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Cometabolic reduction of bromate by a mixed culture of microorganisms using hydrogen gas in a gas-lift reactor

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Abstract The discharge of bromate, a suspected carcinogen, will be restricted in the near future. To assess the possibility of biotechnological treatment of bromate-containing wastewaters, the removal of bromate by chlorate-reducing microorganisms was studied. The removal of bromate and chlorate was studied in laboratory gas-lift bioreactors supplied with hydrogen gas as electron donor in the absence of molecular oxygen. In these reactors, bromate was reduced cometabolically by chlorate-respiring microorganisms. To allow the cometabolic reduction of bromate, a chlorate:bromate molar ratio of at least 3:1 was required. The cometabolic conversion permitted almost complete reduction of bromate into bromide at hydraulic retention times of at least 6 h. Optimal bromate reduction activity was observed at approximately 35°C. The pH optimum was between 7 and 8. Bromate reduction in excess of 80% and a maximum bromate reduction rate of 2.3 g l^{-1} day^{-1} in a pilot-scale gas-lift bioreactor demonstrates that the process is sustainable.

Introduction

Contaminants in the off-gas of incinerators are treated in scrubbers and consequently effluents are generated with high levels of inorganic compounds. Chloride, chlorate, bromate, and hypochlorite are present in these effluents (in decreasing order of concentration). Wastewaters containing these inorganic compounds are traditionally not treated. In the Netherlands, more stringent water quality guidelines have been promulgated due to the suspected carcinogenicity of bromate [17]. The carcinogenicity of potassium bromate is believed to be due to its ability to oxidize DNA [14, 25]. In anticipation of the stricter discharge regulations, a technology that is appropriate for the treatment of bromate-containing wastewaters is required.

The levels of bromate may be lowered by microbial reduction to bromide. The potential of biological treatment of bromate-containing wastes has been enhanced by findings relating to (per)chlorate degradation. Bacteria utilize (per)chlorate as sole electron acceptor and an organic substrate as both electron donor and carbon source [16, 21, 24, 27]. The biochemical pathway of these microorganisms appears to involve a (per)chlorate reductase that catalyzes the reduction of perchlorate via chlorate to chlorite [15]. Chlorite is subsequently disproportionated into chloride and oxygen by a chlorite dismutase [8]. These bacteria, which can utilize high concentrations of (per)chlorate for growth, are a promising source for the biotreatment of bromate because they are capable of cometabolizing bromate [15]. The reduction of bromate is initiated by the enzyme (per)chlorate reductase, catalyzing the following reaction:

$$BrO_3^- + XH_2 \rightarrow BrO_2^- + H_2O + X$$

The bromite formed is a strongly oxidizing agent that decomposes rapidly below pH 8, resulting in the formation of bromide [13]. The microbial conversion of bromite has not been investigated. The removal of (per)chlorate from wastewater is accomplished with organic compounds and has already resulted in economically competitive processes [1, 2, 20, 21, 29]. Hydrogen gas may be an attractive alternative electron donor [6, 7, 9, 23]. The use of hydrogen gas as a reductant in biological wastewater treatment offers several important benefits, such as process reliability, low excess sludge production, and no need for the removal of residual reductant [3, 4 10, 12, 18, 22]. So far, the reduction of

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bromate by chlorate-reducing microorganisms utilizing hydrogen gas as electron donor has not been studied.

In this paper, we describe the reduction of chlorate and bromate by microorganisms in both laboratory- and pilot-scale gas-lift reactors supplied with hydrogen as sole reductant and carbon dioxide as sole source of carbon. Reactor performance, reaction stoichiometry, and the chlorate:bromate molar ratio required are presented. We also investigate the influence of pH, temperature, salt, and oxygen.

Materials and methods

Materials

Potassium bromate was purchased from Acros Organic (Geel, Belgium). Hydrogen gas was purchased from BOC GAS (Zaventem, Belgium). All other chemicals used were of analytical grade. Pumice particles (Aqua-volcano) used as carrier material were obtained from Aquatechniek (Papendrecht, the Netherlands). Pumice is highly porous volcanic rock. The particles (0.2–0.6 mm diam., 2.4 kg m^{-3}) consisted of 60–75% SiO_2, 13–17% Al_2O_3, and smaller quantities of Fe_2O_3, CaO, Na_2O, and K_2O.

Sludge

Several kinds of sludge were used as inocula for the bioreactors. The laboratory-scale bioreactor was inoculated with activated sludge from a plant treating primarily domestic wastewater. The pilot-scale bioreactor was inoculated with granular sludge from an upflow anaerobic sludge blanket (UASB) reactor and an activated sludge plant treating industrial wastewater from an Akzo Nobel site in Rotterdam, the Netherlands.

Mineral salts medium

Bromide-free mineral salts medium was used to feed the laboratory-scale gas-lift reactor. This medium contained the following minerals salts (per liter of deionized water): 0.10 g $MgSO_4 \bullet 7H_2O$, 0.50 g $(NH_4)_2HPO_4$, 3.10 g K_2HPO_4, 1.70 g NaH_2PO_4, 1.7 mg Na_2SeO_3, 0.13 mg $NiSO_4 \bullet 6H_2O$, 0.5 mg resazurin (redox indicator), 0.1 ml trace element solution [28]. Bromate and chlorate were added to the mineral salts medium as sole electron acceptors. The chlorate and bromate concentrations were varied during the experiments. Only bromate was added to bromide-free mineral salts medium to assess the bromate-reducing activity.

Influent of the pilot-scale reactor

The pilot-scale reactor was fed with effluent from the scrubber of an incinerator. The effluent used contained high levels of inorganic compounds. Besides chloride, chlorate, and bromate, the effluent from the incinerator also contained small amounts of hypochlorite. Since hypochlorite is a biocide, removal of this compound before biological treatment is a prerequisite. Hypochlorite was therefore reduced to chloride with an excess of urea. The urea also acted as the nitrogen source. The water used was also supplemented with 15 mg l^{-1} PO_4^{-3} and micronutrients [28]. The carbon dioxide used by hydrogen-utilizing microorganisms as a carbon source was sufficiently present in the wastewater as carbonate and bicarbonate. The effluent of the scrubber was diluted with process water to obtain an influent of the bioreactor with a conductivity of 25 ± 5 mS cm^{-1}. Conductivity quantifies the anions such as chloride, carbonate, and bicarbonate present in the influent.

Laboratory-scale gas-lift reactor

The laboratory-scale gas-lift bioreactor used in this study was made of glass with an external gas loop (Applikon, Schiedam, the Netherlands). The working volume of the reactor was 1.3 l and the volume of the settler was 1.2 l (Fig. 1). The reactor contained 80 g l^{-1} pumice particles as a support material for biofilm formation. The reactor was kept at 30°C with a water jacket. Hydrogen was sparged into the reactor through a stainless steel sintered plate (20 μm). The gas flow was

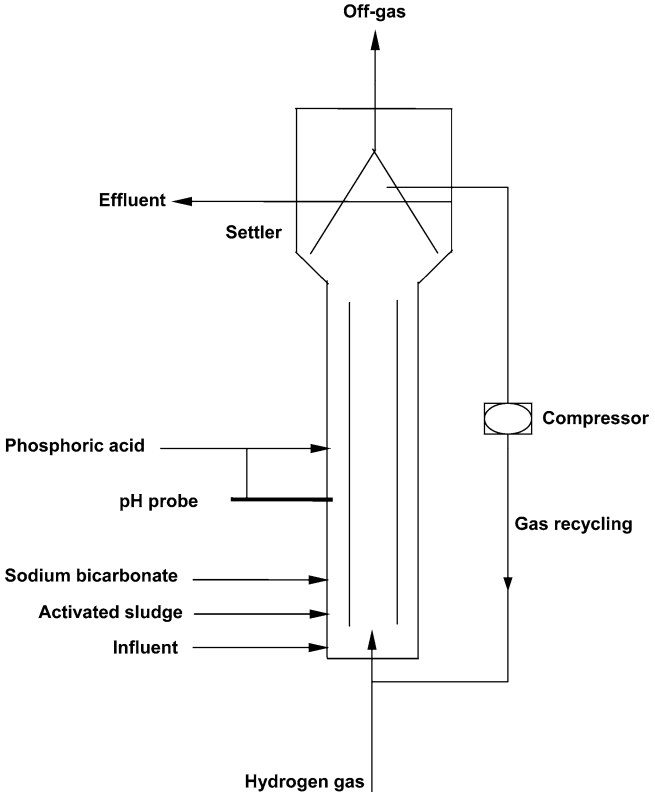

Fig. 1 Schematic representation of the laboratory-scale hydrogen gas-lift bioreactor

recycled with a compressor pump (KNF Neuberger, Freiburg, Germany) at a flow rate of 200 l h^{-1}. Influent hydrogen gas was delivered into the gas recycle stream at a rate of 3 l h^{-1}. Influent hydrogen gas flow, off-gas flow, and total gas volumes were monitored with mass flow controllers (type 5850S controller, 5860S meter, flow computer 405A; Brooks Instrument, Veenendaal, the Netherlands) connected to a user interface program (Smart control series 0160; Brooks Instrument). The pH was maintained at 7.5 with a 7.5% solution of phosphoric acid, using a pH-electrode connected to a pH controller (ADI 1020; Applikon, Schiedam, the Netherlands). The influent (mineral salts medium with chlorate, bromate) and excess sodium hydrogen carbonate (halo-oxo acid:sodium hydrogen carbonate molar ratio of 1:1) were supplied to the reactor separately, using peristaltic pumps (Gilson Minipuls 3; Meyvis & Co., Bergen op Zoom, the Netherlands). All tubing used for the experimental set-up was made of polytetrafluoroethylene. Inoculation of the reactor was conducted by the continuous addition of an activated sludge suspension (500 mg l^{-1} dry weight) at a rate of 1 ml h^{-1}.

Pilot-scale gas-lift bioreactor

The pilot-scale gas-lift bioreactor experiments were performed in a polyethylene reactor with a working volume of 45 l and a 30-l settling tank with an external gas loop. The diluted pretreated effluent of the scrubber was pumped from a storage tank into the gas-lift bioreactor. The reactor and storage tank were placed in a container. The pH was maintained at pH 8.0–8.5 throughout the pilot study. The temperature varied over 34–36°C. To increase the diversity of microorganisms present in the inoculum of the reactor, a mixture of activated sludge and granular sludge (1:1) was used. Chlorate-reducing bacteria have been detected in many ecosystems and wastewater treatment plants [7, 30]. In the pilot-scale gas-lift reactor, microbial cells occurred as flocs formed due the use of a flocculating agent, the density of which was sufficient for settling in the clarifier. Initially, the reactor was fed with a batch of diluted effluent from the scrubber. The hydraulic retention time (HRT) was decreased stepwise from 24 h to 6 h. Subsequently, the reactor operated at HRTs of 6 h and 4 h and received diluted effluent from the scrubber with varying concentrations of bromate and chlorate. Samples were collected at different time-intervals. Chlorate, bromate, chloride, and bromide were estimated in the influent and effluent of the bioreactor. The use of hydrogen gas was calculated from the influent-gas and off-gas flows and the hydrogen gas concentration in the off-gas.

Determination of activities

The bromate-reducing activity of the biomass from the laboratory-scale reactor was determined in 110-ml gas-tight glass bottles, which were 10% filled with bromide-free mineral salts medium. Active biomass on pumice particles was withdrawn from the laboratory-scale reactor whenever steady-state conditions were reached at a HRT of 24 h with chlorate and bromate concentrations of 6.3 g l^{-1} and 0.8 g l^{-1}, respectively, in the influent. The pumice particles were washed with a potassium dihydrogen phosphate buffer (2.7 g l^{-1}, pH 7) twice before use. Washed pumice particles containing 50 mg biomass-carbon g^{-1} pumice particles were added to the bottles. The gas phase and the medium were flushed with nitrogen immediately after inoculation. Hydrogen gas was supplied by injection of 20-ml volumes, using a gas-tight syringe. The activity of the microorganisms was determined by measuring the increase in bromide from bromate over 8 h at 30°C. First, the activity was determined at bromate concentrations of 13, 27, and 54 mg l^{-1}. The effect of temperature on the activity at 27 mg l^{-1} bromate was checked in a temperature-controlled shaking water bath (GFL, Burgwedel, Germany). To obtain various salt concentrations, batch cultures were augmented with 0, 10, 20, 30, 40, and 80 g l^{-1} sodium chloride before the start of each experiment. For the pH-dependence experiments, the pH values of the batch cultures were adjusted with either potassium dihydrogen phosphate buffer (18.8 g l^{-1}) or sodium borate buffer (3.1 g l^{-1}), to attain the desired pH values. Bottles used to assess the influence of salt concentration and pH on the bromate-reducing activity were incubated at 30°C. The activities were determined in triplicate; and analyses did not vary by more than 20%.

Analytical methods

The nonpurgeable organic carbon and total inorganic carbon were determined using a total inorganic carbon apparatus (Shimadzu, s'Hertogenbosch, the Netherlands). For biomass-carbon determinations, the biomass was liberated from the pumice particles, using an ultrasonic treatment (10 min, 375 W). A period of 30 min of ultrasonic treatment did not result in an increase in biomass-carbon. Samples were acidified to permit the removal of carbon dioxide by purging with nitrogen prior to injection into the apparatus.

Chlorate, bromate, chloride, and bromide were determined by ion chromatography (Dionex −120), using (suppressed) conductivity detection. The columns used were AG9-HC (guard) and Ionpac AS-9-HC. The eluent consisted of 0.95 g l^{-1} Na_2CO_3 at a rate of 1.0 ml min^{-1}. The injection volume was 50 µl.

Hydrogen gas was determined with an Interscience HR GC 8,000 S gas chromatograph equipped with a thermal conductivity detector (HWD 430; Carlo Erba, Milan, Italy) at 300°C. The injection (100 µl, split ratio 1:25) temperature was 200°C. The capillary column (Chrompack, Middelburg, the Netherlands) used was a molecular sieve (5 Å, 30 µm film) with a length of 25 m.

The column temperature was set at 80°C and the nitrogen gas flow was 50 ml min^{-1}.

Proton activity was measured with a model P207 pH meter (Consort, Turnhout, Belgium). Conductivity was estimated with a model LF 318 conductimeter (WTW, Weilheim, Germany).

Results and discussion

Reduction of halo-oxo acids in gas-lift reactors

Feeding of influent that contained 2 g l^{-1} chlorate was immediately started and the HRT was set at 48 h. Biological activity in the gas-lift bioreactor became evident as complete chlorate reduction; and the concomitant stoichiometric formation of chloride was noticed within 2 weeks. Within another 2 weeks, the hydraulic retention time was reduced from 48 h to 6 h without loss of complete chlorate removal. From this moment (day 0), the bromate concentration in the influent was set at 0.34 g l^{-1} (Fig. 2). Complete bromate removal was observed after 10 days of operation. The stoichiometric formation of bromide demonstrated that no accumulation of intermediates occurred. Next, the effects of varying concentrations and ratios of bromate and chlorate were investigated. An increase in the bromate concentration in the influent from 0.34 g l^{-1} to 0.68 g l^{-1} resulted in a decrease in the degradation efficiency of chlorate. Complete chlorate removal was recovered within a few days. However, only a partial reduction of bromate was achieved. Upon increasing the chlorate concentration from 2.0 g l^{-1} to 4.0 g l^{-1}, complete reduction of both bromate and chlorate to bromide and chloride, respectively, was accomplished. A further increase in the bromate loading rate by doubling the bromate concentration from 0.68 g l^{-1} to 1.36 g l^{-1} resulted in a full decline in bromate and chlorate reduction. This indicates that bromate exerts a toxic effect that probably depends on the ratio of chlorate and bromate in the influent. Omitting the bromate from the influent at day 48 resulted in a complete recovery of the total reduction of chlorate present at 4.0 g l^{-1} in the influent within 2 days (Fig. 2). Taking just 2 days to recover from inactivation is very rapid, compared to the bioreactor start-up period. The ready recovery of chlorate reduction upon the omission of bromate suggests that only de novo protein synthesis of chlorate reductase is required.

To determine the chlorate required for bromate removal more accurately, an experiment was undertaken by running the gas-lift reactor with concentrations of chlorate and bromate of 6.3 g l^{-1} and 0.8 g l^{-1}, respectively (Fig. 3). The HRT was set at 24 h. Under these conditions, both chlorate and bromate were stoichiometrically converted into chloride and bromide, respectively. A stepwise decrease in the chlorate concentration to 2.5 g l^{-1} did not show any decrease in the removal of bromate (Fig. 3). A further decrease in the chlorate concentration to 1.8 g l^{-1} resulted in a decline in bromate removal. A chlorate:bromate molar ratio of at least 3:1 therefore allowed chlorate-reducing microorganisms to reduce bromate to bromide. Influent containing chlorate and bromate at a molar ratio of 2:1 resulted in complete inactivation of the reducing activity in the gas-lift bioreactor (Fig. 3).

Cometabolic reduction of bromate was also studied in a fixed-bed bioreactor with denitrifying bacteria operated at a hydraulic retention time of 30 min [11]. Nitrate present in the influent of the bioreactor supported a microbial population capable of converting the bromate. The bioreactor removed nitrate (ca. 90 mg l^{-1})

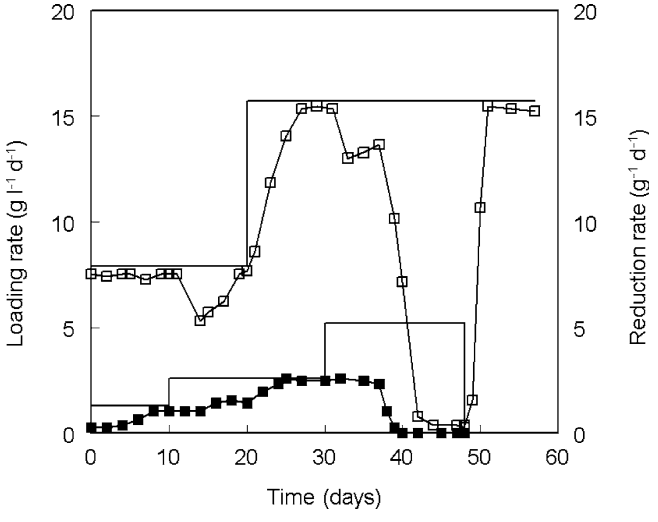

Fig. 2 Reduction rates of bromate (*filled squares*) and chlorate (*open squares*) in a laboratory-scale hydrogen gas-lift bioreactor operated at an HRT of 6 h with varying concentrations of chlorate and bromate in the influent. The *solid lines* represent the loading rates of the halo-oxo acids

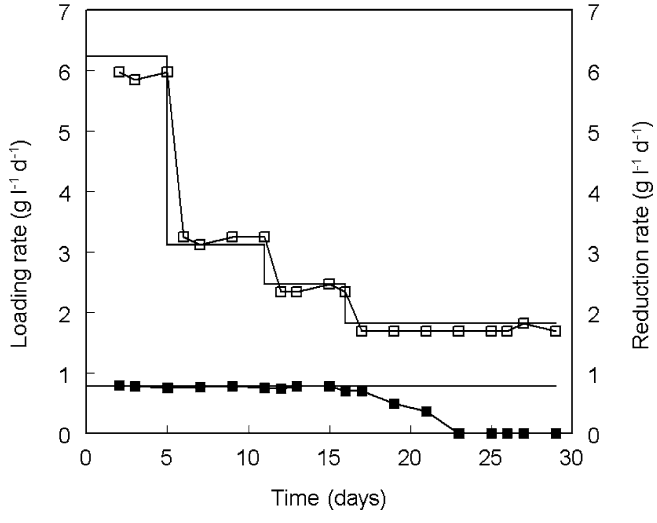

Fig. 3 Reduction rates of bromate (*filled squares*) and chlorate (*open squares*) in a hydrogen gas-lift bioreactor operated at an HRT of 24 h with decreasing concentrations of chlorate in the influent. The *solid lines* represent the loading rates of the halo-oxo acids

and bromate (10–30 μg l^{-1}). The nitrate:bromate molar ratio required to remove bromate was high, compared with the chlorate:bromate molar ratio.

Optimal conditions for bromate reduction

To test the ability of the microorganisms present in the gas-lift bioreactor to reduce bromate under various conditions, pumice particles from the gas-lift bioreactor were incubated in batch cultures with bromate. The bromate-reducing activity at a bromate concentration of 27 mg l^{-1} produced 0.44 mg bromide min^{-1} mg^{-1} biomass-carbon. The bromate-reducing activity at 54 mg l^{-1} bromate was not inhibited, compared with the activities measured at 13 mg l^{-1} and 27 mg l^{-1} bromate.

Perchlorate- and chlorate-reducing microorganisms are inactivated by molecular oxygen [1, 7, 27]. As expected, replacing 20% of the hydrogen gas by oxygen in the headspace of batch cultures with resulted in a total loss of bromate-reducing activity. The activity could be restored after the oxygen was removed [26].

To test the effects of pH on bromate-reducing activity, batch cultures were incubated at 30°C at various pH values. No activity was observed at pH 6 and pH 10. The highest activity was observed at pH 7–8 (Fig. 4). The slightly alkaline pH optimum found for bromate-reducing microorganisms is common among lithoautotrophic organisms [5]. The highest bromate-reducing activity was observed at approximately 35°C (Fig. 5). No activity was observed at 45°C. Activities measured in the batch experiments showed that the biological bromate reduction was not influenced by sodium chloride concentrations ranging from 0 g l^{-1} to 40 g l^{-1}. A 50% reduction was only found at 80 g l^{-1} sodium chloride. Growth of perchlorate-degrading microorganisms was observed at salinities of 1–15% [19]. The limited effect of sodium chloride on chlorate-reducing microorganisms may be the result of an adaptation to the end-products of chlorate and bromate reduction.

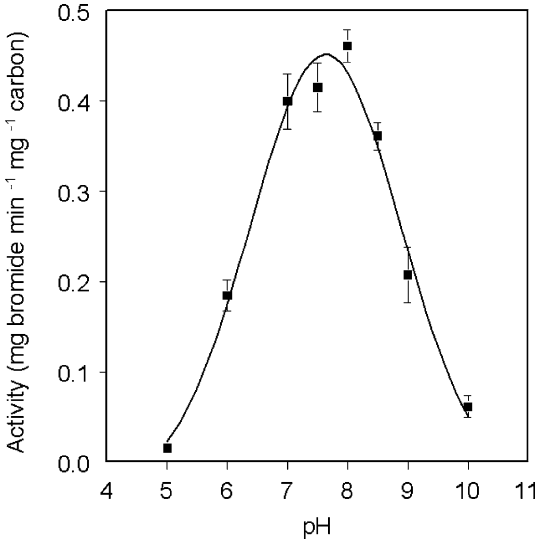

Fig. 4 Effect of pH on the reduction rate of bromate to bromide by microorganisms attached to pumice particles from the gas-lift reactor. The activities were measured at 30°C. Each point represents the mean (±SD) of three replicates

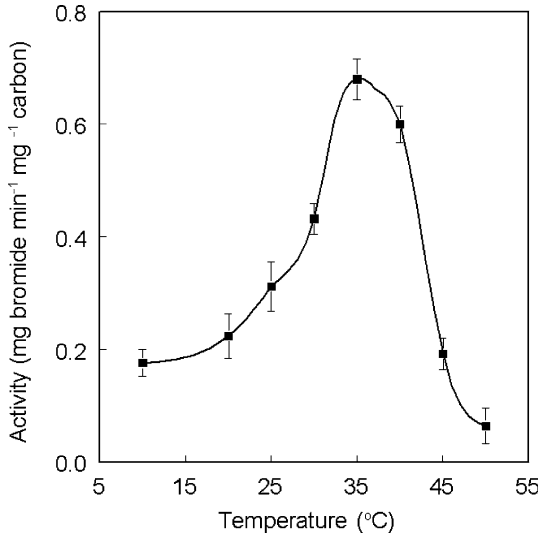

Fig. 5 Effect of temperature on the reduction rate of bromate to bromide by microorganisms attached to pumice particles from the gas-lift reactor. The pH was kept constant at pH 7.5. Each point represents the mean (±SD) of three replicates

Bromate reduction in a pilot-scale reactor

The concept of a gas-lift bioreactor for treating bromate- and chlorate-contaminated effluents was further tested in a pilot-plant reactor. Initially, halo-oxo acid reduction was tested with one batch of pretreated diluted effluent from the scrubber containing 1.9 g l^{-1} chlorate and 0.2 g l^{-1} bromate. The influent also contained high concentrations of (bi)carbonate, i.e. 7 g l^{-1} of inorganic carbon. At a HRT of 24 h, microorganisms used chlorate and bromate following an acclimatization period of less than 2 weeks. A minimum HRT of 6 h was necessary to achieve chlorate and bromate removal in excess of 90%. In the pilot reactor, 5 mol hydrogen were consumed to reduce 1 mol halo-oxo acid. The stoichiometric relationship for the reduction of halo-oxo acids with hydrogen gas is as follows:

$$XO_3^- + 3H_2 \rightarrow X^- + 3H_2O$$

Consequently, approximately 40% of the hydrogen gas was utilized for anabolic reactions.

During the last period, pilot tests were conducted with fluctuating halo-oxo acid concentrations in the influent. The concentrations of chlorate in the influent of the bioreactor ranged from 0.4 g l^{-1} to 1.6 g l^{-1}. The feed concentrations of bromate varied between 0.1 g l^{-1} and 0.4 g l^{-1}. The effluent concentrations remained to some extent constant with the fluctuating influent concentrations. An increase in the concentrations of the halo-oxo acids by a factor of two did not result in a decrease in the

conversion of the halo-oxo acids. The chlorate:bromate molar ratio was usually higher than six. A chlorate:bromate molar ratio of four resulted only in a temporary decrease of the bromate reduction (ca. 80%). During this period, chlorate reduction was always >95%. Almost complete loss of bromate reduction was observed during a malfunction, effecting an influent with a conductivity of 45 μS cm^{-1}. Finally, at a HRT of 4 h, the maximum conversion rates achieved for chlorate and bromate were 9 g l^{-1} day^{-1} and 2.3 g l^{-1} day^{-1}, respectively. The maximum conversion rate of bromate was comparable with the maximum rate (i.e. 2.5 g l^{-1} day^{-1}) achieved in the laboratory-scale reactor.

Conclusions

The ability of microorganisms to reduce chlorate and bromate under a variety of conditions demonstrates that halo-oxo acid-contaminated water can be treated. Almost complete removal of bromate was maintained at a HRT of 6 h, using a hydrogen gas-lift bioreactor with external gas recirculation. The pilot-plant studies demonstrated the operating characteristics, reliability, and effectiveness of the process for treating bromate-containing wastewater. The gas-lift bioreactor thus looks very promising for the treatment of wastewater containing both chlorate and bromate generated by an incinerator.

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