Membrane Biofilm Reactors (MBfRs) for DrinkingWater Treatment

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Abstract: Increase demand on water resources make ground waters essential due to the fact that surface waters don't actually meet the water requirements for agricultural, industrial, recreational and drinking purposes. Provided that their quality and quantity are ensured, ground waters are a good source as drinking waters. However, they are threatened by various micro compounds coming from industrial, municipal, and agricultural activities such as; perchlorate, chlorinated solvents, oxidized contaminants, and heavy metals. Therefore a reliable treatment method should be applied to remove these micropollutants. Among the treatment technologies used for water supply, biological methods are widely used for the treatment purposes of drinking waters. Recent studies focus on the removal of micro pollutants by using membrane biofilm reactors (MBfRs) which allow gaseous substrate to move across the membrane for gas delivery and support biofilm formation on the outer surface of the membrane. This paper reviews several applications of MBfRs for water treatment.

• Introduction

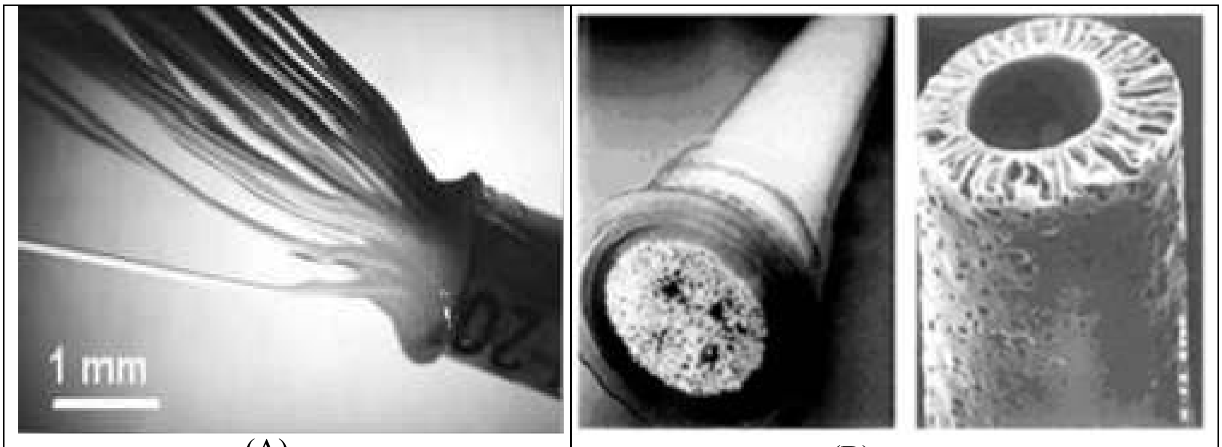
Increase in population and developments in industrialization have resulted in higher use of chemicals leading to faster transport rates between environmental compartments such as ground waters which drinking water is mainly produced. So many pollutants are known as danger for ground waters even if in micro levels such as; oxidized pollutants, chlorinated solvents, heavy metals and pesticides (Nerenberg and Rittmann, 2004; Modin et al., 2008; Chung and Ritmann, 2008). These pollutants are mainly the reason for industrial, municipal, and agricultural activities. In this respect, increasing chemical pressure on drinking water sources should be taken into account especially to be able to meet drinking water needs. Thus, due to the harmful effect on human health, the contamination of drinking water sources with inorganic compounds is a matter of concern. Therefore a reliable treatment method should be applied to remove these contaminants. Technologies available for the treatment of contaminated ground waters include physical, chemical and biological processes. Application of chemical and physical methods has been some disadvantages due to the toxic characteristics of these contaminants that needs to transform less toxic forms (Modin et al., 2008; Xia et al., 2009). But by the help of chemical and physical methods, these contaminants can only be transformed other toxic forms or even more toxic. Applied chemical and physical methods includes; ion exchange, reverse osmosis, adsorption, and electro dialysis or more than one of them. However; biological treatment methods have the advantages of being relatively inexpensive and having the ability to completely destroy the contaminants rather than producing another waste. Biological treatment has long been known as a promising technology that use microorganism to remove any pollutant. Biological processes are classified as attached or suspended growth has been the most popular treatment configuration. In attached growth processes normally occur between microorganisms and a surface that allow microorganism to make biofilm (Hasar, 2009). Membrane biofilm reactors (MBfRs) are among the attached growth biological treatment applications which are newly adapted technologies that allow biofilm growing on the membrane. This configuration of the MBfR allows gaseous substrate to move across the membrane for gas delivery and support biofilm formation on the outer surface of the membrane. This exciting new technology for removal of contaminants from ground waters has been among the most promising trends. Therefore, to be able to operate the membrane biofilm reactors, system configurations, applications and also limitation of MBfRs should deeply investigated. These factors will briefly be discussed in subsequent sections.

• Main MBfR components

MBfRs are among the biological treatment technologies that let biofilm grow on the membrane fiber where pressurized gas diffuses through the membrane lumen in order to oxidize or reduce the soluble constituents present outside the membrane lumen. The main difference between the membrane biofilm reactors (MBRs) and MBfRs are that MBRs are only functional to separate biomass from effluent water, be sort of clarifier (Nerenberg, 2004). Nevertheless; in MBfRs, membranes let naturally- forming biofilm that catalyzes desired reactions. A gaseous substrate is also essential for this treatment technology. Depending on the treatment aims; air, oxygen, hydrogen or methane can be used as gas. Thus a gas and a membrane that allows microorganism accumulation represent the MBfR's main components. The main advantages in use of MBfR for the ground water treatment purposes are that contaminants available in these waters are mostly micro levels with toxic properties and they cannot be removed with conventional biological treatment methods. Also, biological treatment occurs with biochemical reactions in which a substrate acts commonly an electron donor for microorganisms. However, ground waters are lack of electron donors essential for the treatment purposes; usage of gases electron donors and its efficiency make MBfRs solve these problems.

• Membranes

Membranes are one of the indispensable components in MBfRs. Membranes can be made of organic and inorganic materials. Sheet or hollow-fiber geometries are generally applied for membrane design in which hollow-fiber membranes are commonly used.



(A) (B)

Figure 1. (A) A bundle of hollow-fiber membranes; (B) Cutaway view of one fiber (Ritmann, 2006)

A schematic bundle of hollow fiber and a cutaway view of one fiber are represented in Figure 1. This membrane type has very small diameter as small as 0, 1 mm and consist of large number of membranes in a module. Materials used for hollow-fiber membranes are usually made of hydrophobic materials in order to keep their pores dry and thus make gaseous molecules diffuse much more quickly through dry pores. By this way, efficiency of the gaseous distribution can be maintained. Dry pores also eliminate the fiber clogging from liquid and biofilm infiltration. In Figure 2, scanning electron micrograph of pore structure on the hollow fiber membrane is depicted.

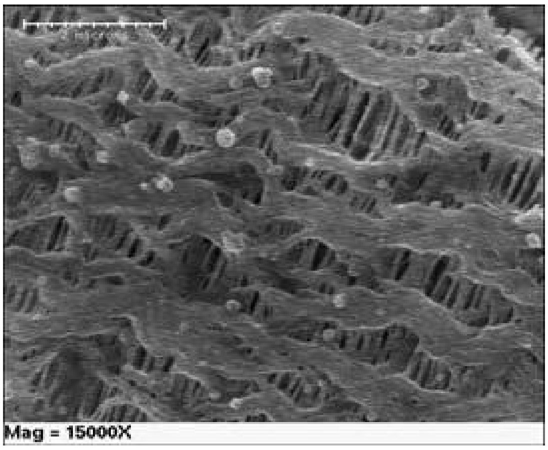


Figure 2. Pore structure on the hollow fiber membrane (Nerenberg, 2005)

- **Biofilm**

Biofilms are formed on the membrane surface naturally. They are the accumulated and attached microorganisms and are responsible for the removal of the contaminants in the effluent. Normally biofilm-based treatment methods supply both electron donor and/or acceptor for biofilm formation from the bulk solution via diffusion. But the mechanism in MBfRs is rather different since electron donor, which is normally a gaseous substrate, is diffused into the biofilm from the membrane and other from the bulk liquid.

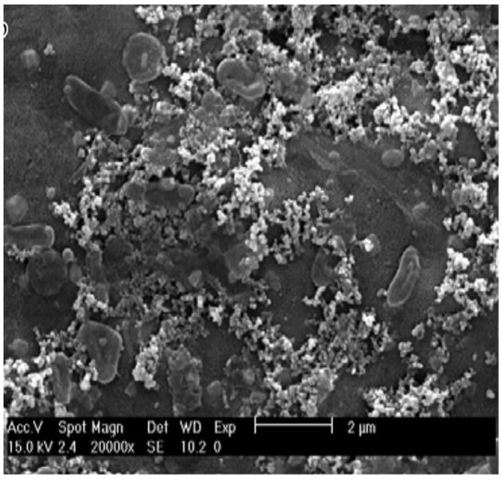


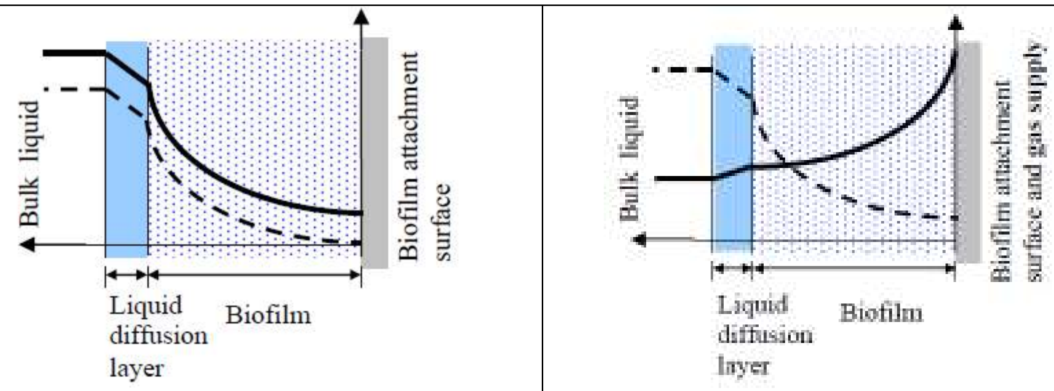
Figure 3. Biofilm microorganisms from MBfR (Xia et al., 2009)

Figure 3 indicates the surface morphology of the hollow fiber with biofilm formation. Actually biofilm formation is a key factor to be control since it directly affects the MBfR efficiency. It has been reported that biofilm structure such as; thickness, density and composition is vital for MBfRs. For instance, excess biofilm development is undesirable because of the fact that it can result in biofilm sloughing, non-uniform flow distribution, inhibition of substrate or gas diffusion. The detachment or sloughing of biomass needs to be balanced with biomass accumulation (Hwang et al., 2009). Hence, many researchers identified biofilm control as one of the most challenging aspect of MBfR operation (Hwang et al.,2009; Celmer et al., 2008).

- **Gas substrate**

Mostly biological treatment processes are based on oxidation reduction reactions. In MBfR technologies microorganisms use electron donors as an electron and energy source. Electrons released from electron donors (normally H_2) are transfer to the electron accepting contaminants. The few rate of these electrons are used for microbial growth and hence biofilm formation on the surface of membrane. The most known advantage of the MBfR technology is the use of a gaseous substrate which prevents regrowth caused by organic donor materials used as electron donors such as ethanol, methanol, and acetate. Published reports have been showed that organic materials used for electron donor results in recontamination of waters by residual of these organic donors. By this respect, substrate as gaseous form is usually used as electron donor but some cases as electron acceptor. For the electron donor purposes, methane, hydrogen and for the electron acceptor purposes oxygen has been mostly used in recent studies (Nerenberg, 2005).

Hydrogen is the ideal electron donor that has been used in most MBfR studies due to the inherent advantages over other organic donors. H_2 is non toxic to human and cost effective. Supporting autotrophic bacteria eliminates the need for an organic carbon source since the growth rate of autotrophic bacteria is slow; amount of produced microorganism per removed substrate is rather scarce. So H_2 produces far less excess biomass than organic donors. On the other hand, its low water solubility prevent the residual in the water which means it cannot be over-dosed to increase effluent BOD and be wasted at the same time (Ritmann, 2006). Additionally, it was reported in a study that use of H_2 as gaseous substrate reduce the cost about 3-15 times compaired to other common organic donors used (Lee and Rittmann,2000).



10. (B)

Figure 4. (A) Normal biofilm and (B) MBfR biofilm; The bold line is the dissolved gas concentration, while the dotted line is the substrate from the bulk liquid (Nerenberg, 2005).

Figure 4 compares the ways in order to supply gas (electron donor) into the bulk solution and represents the advantages and disadvantages of these ways. Normal biofilm and biofilm formed on the MBfR have the dissimilarities with respect to gas diffusion. The amount of required electron donor is much less in MBfRs compare to the conventional biofilms. This promotes the usage of the membrane biofilm reactors especially for the cost-effectiveness of the process.

• MBfR applications

This part of the review paper includes research articles mainly focusing on MBfR applications. Besides drinking water treatment processes, there are applications of MBfRs for industrial and domestic wastewater treatments. Researches on the applications of MBfRs have been focused on the denitrification processes and the treatment of oxidized contaminants (Nerenberg et al., 2002; Chung et al., 2006).

Removal of nitrogen

Nitrate contamination is a widespread problem for drinking water around the world. Nitrogen is mainly found in ground waters as mainly in the form of nitrate (NO_3^-) and nitrite (NO_2^-). Contamination of ground waters with nitrate mainly the reason for the usage of nitrogen fertilizers and the irrigation with domestic wastewater (M. Shrimali, K.P. Singh,2001). Nitrate should be regulated in drinking water since the excess levels can cause methemologlobinemia or blue baby disease in humans. Nitrate removal in biological systems involves denitrification processes which require anaerobic conditions. Denitrification occurs in two ways according to the carbon source, heterotrophic and autotrophic; respectively. In heterotrophic denitrification processes, electron donor source is normally organic compounds. However, due to a very low organic carbon sources in ground waters nitrate cannot be removed effectively through heterotrophic biological methods. Hopefully, autotrophic denitrification has advantages over the heterotrophic denitrification, such as usage of inorganic electron donor which makes biomass yields low (Shin et al., 2007). In a research article it has been found that denitrification rate can be affected from gas pressure and nitrate loading (Celmer et al., 2006).

The reactions involved in autotrophic denitrification consist of oxidation of H_2 gas to hydrogen ions and reduction of nitrate to nitrogen gas. Overall half reactions and the schematic diagram of the MBfR for denitrification process are represented in Figure 5.

Oxidation of hydrogen gas :

$$H_2 \rightarrow 2e^- + 2H^+$$

Reduction of nitrate:

$$NO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}N_2 + 3H_2O$$

Overall denitrification reaction:

$$NO_3^- + 2.5\,H_2 \rightarrow \frac{1}{2}N_2 + 2H_2O + OH^-$$

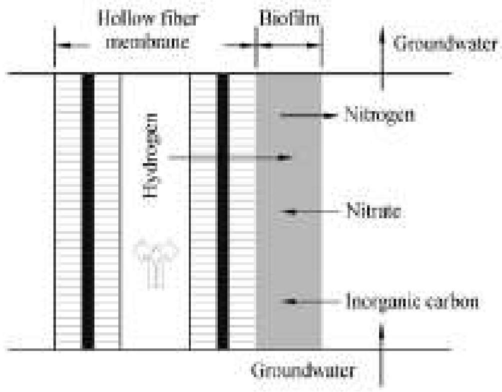


Figure 5. Principle schematic diagram of MBfRs for autotrophic denitrification and reactions involved (Xia et al., 2009)

- **Removal of micro contaminants**

Hydrogen-based MBfR is a successful tool of reducing many oxidized pollutions such as such as; arsenate (AsO43−), perchlorate (ClO4−), selenate (SeO42−), chromate (CrO4−), trichloroethene (TCE), and nitrosodimethylamine (NDMA), hexavalent chromium which are difficult to remove in conventional biological treatments (Ergas and Reuss, 2001; Lee and Rittmann, 2002; Nerenberg et al., 2002). These contaminants are usually found in micro levels in ground waters. Origin of the perchlorate in water mainly is the improperly disposed-of rocket fuel. It inhibits thyroid function even if at low levels (Espenson, 2000). Level of 4 µg/L has been determined in California for perchlorate in spite of the fact that there is no standard for perchlorate. Arsenic is another micro pollutant exclusively found in groundwater which can cause gastrointestinal damage and cardiac damage. Hence it has been considered as a human carcinogen. Level of 10 µg/L arsenic is determined by Protection Agency (EPA) Maximum Contaminant Level Goal (MCLG). Bromate is regulated under the Stage 1 Disinfectants/Disinfection By-Products Rule at 10 µg/L (Kirisits et al., 2001). Chromium is also an inorganic contaminant. It is released to drinking water sources from electroplating facilities, old mining operations, and fossil-fuel power plants. It has been known that chromium can cause liver and kidney damage, and the maximum contaminant level for drinking water is 0.1 mg/L total chromium. DCM (CH_2Cl_2), methylene chloride, which is carcinogenic, highly soluble in water, and one of the most common groundwater contaminant (Kohlerstaub et al., 1995). Consequently, these micro contaminants should be removed due to their adverse affects. In a published report, it has been found that a wide range of oxidized contaminants (arsenate, perchlorate, selenate, chromate, and dichloromethane) can be successfully removed by the hydrogen based hallow-fiber membrane biofilm reactor and removals were greater than 75% without any community adaptation. It has been noted that when the contaminants need to be reduced to very low levels nitrate or oxygen can serve as primary electron acceptors, on the other hand; many of the contaminants can serve as primarily electron acceptors at higher concentrations. (Nerenberg and Rittmann, 2004).

Conclusion

MBfR is a novel system that uses membranes to supply dissolved gaseous directly without bubbling to a biofilm growing on the membrane surface. The H_2-based MBfR has great potential to solve emerging problems in water quality and has kept increasing since it appears in the early 1980s. Especially after 2000, more research studies have been published from all around the world. MBfR is a promising technology by the means of gaseous substrate usage, which prevents regrowth caused by organic donor materials used as electron donors. By utilizing H_2 gas as the electron donor, some of the major problems such as; a large increase in excess biomass generation, over- or under-dosing of donor, safety concerns can be able to be solved. Application studies of MBfRs have shown promising potential and suggest the possibility of utilizing MBfR in biological treatment technologies also for industrial and domestic wastewater treatments but mainly for the purpose of removing micro pollutants found in ground waters. The results of the published reports confirm that the wide variety of oxidized contaminants can be successfully reduced and removed immediately in a hydrogen-oxidizing MBfR with oxygen or nitrate as primary acceptors. However, so many research articles has emphasized that there are some outstanding challenges associated with MBfRs in the near-future. The principal obstacle to full scale implementation is the problem of excess biomass control which can lead to significant performance deterioration. Hence, field studies are needed to focus on biofilm thickness and activity control to make commercial scale applications feasible. Additionally, possible developments in this area are likely to focus on membrane material and module design improvements in along with selection of appropriate liquid/gas scouring methodologies.

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