 and has a COD greater than 50,000 mg/liter, consisting largely of protein and sulfide. The auto-oxidation pilot plant in static tests effectively and rapidly removed sulfide from the waste. Removal of COD, nitrogen, and suspended solids was considerably less effective. Combining the auto-oxidation with ultraviolet light and a hydrogen peroxide addition improved the COD removals very little.

Introduction

In 1968, the Hides and Leather Laboratory was approached by Technical Associates for Industry (TAFI) with a proposal to test an innovative process for treatment of tannery lime-sulfide unhairing wastes. TAFI is a small, private consulting firm. Their general interest was in treatment of industrial and municipal wastes to meet regulatory limits. Their experience to date, on treatment of wastes with this process, was on municipal sludges and industrial wastes with high carbohydrate content. The process is based on a free-radical, auto-oxidation mechanism of breakdown of the waste. The free radicals are produced by passing the solution under pressure through an orifice. The basis for free radical production was proposed by N. Zaleiko during treatment. The collapse of gas bubbles in cavitation can develop very high local temperatures. Under adiabatic conditions, gas temperatures at the minimum bubble radium can reach 2,000°F. There, local high temperatures can be expected to lead to ionization effects and the production of hydroxy-free radicals and peroxides. Extensive cavitation effects on the oxidation of phenol are described by Chen et al.

The effluent stream from the unhairing process in a tannery is a difficult waste to treat by conventional methods. Typical composition of unhairing waste is: BOD, 20,000 ppm; COD, 40,000 to 60,000 ppm; solids, 50,000 ppm; pH, 12.5; and sulfide, 1,000 to 3,500 ppm. The beamhouse process starts by soaking hides in water in order to rehydrate them and to remove salt. The soaked hides are then placed in a 2-4% calcium hydroxide suspension along

with approximately 2% by weight of the hide of sodium sulfide in order to dissolve the hair. The hides may then be relimed with additional calcium hydroxide or simply washed. From this stage they continue into the actual tanning process.

Conclusions

The innovative treatment of tannery wastes, using the oxidative pilot plant manufactured by TAFI, rapidly removed sulfide from tannery limesulfide unhairing effluent. Removal of COD, suspended solids, and nitrogen under the conditions studied was not effective. The excessive formation of foam in this waste might have been responsible. No estimate of cost effectiveness was made to determine whether this process could be used commercially to treat beamhouse effluent.

Experimental Procedures

The apparatus which is the basis of this treatment process, the oxidation pilot plant, is detailed in Figure 1. The material to be treated was pumped from a feed tank (250 gal) into a reservoir which was maintained at a level of approximately 18 gal. The treated solution flows out of the system through the overflow at the same rate that feed was pumped into the system. Solution from the reservoir was pumped by a 5 hp circulation pump through the oxidation nozzle and back to the reservoir through a ¾" ID copper pipe at a rate of 5 gal/min. The oxidation nozzle was essentially a constriction in the recycle loop. As the solution flowed out of the nozzle, the pressure on the solution was rapidly reduced causing cavitation. At the same time, air was incorporated into the loop to prevent the level of dissolved oxygen from dropping to zero. Two types of tests were run on the apparatus. The first, referred to as a static test, consisted of recycling the solution to be treated from the reservoir, through the pump and around the loop, through the oxidation nozzle and back into the reservoir. No additional feed was added. In a continuous run, the second type of run, the reservoir and the overflow from the treatment was allowed to flow out into a final tank or into a drain. At a later stage of the research, an ultraviolet lamp was added to the system positioned directly at the end of the oxidation nozzle. When used in the experiments, hydrogen peroxide was pumped into the system as indicated just before the pump. Metal salts, when added for catalysis, were added in the reservoir or dissolved in the feed tank. In a continuous run, the feed was typically added at a rate of 0.3-0.5 gal/hr. Samples were taken for evaluation of treatment from the overflow. The analyses were performed according to standard methods except as indicated. Analyses reported are:

1. Sulfide (s=),
2. Total Kjeldahl nitrogen using a Technicon autoanalyzer (n),
3. TOC (total organic carbon) using a Beckman TOC instrument,
4. COD (chemical oxygen demand) performed by the techniques developed by Oceanography and accepted by Standard Methods,
5. Suspended solids (ss), and
6. Volatile suspended solids (vs).

Results

The removal of sulfide by this method was consistent and rapid in the static tests. Initial sulfide concentrations in these runs were between 150 to 500 ppm. In less than 100 min, the sulfide concentrations were reduced to less than 2 ppm in each of the trial runs. This was consistent even when the pH dropped as low as 8.5. Presumedly, the sulfide was oxidized to sulfate. The changes in TKN, TOC, COD, suspended solids and volatile solids were small and not consistent.

Continuous waste treatment was done with a 10:1 dilution of the original waste. A continuous trial can be started in two ways. The reservoir and oxidation loop can be filled with the diluted waste solution to be treated or with tap water. Approximately 150 min at 0.5 gal/min was required to approach a steady state between the solution being added and the contents of the reservoir, when the system starts with water. Sulfide reduction under these conditions was between 25 and 50%. Little change in TOC, suspended solids, and volatile solids was observed, although there was a small overall reduction.

Continuous runs were repeated using a more conventional 2-hr settled waste as the starting material. The dilution was again 10:1. In these runs, samples were taken from the storage or feed tank as well as from the reservoir overflow. Only slight reductions were observed in any of the parameters when compared to those from the feed-tank solution. Within the scatter of the values obtained, no trend is apparent.

A preliminary bench-top experiment was performed to examine the effect of addition of peroxide, ultraviolet light, and copper ions to tannery limesulfide unhairing solutions. The procedure followed was to place 1 liter of unhairing waste in a beaker with constant stirring under a Phipps-Bird apparatus. Samples were then taken at 0, 15, 36, 90, and 120 min and at 20 hr. Samples were analyzed for pH, sulfide, tota

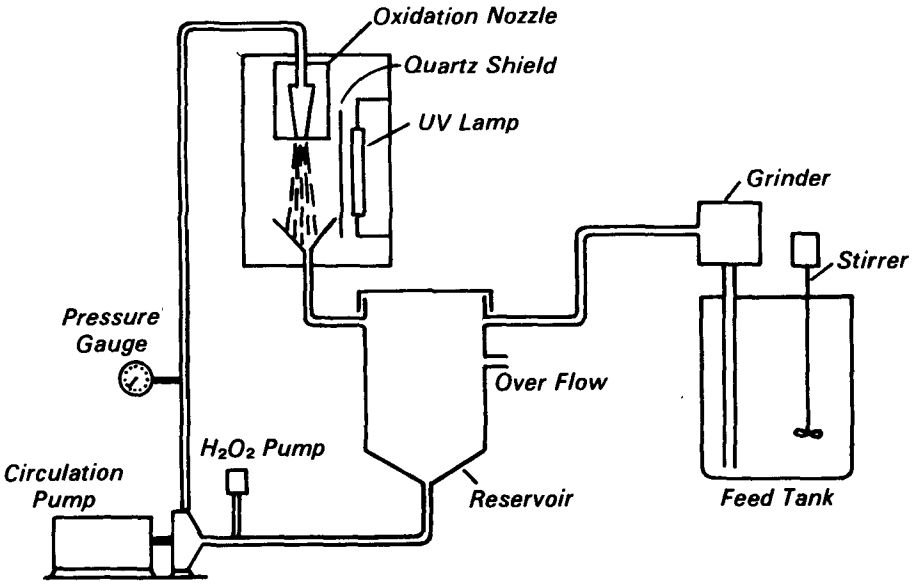

Figure 1. Schematic of auto-oxidation pilot plant.

Kjeldahl nitrogen, TOC, COD, suspended and volatile solilds. The control samples showed no change. Addition of ultraviolet light to the solutioin did not alter values over the 20-hr period.

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The complete report, entitled "Innovative Destruction of Complex Industrial Wastes—Auto Oxidation of Tannery Beamhouse Wastewater," (Order No. PB 81-129 025; Cost: $6.50, subject to change) will be available only from:
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