HYBRID ADSORPTION-MEMBRANE BIOLOGICAL REACTORS FOR IMPROVED PERFORMANCE AND RELIABILITY OF PERCHLORATE REMOVAL PROCESSES

L.C. Schideman*, K.J. Hegger, E. Morgenroth
University of Illinois at Urbana-Champaign
Urbana IL, 61801, USA

B.J. Kim
U.S. Army Engineer Research and Development Center
Champaign, IL 61826, USA

ABSTRACT

This study introduces the novel HAMBgR process (Hybrid Adsorption Membrane Biological Reactor) and presents an application for the efficient removal of perchlorate from contaminated waters. This process combines the economic advantages of a microbiological treatment with the reliability of a physicochemical process. Batch isotherm experiments show that the ion-exchange adsorbents from this study can be effectively and continuously regenerated biologically in a single membrane bioreactor that is used for treating perchlorate contaminated waters. The presence of the ion-exchange resin in the HAMBgR process provides a physico-chemical backup to the biological process that was shown to reduce effluent perchlorate spikes by up to 97% in comparison to a conventional MBR that was subject to sudden changes in influent conditions.

1. INTRODUCTION

It is critical to the long-term success of the army mission to have efficient and reliable treatment techniques that can mitigate the potential environmental and health effects of core military functions to enhance soldier welfare, facilitate public acceptance, and maximize the impact of resources devoted to environmental management. Microbiological treatment processes can provide very cost-effective removal of many environmental contaminants that are produced and released as a result of core military activities. However, the application of microbiological treatment processes is often significantly hindered by unstable performance in the face of natural variations of influent concentrations, temperature, pH, etc. Additionally, microbial processes can experience problems related to the carryover of biomass to the effluent water.

To address the key limitations of currently available microbiological treatment processes, a new treatment process is introduced, the hybrid adsorption-membrane biological reactor (HAMBgR). The HAMBgR process integrates a granular adsorptive media into the mixed liquor of a membrane bioreactor (MBR), which addresses the biological instability problem by providing a temporary physicochemical sink for contaminants that maintains low effluent contaminant concentrations even while microbes are adapting to changing reactor conditions.

This novel hybrid process combination also improves on exclusively adsorption processes because continuous biological adsorbent regeneration avoids the cost, effort and undesirable sidestreams of concentrated contaminants that typically occurs during physicochemical adsorbent regeneration. Finally, the membrane used in the HAMBgR process serves to retain the adsorbent and all microbes in the reactor-- thus providing a reliable barrier to microbial carryover.

The key issue for the HAMBgR process concept is to demonstrate that biological adsorbent regeneration over many loading cycles can maintain significant working capacity after prolonged exposure to the microbial suspension. This paper presents original bench- and pilot-scale experimental work demonstrating this key feature of the HAMBgR treatment concept as it was developed and applied for the removal of aqueous perchlorate (ClO_4^-) from waters impacted by military activities. Perchlorate is an important emerging contaminant because it can impair proper thyroid function at low μg/L concentrations and has widespread occurrence in environmental water sources (Greer et al., 2005; Gullick et al., 2001; Tikkanen, 2006). Although there are some natural sources, perchlorate is most commonly associated with military applications, where it has been used as an oxidizer in mass quantities for munitions and solid rocket fuel.

Past studies have shown that perchlorate can be biologically converted to a harmless chloride ion form under anaerobic conditions using both organic electron donors and inorganic ones like hydrogen (Xu et al., 2003). Most previous work has focused on fixed-film processes

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using biologically active granular media filters or membrane diffuser reactors that use a membrane to feed hydrogen gas to a biofilm (Logan and LaPoint, 2002; Nerenberg and Rittmann, 2004). Ion exchange processes with strong and weak base anion resins have also been shown to effectively remove perchlorate although concentrated brine disposal can be problematic. In this study, we measured the performance of a conventional MBR and a HAMBgR process and compared them with each other.

2. MATERIALS AND METHODS

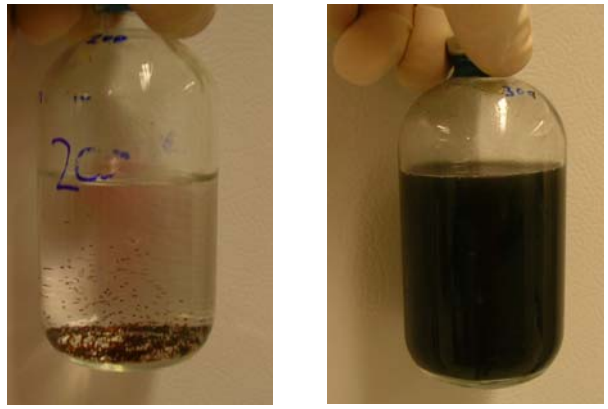
2.1 Ion Exchange Resins

Two different types of commercial anion exchange resins manufactured by Rohm and Haas (Philadelphia, PA) were selected for this study. Amberjet-4400 is a strong base anion (SBA) resin with a quaternary ammonium functional group, initially in the hydroxide form. Amberlite IRA-92 has a macroporous polystyrene matrix and a binary amine functional group that results in a weak base anion exchange (WBA) resin that is generally easier to regenerate. The amine functional group is in the free base form, which means that pH must be acidic for the resin to be fully effective, whereas SBA resins can generally operate indiscriminate of pH.

2.2 Batch Isotherms with Fresh and Biologically Regenerated Resins

To quantify and compare resin capacity over multiple cycles of biological regeneration, batch isotherm tests were conducted with fresh resin and biologically regenerated resins over sequential cycles of abiotic loading followed by biological regeneration. For these tests, serum bottles were first loaded with varying amounts of resin and 100mL of influent solution with a target initial ClO_4^- concentration of 100 mg/L (See Figure 1(a)). The bottles were then placed on a shaking table at a mixing rate of 240 rpm and effluent samples were analyzed periodically for perchlorate concentration until equilibrium was reached. Perchlorate samples were analyzed by ion chromatography using Dionex ICS-2000 with an AS-16 column.

After the resins reached equilibrium, active perchlorate reducing biomass (PRB) from the pilot reactor described below was added to the bottles along with hydrogen gas up to a pressure of 20-25 psi, simulating the excess hydrogen conditions of the pilot reactor (See Figure 1(b)). The bottles were replaced back on the shaking table and temperature was controlled at 34°C so that PRB could degrade all perchlorate in the bottles to below detection limit. Bottles were then decanted of the liquid, leaving behind only the biologically regenerated resin. The cycle was repeated up to six times with a fresh 100mL of influent feed for each resin amount, which varied from 30 – 650 mg per jar.



(a) (b)

Figure 1- Example of batch isotherm serum bottles during (a) abiotic loading (i.e., resin and influent water only) and (b) biological regeneration cycle (i.e., after adding hydrogen and biomass).

In addition, the same type of isotherm test was completed with resin used for one month in the pilot reactor described below to ascertain the resin capacity loss associated with longer-term continuous biological regeneration as would be typical of routine HAMBgR operations.

2.3 Pilot-scale MBR and HAMBgR Process Operations

A pilot-scale membrane bioreactor (Figure 2) was operated for 15 months switching back and forth between a conventional MBR mode and a HAMBgR mode by the addition of an anionic exchange resin to the microbial suspension and subsequent resin removal by sieving. The total reactor capacity is 12 L, but during operation the liquid volume was maintained at 10 L. At startup, the reactor was seeded with anaerobic digester sludge from the local wastewater treatment plant and anaerobic conditions were maintained by feeding both gaseous hydrogen as an electron donor and carbon dioxide for both pH control and to insure adequate inorganic carbon supply for the autotrophic perchlorate reducing bacteria. The membrane used in the reactor is a hollow-fiber microfiltration membrane made from a polyvinylidene fluoride (PVDF) material, which is widely used in large-scale water treatment applications. The membrane module was manufactured by GE-Zenon with a nominal pore size of 0.04 μm. The membrane module was operated in a submerged mode with suction applied to the downstream side of the membrane and gas scour on the upstream external side of the membrane to control fouling. This configuration allows for operation with increased biomass concentrations and provides efficient use of the recirculating hydrogen and carbon dioxide gas stream for reactor mixing, hydrogen mass transfer, and membrane surface scouring.

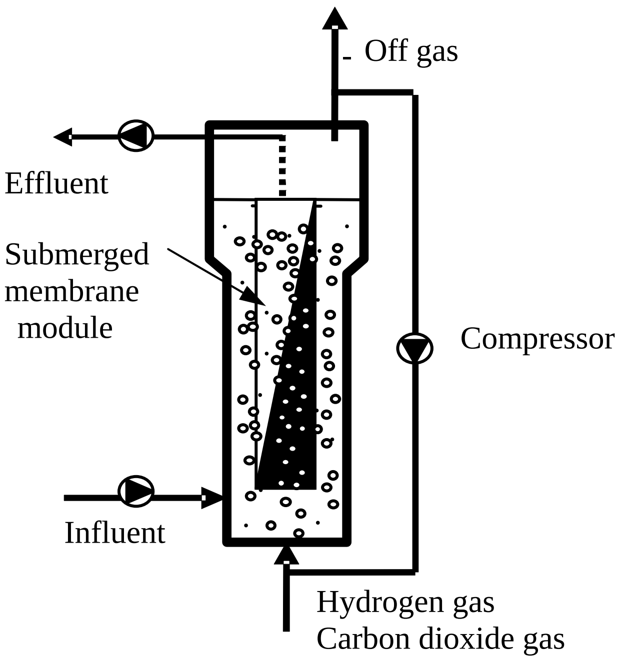


Figure 2- Schematic diagram of membrane reactor system.

3. RESULTS AND DISCUSSION

3.1 Comparison of resin isotherms

As shown in Figure 3, the batch isotherm tests with fresh resin indicated that the WBA resin (IRA-92) had a capacity that was 25-70% lower than the SBA resin over the range of effluent concentrations tested. However, both resins have significant capacity for perchlorate. Note that the WBA resin requires its functional group be protonated to most effectively exchange anions. By operating these batch tests at slightly above neutral pH, which is beneficial for biological perchlorate removal, the WBA resin would have been limited in its ability to exchange for perchlorate. SBA resins, on the other hand are effective for pH ranging from 0-13.

After the abiotic isotherm test with fresh resin, each of the resin bottles was dosed with hydrogen and biomass from the pilot reactor, which were subsequently allowed to degrade perchlorate until the serum bottle concentration was below detection. Afterwards, the biomass was decanted off and another abiotic loading cycle ensued. This process was repeated multiple times and showed that both the resins could be successfully regenerated biologically with perchlorate reducing bacteria (PRB).

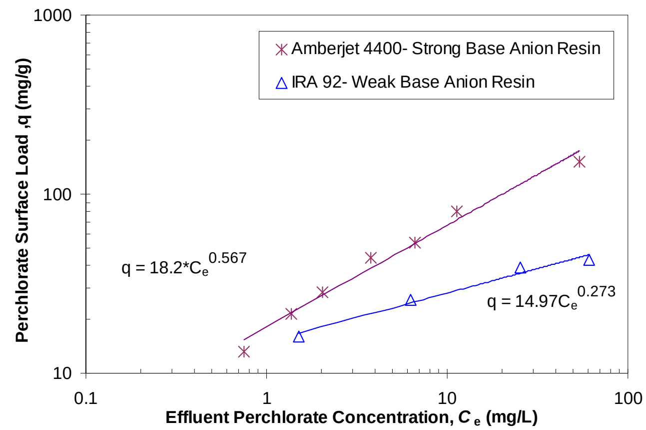


Figure 3- Comparison of isotherms for fresh anionic exchange resins before bioregeneration.

Amberjet-4400, a SBA resin, was sequentially loaded and biologically regenerated over 6 cycles and showed that resin capacity declined by about 40% over the first 2 to 4 loading cycles, but then approached a steady-state working capacity that was maintained over subsequent cycles. Figure 4 shows the isotherm with IRA-4400 after the first third and sixth abiotic loading cycle, which indicates that a significant and consistent working capacity was restored in the resin over several regeneration cycles.

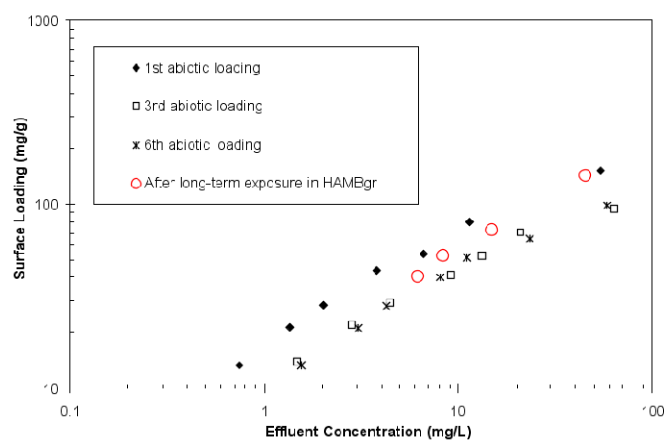


Figure 4- Comparison of isotherms for IRA-4400 SBA Resin after multiple biological regeneration cycles.

In an identical biological regeneration test, the IRA-92 weak base resin decreased in capacity slightly more than IRA-4400, which may be explained by increased organic fouling of its looser macroporous matrix structure. In direct contact with suspended biomass, the large pores of the WBA resin may trap more organics. The more tightly arranged structure of the SBA resin may make it more resistant to infiltration by excess organics and possibly a better candidate for direct biological regeneration. However, this proposed explanation needs further study before definitive conclusions can be drawn.

To further assess resin longevity and the ability to handle longer-term continuous contact between the resin and the regenerating biomass, another isotherm was conducted with IR-4400 that had been exposed to the pilot reactor biomass for a month. As shown by the red circles in Figure 4, the longer-term continuously regenerated resin isotherm also showed that no more than 40% loss of its original capacity.

All in all, these batch isotherm results suggest that the HAMBgR process could be an attractive alternative for continuous treatment of perchlorate contaminated water. The sequential nature of the tests clearly showed that the biomass could degrade previously adsorbed perchlorate and effectively regenerate a substantial working capacity for the resins. These results also indicate that brine regeneration of the resin will not be frequently needed and may not be necessary at all. If however, infrequent brine regenerations are needed for long-term, multi-year operations, this is readily accommodated in the HAMBgR process by sieving out the resin from the suspended growth biomass in the MBR. The next step was to assess the benefits of the HAMBgR process for dealing with upsets and spike loads in a continuous biological reactor.

3.2 Comparison of MBR and HAMBgR process under dynamic loading conditions.

In a conventional MBR and other biological reactors, there can be a lag time for the microorganisms to grow or adjust to changing influent conditions. In such cases, the HAMBgR process provides a physicochemical backup to the biological process that can attenuate or eliminate the spike in effluent contaminants that would normally occur while the biological process adjusts. To demonstrate this feature, the continuous flow pilot MBR process was operated at steady state with full perchlorate removal for several days. Then, an instantaneous spike load of 500 mg of perchlorate (50 mg/L of reactor) was dosed to the MBR and allowed to attenuate. As shown on the left hand side of Figure 5, the resulting effluent spike of perchlorate from the MBR peaked quickly at above 40 mg/L and took more than 300 minutes to return to return to baseline conditions.

After a few hours, the reactor was switched over to HAMBgR mode by adding 220 grams of IRA-92 resin to the MBR (22 grams per L of reactor), and then was dosed with another instantaneous spike of perchlorate at 50 mg/L. Even though the pilot reactor was operating between pH 7.5 and 8.0-- a rather unfavorable environment for a free base resin, the HAMBgR system was able to significantly reduce the effluent pulse of perchlorate in comparison to the conventional MBR mode of opertion. Figure 5 shows that following the pulse spike, effluent perchlorate concentrations peaked at 16mg/L for the HAMBgR process. Additionally, effluent concentrations returned to baseline levels in 15 minutes, more than 20 times faster than the conventional MBR. The perchlorate spike with the HAMBgR operating mode was repeated two days later and yielded essentially the same result, which is also shown on Figure 5. Integrating under the line in Figure 5, indicates that the HAMBgR process reduced the amount of effluent perchlorate resulting from the spike by 97%. Similar tests with the Amberjet-4400 also showed a significant benefit of the HAMBgR process for handling perchlorate spikes and also for process upsets like a pH excursion.

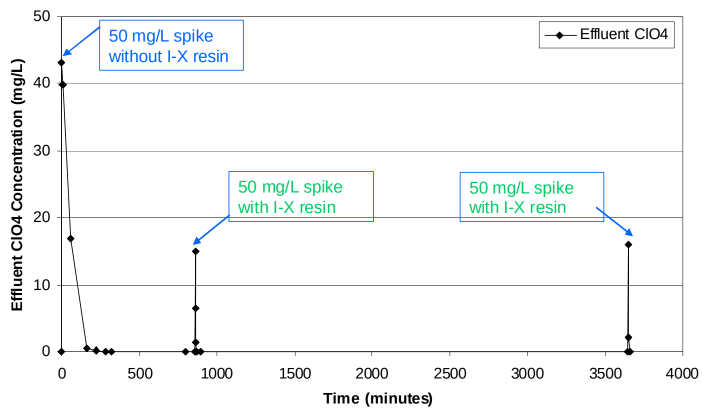


Figure 5- Comparison of perchlorate removal for MBR and HAMBgR processes in response to a spike load of perchlorate (50 mg/L).

CONCLUSIONS

This study introduced a novel process configuration for more reliable and cost-effective systems to treat wastewaters associated with various military operations. In particular, the novel process is referred to as HAMBgR (Hybrid adsorption-membrane biological reactor) and involves adding an ion-exchange resin to a membrane bioreactor system for removal of perchlorate. We clearly showed that it is possible to biologically regenerate ion exchange resin and thus the HAMBgR process provides an efficient physicochemical backup to unexpected shock loads or temporary upsets in reactor stability, such as pH disturbances or DO increases that can cause biological perchlorate reduction to cease or slow down. By having adsorptive media acting within a biological reactor, these high levels of target contaminants will be trapped until the microorganisms can recover and continue feeding. At resin concentrations of only a few grams per liter, HAMBgRs can be a very cost effective improvement to conventional MBRs.

This process can support various army operations because reliable and cost-effective treatment of munitions waste streams can help ensure that the best tools are available to the soldier and not restricted by undesirable environmental impacts. Moreover efficient pollution prevention can improve the environmental and health aspects of military operations to enhance soldier morale and public support.

REFERENCES

Greer, M.A., Goodman, G., Pleus, R.C. and Greer, S.E. (2005) Health effects assessment for environmental perchlorate contamination: The dose response for inhibition of thyroidal radioiodine uptake in humans (vol 110, pg 927, 2002). Environmental Health Perspectives 113(11), A732-A732.

Gullick, R.Q., Lechvallier, M.W. and Barhorst, T.A.S. (2001) Occurrence of perchlorate in drinking water sources. Journal American Water Works Association 93(1), 66-77.

Logan, B.E. and LaPoint, D. (2002) Treatment of perchlorate- and nitrate-contaminated groundwater in an autotrophic, gas phase, packed-bed bioreactor. Water Research 36(14), 3647-3653.

Nerenberg, R. and Rittmann, B.E. (2004) Hydrogen-based, hollow-fiber membrane biofilm reactor for reduction of perchlorate and other oxidized contaminants. Water Science And Technology 49(11-12), 223-230.

Tikkanen, M.W. (2006) Development of a drinking water regulation for perchlorate in California. Analytica Chimica Acta 567(1), 20-25.

Xu, J.L., Song, Y.U., Min, B.K., Steinberg, L. and Logan, B.E. (2003) Microbial degradation of perchlorate: Principles and applications. Environmental Engineering Science 20(5), 405-422.