Chapter 18
EVALUATION OF BIOLOGICAL REACTORS TO DEGRADE PERCHLORATE TO LEVELS SUITABLE FOR DRINKING WATER

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INTRODUCTION

Perchlorate (ClO₄⁻) contamination of groundwater has been estimated to potentially affect the drinking water supplies of at least 12 million people in the United States.¹² Perchlorate is used as an oxidizer with solid missile and rocket fuels (up to 70% w/w), in automobile air bag inflation systems, and is reported to be present in lawn fertilizers (< 0.84%).³⁴ Perchlorate is a human health concern due to its ability at high doses to interfere with iodine uptake and the ability of the thyroid to regulate hormones and metabolism. There is currently no federal drinking water standard for perchlorate, but many states have adopted an interim provisional drinking water standard of 18 ppb. Perchlorate is stable and extremely soluble in water, and is not efficiently removed by conventional activated carbon and ion exchange processes. However, perchlorate is used as an electron acceptor by a number of bacterial strains under anoxic conditions.⁵

The use of a biological water treatment system in the U.S. presents both societal and engineering challenges. The societal challenge results from the fact that biological treatment of drinking water is not generally accepted or practiced by the water industry. There is currently only one specific-contaminant biological treatment system in the U.S. that treats water for potable uses.⁶ This system, located in Coyle, Oklahoma, is designed to biologically reduce

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nitrate in water from average concentrations of 12 mg L⁻¹ to <10 mg L⁻¹. The biological treatment system removes nitrate to lower levels (2 mg L⁻¹), but in order to minimize treatment costs part of the water is bypassed around the system and recombined with treated water to achieve system design specifications. In Europe, there are many biological systems have been used to pretreat drinking water and remove nitrate.⁷ All around the world unintentional biological treatment of water occurs indirectly as a result of water filtration in a sand or granular activated carbon (GAC) filter, unless deliberate steps are taken to periodically chlorinate the filter media.⁸ Bacteria naturally occur at concentrations of about 10⁴ - 10⁷ cells per mL in streams, lakes and rivers. When this water is filtered, both the bacteria and particulate organic matter are removed, producing a bacterial biofilm on the support medium. These attached bacteria can grow and degrade filtered particles and dissolved organic matter in the water. Under such conditions, biological treatment of the water occurs resulting in lower effluent concentrations of organic matter. In order to limit the distribution of potentially pathogenic bacteria in the water distribution system, water is disinfected before leaving the treatment plant.

The biological treatment of water to remove perchlorate presents some unique engineering challenges relative to nitrate. Although biological systems have been designed to remove nitrate, firms in the U.S. have little experience in designing such systems. A more important factor in design than experience of a particular firm, however, is the engineering challenge that arises from designing a system to achieve the level of treatment required for perchlorate compared to that for nitrate. Nitrate must be removed to only <10 mg L⁻¹ for drinking water standards. Most systems are therefore designed to treat nitrate in water from concentrations less than one order-of-magnitude higher to a concentration that is still relatively large compared to a perchlorate concentration of <0.018 mg L⁻¹. Perchlorate concentration in contaminated sources vary from these levels up to on the order of 10⁵ mg L⁻¹, thus potentially requiring removal over five orders of magnitude (from 10³ to 10⁻²). The engineering challenge for the design of perchlorate bioreactors is therefore how to ensure this level of treatment efficiency over such a large concentration range.

There are few alternatives to biological treatment of perchlorate contaminated water, whether the water is used as a potable water source or simply treated and released back into the environment. Physical removal using ion exchange, for example, is possible, but removal must be coupled to a process (chemical or biological) to treat the contaminated brine solution. Even if the perchlorate in the brine is destroyed, the concentrations of other anions in high-salinity brine solutions present residual treatment difficulties. There is recent work on suggesting that ammonia-based regeneration solutions could be used instead of salt to eliminate the production of salting brine solutions,⁹ but this technology is not fully developed. Although biological treatment therefore appears to be the most cost effective method of perchlorate treatment, there remain engineering issues on how to design the most effective treatment system. The purpose of this paper is therefore to discuss the options for different types and configurations of reactors, and to comment on advantages and disadvantages of these methods to treat perchlorate contaminated water to drinking water levels.

EXPERIMENTAL

Perchlorate is used by bacteria under anoxic conditions (in the absence of oxygen) as an electron acceptor. Typically, in situ organic substrate concentrations under natural conditions limit bacterial growth. To achieve perchlorate reduction in a reactor requires the absence of oxygen (or its consumption by the bacterial assemblage), a source of energy (either organic matter or inorganic sources such as hydrogen gas), and carbon (organic matter or dissolved
CO$_3$). Thus, the primary purpose of the reactor is to selectively stimulate the growth of perchlorate reducing microbes (PRMs) over the growth of other microbes capable of growing in the reactor.

**Reactor Kinetics**

Bacteria growth can be assumed to limited by the concentration of one substrate (electron and energy donor) and one electron acceptor (such as oxygen or perchlorate). The rate of cells growth, $r_X$, is

$$ r_X = (\mu - b) X = \left( \mu_{\text{max}} \frac{S}{K_S + S} \frac{E}{K_E + E} \right) - b \right) X \tag{1} $$

where $\mu$ is the growth rate, $b$ the decay rate, $\mu_{\text{max}}$ the maximum growth rate, $X$ is the biomass concentration, $S$ the substrate and $E$ the electron acceptor concentrations, and $K_S$ and $K_E$ the half saturation constants of the electron donor and acceptor. Assuming bacterial growth is coupled to uptake (i.e., cells do not store substrate without cell division) and that by definition no substrate is used during cell decay, the rate of substrate utilization is

$$ r_S = -\frac{\mu X}{Y_{XS}} = -\frac{\mu_{\text{max}} X}{Y_{XS}} \frac{S}{K_S + S} \frac{E}{K_E + E} \tag{2} $$

where $Y_{XS}$ is the cell yield defined as the mass of cells produced per mass of substrate used. The utilization rates of substrate and electron donor ($r_E$) are assumed to be coupled and cell decay requires cell respiration, so that

$$ r_E = Y_{SE} (r_S + bX) \tag{3} $$

where $Y_{SE}$ is the mass of substrate used per mass of electron acceptor. This assumes that all biomass is degradable, although typically 20% of the cell mass is not $^{10}$.

There is also a minimum concentration of substrate necessary to maintain cells due to energy requirements for cell maintenance, which can be calculated$^{10}$ as

$$ S_{\text{min}} = \frac{b K_S}{\mu_{\text{max}} - b} \tag{4} $$

With this relationship we can see that some oxidizable substrate will remain in the reactor.

The detention time necessary in a CSTR for a given substrate concentration is:

$$ \theta = \frac{1}{\mu - b} \tag{5} $$

Because a CSTR is completely mixed, $\mu$ is the cell growth rate at the effluent substrate concentration.

**Kinetic Constants**

There is little information available on perchlorate degradation kinetics, and therefore for the purposes of comparing potential reactor advantages and disadvantages, we will have to
allow for assumption of typical values. A typical endogenous decay constant\textsuperscript{10} is $b = 0.01 \text{ d}^{-1}$ and we can assume a typical cell yield of $Y = 0.5 \text{ g cells (g acetate)}^{-1}$ and perchlorate yield\textsuperscript{11} of $1.9 \text{ mg acetate (mg-perchlorate)}^{-1}$. Kinetics constants recently measured in our laboratory suggest values of $\mu_{\text{max}} = 0.2 \text{ h}^{-1}$, $K_p = 20 \text{ mg perchlorate L}^{-1}$ and $K_A = 300 \text{ mg acetate L}^{-1}$.

<table>
<thead>
<tr>
<th>Suspended Cell Reactors</th>
<th>Fixed-film Reactors</th>
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<tbody>
<tr>
<td>- Completely mixed reactor (no cell recycle): CSTR</td>
<td>- Packed bed-saturated flow: PFR</td>
</tr>
<tr>
<td>- Activated sludge- mixed reactor with cell recycle (many configurations): CSTR and PFR</td>
<td>- Packed bed- unsaturated flow (trickling filter): PFR</td>
</tr>
<tr>
<td>- Upflow anaerobic sludge blanket: PFR</td>
<td>- Fluidized bed: CSTR</td>
</tr>
<tr>
<td></td>
<td>- Rotating biological contactor: CSTR</td>
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</tbody>
</table>

**Reactor Types**

The different types of reactors that could be used to treat perchlorate contaminated water are listed in Table 1 according to whether they are based on suspended cells or fixed-films attached to either a carrier particle or fixed medium. These reactor types are also indicated as a plug flow reactor (PFR) or completely mixed/stirred constant-flow reactor (CSTR). Of the different reactors listed in Table 1, only a few have been used for biological water treatment for nitrate or perchlorate removal (Table 2). These reactors are all fixed film systems, with both PFR (packed bed) and CSTR (fluidized bed) reactors having been used to date.

**RESULTS AND DISCUSSION**

To compare the potential for different bioreactor systems to treat drinking water, it was assumed that perchlorate needed to be removed to essentially non-detectable levels and that the acetate feed had to be removed to very low levels. Low levels of acetate can also be achieved outside the main reactor in a downstream polishing unit (for example an aerobic filter) but for economic reasons (to minimize purchasing costs of acetate) we would like to have the lowest possible acetate concentrations entering and leaving the reactor. Using the above equations and estimates of kinetic constants, a suspended growth reactor does not appear to be feasible for perchlorate degradation. If we assume for the moment that only acetate limits the growth rate of the cells, then the detention time would be calculated as:

$$
\mu = \frac{\mu_{\text{max}} S}{K_S + S} = \frac{0.2 \text{ h}^{-1} (1 \text{ mg L}^{-1})}{(300 \text{ mg L}^{-1}) + (1 \text{ mg L}^{-1})} \frac{24 \text{ h}}{d} = 0.016 \text{ d}^{-1}
$$

(6)

$$
\theta = \frac{1}{\mu - b} = \frac{1}{(0.016 \text{ d}^{-1}) - (0.01 \text{ d}^{-1})} = 62 \text{ d}
$$

(7)

Thus, we would have to have a cell detention time of 62 days to remove acetate and perchlorate to low levels. This detention time would not permit any type of suspended growth reactor unless the reactor had a cell recycle line such as an activated sludge system. However, this is an unusually long detention time (2 months) and therefore makes even an activated sludge system questionable. If effluent substrate concentrations are allowed to be higher, the required detention time could be dramatically reduced making this system feasible for
Table 2. Reactors used to remove nitrate and perchlorate

<table>
<thead>
<tr>
<th>Named Reactor</th>
<th>Type of system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biological Activated</td>
<td>Packed bed reactor using an ethanol feed, located in Eragny, France.</td>
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<tr>
<td>Filter (BAF)</td>
<td></td>
</tr>
<tr>
<td>&quot;Denipour&quot;</td>
<td>Fluidized bed system fed ethanol using buoyant carriers in Germany.</td>
</tr>
<tr>
<td>&quot;Denitropour&quot;</td>
<td>Packed bed reactor in Germany with a hydrogen gas feed.</td>
</tr>
<tr>
<td>&quot;BioDen&quot;</td>
<td>Packed bed reactors in series (anoxic then aerobic) based on an acetate feed.</td>
</tr>
<tr>
<td></td>
<td>First drinking water nitrate removal system in U.S.</td>
</tr>
<tr>
<td>Fluidized bed reactor</td>
<td>GAC and sand supported fluidized bed studies.</td>
</tr>
<tr>
<td>PSU-O4 Systems</td>
<td>Packed bed reactor systems. One system is a saturated-flow packed bed reactor</td>
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<td></td>
<td>system fed acetate; the other is an unsaturated packed bed reactor fed hydrogen gas</td>
</tr>
</tbody>
</table>

wastewater-type treatment. For example, a suspended growth reactor system was developed to degrade perchlorate in wastewaters where brewer’s yeast was used as a feed source. Perchlorate needed to be reduced only to less than 0.5 mg L\(^{-1}\) level, and a high organic matter concentration in the effluent was not a concern since wastewater could be further treated to removed this material. Thus, while a CSTR system is possible for wastewater treatment, from this brief analysis it appears that its use would be limited for water treatment. Therefore, only fixed-film systems need to be further considered.

Fixed Film Reactor Analysis

Among the fixed-film systems, the main factor is whether the system is completely mixed or not. Of the four types of fixed film reactors listed in Table 1, RBCs need not be further considered as they have not been previously used for water treatment. If we neglect consider the unsaturated flow reactor as a variation on a packed bed reactor, that leaves two types of fixed film systems: a packed bed PFR reactor, and a fluidized bed CSTR system. A detailed modeling comparison of these two types of reactors is beyond the scope of this analysis. However, with some simplifications, the advantages and disadvantages of these two reactors can be considered.

First, let us consider the fluidized bed reactor. In a fluidized bed reactor bacteria grow as a thick biofilm on a packing material, and the contents of the reactor (water and biofilm) are recirculated fast enough to keep the system well mixed. As a result, all of the bulk water phase in the reactor is at the same concentration. The concentration of the acetate and perchlorate at the surface of the biofilm is therefore quite low because it is equal to the desired effluent concentration. For nitrate removal, low effluent concentrations allow reactions to proceed at appreciable rates in the reactor biofilm because nitrate must only be removed to < 10 mg L\(^{-1}\). However, because extremely low effluent concentrations are required for perchlorate water treatment, there will be correspondingly low reaction rates at the surface of the biofilm. As the chemicals diffuse into the biofilm, these concentrations are further reduced resulting in even lower growth rates. The minimum substrate concentration that can be achieved under steady growth conditions for acetate removal based on the kinetics given above is
This indicates the lowest acetate concentration that could be achieved is still only around 1 mg L\(^{-1}\). At this concentration, the rate of cell growth in a CSTR will be very low since all cells must be growing in the CSTR at the bulk substrate concentration or lower.

The primary disadvantage of the fluidized bed reactor is therefore the slow growth rates of all cells in the reactor due to the desired low effluent substrate concentration. If the substrate concentration is raised to keep growth rates in the reactor higher, there can be other problems in the reactor. When substrate is present at large concentrations relative to cell growth rates, substrate is not oxidized but instead is processed by the bacteria rapidly into excreted exopolymers. This production of copious amounts of polymer can result in gelatinous particles which stick together and cause the process to fail. If a fermentable substrate is used, it is possible to gradually displace the perchlorate- or nitrate-reducing population with a biofilm that just ferments the substrate. This can cause a loss of reactor performance despite considerable biofilm growth and substrate transformation to other products.

The main advantage of the fluidized bed reactor is the ability to maintain very high biomass concentrations in the reactor creating the potential for small, highly efficient, reactors. However, biomass concentrations can get too high. In nitrate removal systems bed particles are recycled out of the reactor in order to shear off excess biofilm. In perchlorate systems operated at very low effluent perchlorate concentrations, the long detention times of the biomass for a suspended growth CSTR (calculated above) suggest that much of the biomass will decay in the reactor. A second advantage of a fluidized bed reactor is that they are well known to produce suspended cell concentrations in their effluent (because particles are cleaned in a side process) and therefore post treatment filtration is often not necessary. However, the need to ensure complete removal of unused substrate makes it likely that any such system would have a biologically aerated filter following the process.

The packed bed reactor also has advantages and disadvantages. The main advantages of the packed bed reactor configuration result from its operation as a PFR. Because concentrations of substrate and electron donor are large at the reactor entrance, the perchlorate degradation rates at the PFR entry are very large compared to those occurring in a CSTR like the fluidized bed reactor and theoretically a PFR reactor under these conditions can be smaller than a CSTR system. Using equation 2 and assuming that we have an identical biomass concentration and yield and maximum kinetic constants, and neglecting decreases in chemical concentrations in the biofilm, we can compare these rates in the fixed bed to fluidized bed as:

\[
\frac{r_s \text{ (packed bed)}}{r_s \text{ (fluidized bed)}} = \frac{[S/(K_S + S)] [E/(K_E + E)]_{\text{packed bed}}}{[S/(K_S + S)] [E/(K_E + E)]_{\text{fluidized bed}}}
\]

For comparison, we will assume that both reactor achieve a perchlorate reduction from 3 to 0.010 mg L\(^{-1}\) and that acetate is reduced from 6.7 to 1 mg L\(^{-1}\) based on our observed yield. For the fluidized bed reactor, the effluent concentrations are present everywhere in the reactor, but for the packed bed reactor the concentrations vary over the reactor length. Substituting in the values of the constants, we have at the beginning of the reactor:

\[
\frac{r_s \text{ (packed bed)}}{r_s \text{ (fluidized bed)}} = \frac{[6.7/(300 + 6.7)] [3/(20 + 3)]_{\text{packed bed}}}{[1/(300 + 1)] [0.010/(20 + 0.010)]_{\text{fluidized bed}}} = 1720
\]
Thus, we can see that we potentially have rates 1720 times greater at the inlet of the packed bed reactor than the inlet of the fluidized bed reactor. At the reactor exit the rates in the reactors would be equal. These high rates help achieve a small reactor size and help perchlorate-reducing conditions to predominate over other less desirable rates such as fermentation.

The main disadvantage of the PFR is the potential for reactor plugging at the reactor entry, and insufficient biofilm at the reactor exit. Because substrate oxidation rates are very large at the entrance, the biofilm will grow faster and accumulate to a greater extent at the entrance than at the exit. In order to reduce clogging due to biofilm buildup, packed bed reactors are equipped with some method to remove excess biofilm. During the biofilm removal process, flow to the reactor is temporarily halted and the biofilm is removed. One approach to remove biofilm, if the media size is small, is to "backwash" the bed like a water treatment filter. During backwashing, the media is fluidized and the biofilm is knocked off the particles and removed from the reactor. Internal rakes can be placed in the bed to help break up the particles. When heavy packing material such as plastic rings or saddles are used as a support structure, the bed is usually cleaned by an air-scour stream. Although this exposes the biofilm to air, most perchlorate reducing microbes are facultative and will rapidly remove the oxygen when the reactor is placed back into operation. The biofilm produced from either process can be settled out and disposed of as a non-hazardous sludge, and the wash water recycled back to the reactor feed.

Operating Experience with Perchlorate-Degradating Reactor Systems

The treatment of perchlorate in drinking water is a relatively new problem, and therefore there is little data available in the refereed literature at this point to base comments on larger scale system performance. Research at Penn State has centered on two different fixed-film biological treatment processes to determine their feasibility for drinking water treatment. These systems are: a packed bed (slow sand filter) amended with soluble microbial carbon sources (acetate); and a hydrogen gas fed four-phase (hydrogen gas, water, biofilm, and support media), unsaturated trickle-type packed column. The development of the packed bed reactor is more advanced at this time and is being field tested. Our laboratory experiments have demonstrated that perchlorate can be completely removed, from 20 mg L\(^{-1}\) to less than 0.004 mg L\(^{-1}\), at detention times of 13 to 48 min in a sand-packed reactor.

A fluidized bed reactor system using granular activated carbon (GAC) was tested at a site in California. Perchlorate was reduced from 40 µg L\(^{-1}\) to below detectable levels (< 4 µg L\(^{-1}\)) at the same time nitrate removals of 99% were achieved (40–50 mg L\(^{-1}\) reduced to < 0.45 mg L\(^{-1}\)). Ethanol was used for the reactor feed and it was noted that a narrow range in the ethanol feed concentration (75 to 100 mg L\(^{-1}\)) was necessary to achieve ethanol concentrations below the analytical reporting limit (< 5 mg L\(^{-1}\)). Oxygen had to be reduced quickly in the reactor to < 0.1–0.2 mg L\(^{-1}\) for optimum reactor performance. Clumping of the GAC was noted when acetate concentrations exceeded 200 mg L\(^{-1}\), presumably to polymer production by the biomass as discussed above.

A series of laboratory tests using GAC and sand in a methanol- and ethanol-fed fluidized bed reactors. GAC performed better than sand and ethanol was superior to methanol in laboratory tests. A lack of substrate (ethanol) in the reactor effluent limited perchlorate destruction. Field tests are planned to test this system at large scale.

In conclusion, it appears that fixed film systems, such as packed and fluidized bed reactors can be used to treat perchlorate contaminated water to the very low levels suitable for drinking water. It is still too soon to decide what the optimal reactor configuration is for stable, long-term treatment of perchlorate contaminated water. The preliminary comparison of the fluidized
and packed bed reactor types suggests that higher rates of perchlorate reduction could be achieved in a packed bed systems. However, additional laboratory and field tests will be necessary to establish the long term feasibility of both of these reactor systems.

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REFERENCES


