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ANAEROBIC REMOVAL OF CHLORATE FROM BLEACH EFFLUENTS

Å. Malmqvist* and T. Welander**

*ANOX AB, Ideon Research Park, S-223 70 Lund, Sweden
**Applied Microbiology, Lund University, P.O. Box 124, S-221 00 Lund, Sweden

ABSTRACT

Anaerobic biological removal of chlorate was studied on a laboratory and pilot plant scale. Continuous laboratory tests in an anaerobic fixed-film process showed that chlorate can be removed completely from kraft bleach effluent at such a short hydraulic retention time as 0.6 h. The efficiency of biological chlorate removal was confirmed under practical conditions in a 20 m^3 pilot plant, operating at a Swedish craft mill.

Four chlorate reducing bacterial strains were isolated and characterized. All four isolates were gram-negative, catalase- and oxidase-positive, motile rods. None of the four isolates could ferment glucose, while they could all grow aerobically and with nitrate as electron acceptor.

KEYWORDS

Chlorate; anaerobic treatment; bleach effluent.

INTRODUCTION

The discharge of bleach effluents containing chlorinated organic compounds is a main environmental issue in the pulp and paper industry. This problem can be attacked in two principal ways; the formation of chlorinated organics can be decreased by internal modifications in the bleaching procedure or chlorinated organics can be removed from the effluent by some kind of external treatment. In Sweden, modifications of the bleaching procedure has been the dominant way of dealing with the problem. Thus, oxygen delignification has been introduced at all Swedish craft mills and molecular chlorine has to an increasing extent been substituted by chlorine dioxide as bleaching agent. This has resulted in a drastic decrease in the organically bound chlorine discharged by the pulp and paper industry from some 8 kg/tonne pulp in the early seventies to approximately 2 kg/tonne pulp today.

A further increase of the substitution of chlorine dioxide for molecular chlorine is regarded as a major possibility for achieving a further decrease of the emission of chlorinated organics into the environment. However, the use of chlorine dioxide as a bleaching agent creates a new environ-

mental problem, since part of the chlorine dioxide used ends up as chlorate (ClO_3^-) in the effluent. Chlorate is toxic to aquatic plants, e.g. bladder wrack (*Fucus vesiculosus*) (Rosemarin et al., 1986).

Chlorate can be removed from bleach effluents by reduction with sulfur dioxide. However, this method often gives an incomplete removal of chlorate and large amounts of chemicals are consumed. Lately, the possibility to remove chlorate from bleach effluent by means of biological treatment has been demonstrated. The removal of chlorate in a biological treatment system was first shown at Mönsterås craft mill Sweden. As some of the aerators in the aerated lagoon system at the mill were turned off, chlorate was removed from the effluent (Eckerman, 1987). These results indicated that chlorate can be removed biologically in an anaerobic environment. The results at Mönsterås kraft mill have since been verified by several investigations showing the disappearance of chlorate in anaerobic environments (Germgård and Berglund, 1987; Axegård et al., 1989; Yu and Welander, 1990). The need for an anaerobic environment was clearly demonstrated by Yu and Welander (1990). As aerobic and anaerobic treatment of kraft bleach effluent were compared on a lab scale, it could be shown that chlorate was completely removed in the anaerobic system, while not being affected at all in the aerobic reactor.

Although the disappearance of chlorate in anaerobic environments has been proven by several investigators, it was just recently shown that the chlorate removal is indeed due to the activity of microorganisms (Malmqvist et al., submitted). Chlorate reducing bacteria were enriched in continuous culture, using a defined medium. It could be shown that the bacteria used chlorate as electron acceptor for oxidation of organic matter in a previously unknown reaction. The product of chlorate reduction was shown to be chloride. A high biomass yield was obtained in the tests, showing that chlorate reducing bacteria are able to derive a significant amount of energy from the reaction.

Biological treatment is now considered a major alternative for removal of chlorate from bleach effluents in Sweden. The aims of the studies presented in this paper were to learn more about the microorganisms involved in biological chlorate removal and to investigate the possibility to remove chlorate from bleach effluents in a high-rate anaerobic process.

MATERIALS AND METHODS

Analyses

Chlorate and chlorite were analysed by means of an ion-exchange chromatography method. A volume of the sample, estimated to contain approximately 100 mg/l chlorate, was passed through an anion-exchanger (Dowex 1x8, 200-400 mesh, Cl^- form, Carl Roth KG, Karlsruhe, West Germany) in which chlorate and chlorite were retained. The resin was washed with 50 ml distilled water. Chlorite was eluted with 50 ml 0.8 M sodium chloride solution after which chlorate was eluted with 100 ml 1.6 M sodium chloride solution. 25 ml of the chlorite fraction was mixed with 10 ml 0.3 M potassium iodide solution, 5 ml 2 M sulfuric acid and 10 ml distilled water, resulting in an oxidation of iodide to iodine. The iodine formed was determined by titration with 0.0125 M sodium thiosulfate solution and with starch as indicator. 20 ml of the chlorate fraction was treated for two minutes with 40 ml concentrated hydrochloric acid in an evacuated vacuum bottle. A reservoir with a stopcock was connected to the vacuum bottle, allowing for the addition of reagents without releasing the vacuum in the bottle. The reservoir was washed with 30 ml distilled water. 20 ml 0.3 M potassium iodide solution was then added, followed by another washing with 20 ml distilled water. The iodine formed was determined by means of iodometric titration as described above.

Chloride was analysed by potentiometric titration according to Standard Methods (1975).

Isolation and Characterization of Chlorate Reducing Bacteria

Isolation of chlorate reducing bacteria was carried out by the conventional streak plate method, using acetate/chlorate agar plates containing 10 mM $NaClO_3$, 25 mM acetic acid, 1 mM NH_3, 0.1 mM KH_2PO_4, 0.1 mM $MgSO_4$, 0.1 mM $Ca(OH)_2$, 0.05 mM $FeSO_4*7\ H_2O$, 0.05 mM $MnSO_4*H_2O$, 5 μM $NiCl_2*6\ H_2O$, 5 μM $CoCl_2*6H_2O$, 5 μM $ZnSO_4*7\ H_2O$, 0.1 μM H_3BO_3, 0.1 μM Na_2SeO_4, 0.1 μM Na_2WO_4, 0.1 μM Na_2MoO_4 and 15 g/l Bacto-agar.

Samples were taken from a laboratory anaerobic reactor operating continuously on the same defined medium as used for the agar plates. The agar plates were incubated at 37°C in an anaerobic jar (Gaspak System, BBL) for 4 days. Well-isolated colonies were picked, restreaked and recultivated. This procedure was repeated a number of times to ensure that pure cultures would be obtained.

Aerobic growth was checked by transferring the isolates to agar plates of the same composition as given above, except for the chlorate being excluded, and incubating at 37°C for 4 days. The ability of the isolates to use nitrate as electron acceptor was tested by transferring the strains to agar plates for which the chlorate had been replaced by nitrate and incubating in an anaerobic jar at 37°C for 4 days. The strains were examined for Gram reaction by the KOH method (Gregersen, 1978), oxidase reaction (Kovacs, 1956), production of catalase (Enfors et al., 1979), and fermentation of glucose (Hugh and Leifson, 1953). Cell morphology and motility were checked by phase contrast microscopy. Color and morphology of the colonies on the agar plates were checked in a stereo microscope at a magnification of 20x.

Continuous Lab Test

The loading capacity of biological chlorate removal was studied in a laboratory anaerobic fixed-film reactor operated continuously on bleach effluent from a Swedish kraft mill. The chlorate concentration in the effluent was 50 mg/l and the COD was 1600 mg/l. The reactor was operated at 37°C and pH 7. In order to determine the maximum loading capacity of the system, the hydraulic retention time (HRT) was successively decreased until the process failed to remove all chlorate from the effluent.

Pilot Plant Test

In order to study the stability of biological chlorate removal on a larger scale and under practical conditions, a 20 m^3 pilot plant was constructed and operated at a Swedish kraft mill. The process was designed as an anaerobic fixed-film process. The temperature was maintained between 36 and 38°C and pH between 6.2-7. The process was started up at a constant HRT of 12.8 h. The loading was then increased successively as the capacity of the system to reduce chlorate increased.

RESULTS

Characteristics of Chlorate Reducing Bacteria

A number of chlorate reducing isolates were obtained, of which four strains, which differed from each other in colony morphology, were chosen for a closer characterization. All four strains were shown to be gram-negative, catalase- and oxidase-positive, motile rods. None of the four isolates could ferment glucose, while they could all grow aerobically and with nitrate as electron acceptor. The four strains, together with other isolates, are now subject for further characterization and possibly identification.

Continuous Lab Test

The anaerobic fixed-film process removed chlorate efficiently from the effluent. No chlorite was determined at any time during the test and an increase in chloride concentration corresponding to the chlorate removed was obtained. After two months of operation the maximum loading of the process was reached. The critical HRT was found to be about 0.6 h. The chlorate removal rapidly deteriorated as the HRT was further decreased, Figure 1.

Pilot Plant Test

The pilot plant test, which is still going on, has confirmed the efficiency of biological chlorate removal from bleach effluents. Within two weeks from start-up, the chlorate removal was complete at a HRT of 12.8 h. The flow-rate has then been increased successively. Operation at 3.2 h HRT over a rather long period of time confirmed the stability of the process at practical operating conditions, Figure 2. The HRT has later on been decreased to 1.6 h with the chlorate removal maintained over 90%. The critical HRT of the process seems not yet to have been reached.

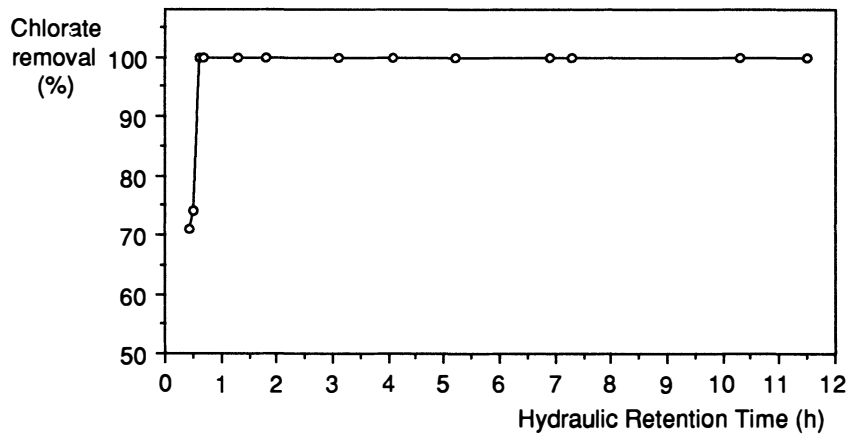

Fig. 1. Chlorate removal versus HRT in a laboratory anaerobic fixed-film process.

DISCUSSION

The results from both the laboratory study and the pilot plant test clearly show that anaerobic treatment is an efficient way of removing chlorate from bleach effluents. A complete removal of chlorate can be maintained at a short treatment time and under practical conditions. This makes biological chlorate reduction a very competitive alternative for removal of chlorate from bleach effluents.

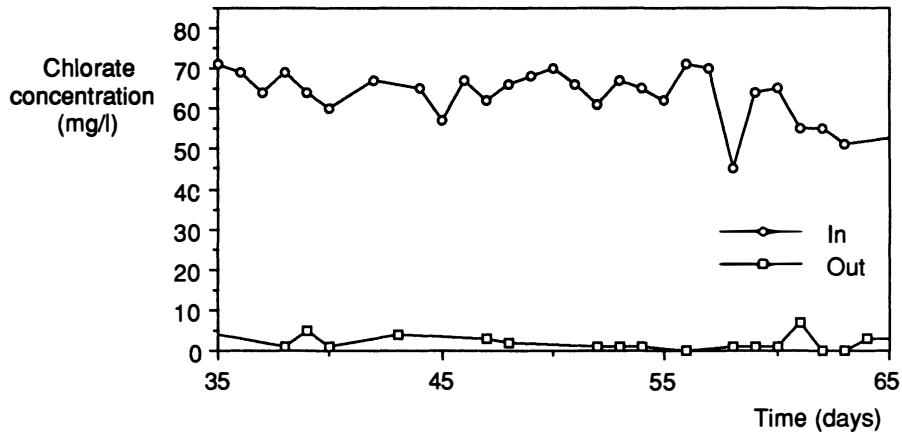

Fig. 2. Chlorate in and out from the pilot plant during 30 days of operation at a HRT of 3.2 h.

Much remains to be learnt about the microbiology of biological chlorate reduction. From the tests made so far, the similarity between biological chlorate reduction and denitrification is obvious and the chlorate reducing isolates studied have been able to use nitrate as well as chlorate as electron acceptor. However, the ability to use chlorate as electron acceptor seems to be far less common amongst bacteria than is the ability to denitrify. A further study of chlorate reducing bacteria is an interesting task for a microbiologist, and a deeper knowledge of the physiology of these bacteria will surely contribute to making biological chlorate removal an even more efficient method.

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