

Role of microorganisms in Permeable Reactive Bio-Barriers (PRBBs) for environmental clean-up: A review

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Abstract

It is an indisputable fact that any environmental clean-up technology generating certain kind of effective result would be easily supported. One of them includes Permeable reactive bio-barrier which is an innovative technology started from 90's to treat a variety of contaminants along the natural gradient flow of groundwater through immobilization or transformation of pollutants into less toxic and harmful form. Despite of any broad acknowledgement, there are lesser known knowledge about use of microorganisms in permeable reactive barriers, mingling of microorganisms with other reactive media and their effect on each other's reactivity. The current review deals with an overview of the types of reactive media used in Permeable Reactive Barriers (PRBs) as well as different bio-barriers (PRBBs) utilized for the treatment of various contaminants, long-term performance of permeable reactive barrier and combination of microorganism and reactive media to look forward for their symbiotic relationship in permeable reactive barrier for environmental remediation.

Keywords: Permeable reactive barriers, Bio-barriers, Remediation, Reactive media

1. Introduction

In Past few decades, groundwater pollution has become a major environmental issue owing to industrial and agricultural applications. The pollution of groundwater resources by organic pollutants like chlorinated organic compounds, pesticides, herbicides, dyes, nitro-aromatic compounds and inorganic pollutants like heavy metals, nitrate, etc. is of paramount importance. Due to a broad range of contaminants emerging from various sources poses a grave threat to the quality of groundwater (Schipper *et al.*, 2010; Wiafe *et al.*, 2013; Rodak *et al.*, 2014). Earlier 'pump-and-treat' has been used for the remediation of contaminated groundwater. In pump-and-treat system, the contaminated groundwater is extracted from the subsurface by pumping, and then it is treated before being discharged to the environment. The treated water is then pumped back to the subsurface. Because of limitations like the long time to meet clean-up goals and high cost this technique fails to work correctly. Apart from

these techniques, various physical and chemical treatment methods like adsorption, coagulation, precipitation, filtration, and advanced oxidation systems have been applied for the treatment of contaminants. Research has been ongoing to meet eco-friendly and sustainable remediation approach (Henderson and Demond, 2007).

An innovative in situ remediation technique known as Permeable reactive barriers (PRBs) technology is accepted worldwide for remediation of contaminated groundwater (Tratnyek, 2003). The reactive media is placed perpendicular to the flow of contaminated groundwater in PRB system. The mechanism behind the treatment of contaminants involves the reaction of contaminants with the reactive media thus generating lesser toxic compounds or infatuation to reactive media. The transformation of highly toxic contaminated groundwater to less toxic form usually takes place inside the barrier or downhill of the wall which is mainly dependent on the type of reactive media used for different kinds of contaminants and the process is generally accomplished by exterminatory and/or non-exterminatory processes (Chen *et al.*, 2011a). However, the reactions within the permeable reactive barriers may be impacted by the presence of micro-organisms within the barrier.

A lot of review paper is published on PRB focusing on different reactive media, advantages, and disadvantages of PRB, and performance of PRB (Henderson and Demond, 2007; Noubactep, 2010; Obiri *et al.*, 2014). This paper portrays on efficiencies of different reactive media along with their limitations, modification in technology, with particular emphasis on the effect of biodegradation within the PRB system with various types of microbes, reported till date.

2. Reactive media used in PRBs

The reactive media zone is the place in the PRBs where contaminants are removed relying on the kind of reactive material used for different type of pollutants. In some PRBs, contaminants are removed by corporal contact while others remove contaminants by changing the biogeochemical processes in the treatment zone, thus providing suitable conditions for contaminant removal or biodegradation. Apart from the design, PRBs primary purpose is to transport the contaminants keen on to the

reactive zone, where the degradation process can take place. The most common reactive material used is Zero-Valent Iron (ZVI). Besides ZVI, the range of reactive material includes zeolites, oxygen releasing compounds (ORC), activated carbon (AC), peat, sawdust, etc. for the removal of contaminants. The major disadvantage with such type of reactive materials is that they are confined to a small cluster of contaminants, and their accessibility is also challenging, and they are expensive too (Kober *et al.*, 2002). The replacement of these reactive materials is still in progress that is not limited to a particular group of contaminants rather that is applicable for a large group of contaminants within PRB (Di-Nardo *et al.*, 2010). Ruhl *et al.*, (2013) performed an experiment for the removal of TCE using a combination of Fe(0) with additional reactive materials in PRB. The reactive media consists of Fe(0), Granulated ferric hydroxide (GFH), Calcite and wood chips. The contaminant removal observed in 184 d having Fe(0) and GFH as reactive media and the reactivity decline thereafter. A complete transformation of TCE to cDCE found with an elevated concentration of cDCE. The use of reactive material generally depends on: (i) different category of contaminants along with their concentrations to be treated (i.e., organic and/or inorganic), and mechanisms involved in their removal (e.g. sorption, biodegradation, or

precipitation) (ii) aquifer hydrogeological and biogeochemical conditions (iii) what are the impacts on environmental/ health; (iv) mechanical stability and (v) the availability and cost of the material. There may be different types of processes for the removal of contaminants, but the dominant removal mechanism involves (i) destructive biotic or abiotic processes such as e.g. complete biodegradation or reductive dechlorination of contaminants into utterly new non-toxic products; (ii) non-destructive processes e.g. surface complexation, adsorption, cation exchange, and precipitation that clutch the contaminants and accordingly reduce their concentrations in the groundwater. It should be taken into consideration that reactive materials that precipitate or immobilize Contaminants must have some properties that adjust geochemical parameters such as pH and redox of the aquifer so that solubility of the contaminants gets reduced or minimize (Panturu *et al.*, 2009). The removal processes in PRBs are dependent on the type of media used, the target contaminants that are to be degraded as well as the biogeochemical conditions prevailing in the aquifer. Table 1 sums up the various reactive materials used for remediation of different type of contaminants in PRBs. Table 2 summarize the locations where PRB have been installed and running successfully.

Table 1. Different types of reactive media used in PRB

| Reactive media | Contaminants type | Mechanism | Efficiency | Optimal condition | Limitations | References |
|------------------|---|---|------------|---|--|---|
| ZVI | Chlorinated Hydrocarbons, Heavy metals, Metalloids, radio-Nuclides, Nutrients, Pesticides | Adsorption, Surface complexation, Reductive precipitation, Co-precipitation | 90-99% | - | Easily oxidized & increases the pH which induces corrosion & leads to poor permeability of reactive material | Yang <i>et al.</i> , 2010b; Naryko <i>et al.</i> , 2014 |
| Activated Carbon | Phenols, PCE, TCE, BTEX | Sorption | - | - | Rapid breakthrough & surface coating lead to decrease in sorption capacity | Di-nardo <i>et al.</i> , 2010 |
| Zeolite | Heavy metals, NH ₄ ⁺ , Radionuclides, PCE & BTEX | Sorption, Ion exchange, precipitation | 80-100% | pH value must be in the range of 3-11 | - | Perric <i>et al.</i> , 2004 |
| Apatite | Lead, heavy metals, U(VI) | Sorption, precipitation, surface Adsorption, incorporation | - | Low pH | - | Naryko <i>et al.</i> , 2014 |
| TRM | AMD, Fe, Cu, Zn, Ni, Pb, Cr | Adsorption, precipitation | 97-99% | Due to fine texture, it should be mixed with sand or gravel to increase permeability of PRB | - | Munro <i>et al.</i> , 2004; Iaponite <i>et al.</i> , 2006 |

Table 2. Locations of various installed PRBs

| Microorganisms used in PRBs | Types of contaminants | Removal efficiency | Time | Temperature | pH | Experiment | References |
|---|---------------------------------|--------------------|-------|-------------|---------|------------------|-------------------------------|
| <i>Trametes versicolor</i> | Orange G dye | 97% | 159hr | 15 °C-25 °C | 6-7 | lab-scale | Folch <i>et al.</i> , 2013 |
| <i>Delftia sp.</i> lp0 (KR 673339) and <i>Pseudomonas sp.</i> wyj10 (KR 673340) | Aniline and Nitro benzene | 98% | 25d | 10 °C | - | - | Wen <i>et al.</i> , 2015 |
| p-CNB-reducing bacteria | pentachloronitro benzene | 95% | 48hr | - | 8.0 | - | Yin <i>et al.</i> , 2012 |
| <i>Arthrobacter viscosus</i> | Polycyclic aromatic hydrocarbon | 80% | 4d | - | 8-9 | Bench scale | Ferreira <i>et al.</i> , 2013 |
| <i>Arthrobacter viscosus</i> | Chromium VI | 79% | 18d | - | 5.6-6.4 | - | Fonseca <i>et al.</i> , 2012 |
| <i>Thiobacillus</i> bacteria | Nitrate | - | 48h | - | - | Batch experiment | Li <i>et al.</i> , 2016 |

3. Bacterial Biobarriers as treatment zone in PRB

Application of biobarriers in the PRBs as a treatment zone contains those materials that are capable of stimulating or enhancing microorganisms to demean contaminants anaerobically or aerobically. Such barriers are termed as Permeable Reactive Bio-Barrriers (PRBB). Since PRBBs are dependent on the use of microorganisms for degradation of contaminants, it is advisable to use the suitable population of microorganisms for a particular pollutant. The microbes are often ever-present, particularly in the upper layers of the aquifer, so it is quite easy to use them for removing contaminants (Di-Nardo *et al.*, 2010; ITRC, 2011). In this technology, the microorganisms that are used as a reactive medium to debase or alleviate the contaminants are clung to a porous support (Tiehm *et al.*, 2008). The main restrictions on this type of approach are that the microorganisms or consortium must form biofilm with the degradative ability for the target pollutants on the reactive materials in PRBB. Microorganisms undergo degradative mechanism by two ways mentioned below:

3.1.1 Aerobic Degradation in PRBBs

Via aerobic biodegradation, removal of some organic contaminants takes place. Such contaminants like petroleum hydrocarbons (such as BTEX and MTBE) have mostly reducing nature. The need for the terminal electron acceptors (TEAs) to stimulate such type of processes from the contaminants that transfer electrons during their degradation is very imperative. O₂, NO₃⁻, CO₂, sulfate, manganese, and ferric iron are the usually present TEAs in the environment. Among the available TEAs, molecular oxygen is, however, more often preferred to other TEAs because of its high energy yielding capacity to the microbes which is, in turn, is helpful in stimulating degradation of contaminants. There are some other oxygen and nitrate-releasing compounds (ORC) such as calcium peroxide, magnesium peroxide, hydrogen peroxide, and sodium percarbonate that have been used to liberate oxygen or create an aerobically active zone in the subsurface. Due to the low cost of ORCs, it has been used mostly in PRBs (Simon and Meggyes, 2000; ITRC, 2011). Mackay *et al.*,

(2002) performed two sets of an experiment to treat Methyl tert-butyl ether (MTBE) in contaminated groundwater at two sites in California using native and non-native bacterial strain, and they found that diffusive release of oxygen into the groundwater or oxygen released through sparging can degrade MTBE aerobically by native microorganism. The result confirmed the biodegradation activity occurred because of direct supply of oxygen through polymeric tubing and air sparging. Aerobic degradation of BTEX contaminated groundwater was also carried out by (Yeh *et al.*, 2010) with column experiments, batch experiments, and bench-scale permeable reactive barrier (PRB) using microbial community obtained from industrial wastewater treatment sludge and organics-contaminated groundwater site in central Taiwan. To provide an aerobic condition for degradation, various amount of CaO₂ added. The experimental result showed that in the batch experiment the degradation was 80 mg l⁻¹. The PRB system shows removal efficiency in the following ascending order: ethylbenzene > toluene > p-xylene > benzene during 100 days of operation. Shock load applied on day 44 and 52 for 4 hrs with an increase in BTEX concentration from 30 mg l⁻¹ to 60 mg l⁻¹ and the level reduced to the original. The addition of oxygen releasing compounds like CaO₂, is of the reason that it could meet the oxygen requirement of bacteria. However, shock loading exerts a negative impact on microbial community thereby reducing their degradation capability.

3.1.2 Anaerobic Degradation in PRBBs

In contrast with the contaminants that are aerobically biodegraded, anaerobically degradable contaminants are oxidized in nature and thus are sooner degraded by reduction. The reactive materials used in PRBs serves as a source of electrons whereas the contaminants that are degraded serve as the electron acceptors for the metabolic process of microorganisms (Obiri *et al.*, 2014). Nitrate, sulfate, carbon dioxide, ferric iron etc. acts as electron acceptors to mediate anaerobic degradation. Materials like ZVI, dithionite may act as reactive barrier materials which can facilitate the anaerobic degradation of contaminants.

3.2 Fungus Biobarriers

Another group of microorganisms has identified by researchers known as, Fungi having higher potential in bioremediation processes because they can degrade a wide variety of organic compounds by co-metabolism under oxic conditions. Specifically, white-rot fungi (WRF) have been known to degrade several xenobiotic compounds at broader scale. Folch *et al.*, (2013) used fungus as biobarrier to remediate groundwater in an artificial aquifer. Fungus *Trametes versicolor*, was used to treat Orange G dye contaminated groundwater. The result of the study revealed that the maximum degradation was 97% and the degradation continues to 85% for about eight days. The results showed that fungus could be used as an active media in PRB.

4. Degradation of Contaminants in PRBBs

4.1 Nitrate

The presence of some low-cost organic materials for the removal of nitrate from groundwater includes sewage sludge, leaves, sawdust, peat, alfalfa, manure, wood waste and compost (Schipper *et al.*, 2010; ITRC, 2011). But there are some microorganisms like denitrifying bacteria such as *Paracoccus denitrificans* and other microorganisms belonging to the *Pseudomonas* group in the presence of organic substrates which are efficient in removal of nitrate. A two layer heterotrophic – autotrophic denitrification PRB was installed by Huang *et al.*, (2015) for the treatment of nitrate- nitrogen contaminated groundwater having pine bark as an upper layer and spongy iron and river sand mixture as the lower layer. The removal mechanism involves biological deoxygenation, heterotrophic denitrification, hydrogenotrophic denitrification, and anaerobic Fe corrosion. Both batch and column experiments conducted and the result showed that the removal efficiency continues up to 504 d having removal of 91%. The NO_3^- -N degradation was achieved at first 65 cm of the column having influent concentration of 23 and 46 mg L^{-1} whereas 79% was depleted having influent concentration of 103 mg L^{-1} . The presence of aerobic heterotrophic bacteria depleted oxygen via aerobic respiration and thus favoring hydrogenotrophic denitrification by providing excess CO_2 .

4.2 Sulfate and Heavy Metals

Reduction of sulfates to sulfides by Sulfate Reducing Bacteria (SRB) utilizes the organic substrates under anaerobic conditions (Waybrant *et al.*, 2002). Generation of dissolved phosphates by reduction process is further taken up by microbes as their nutrient sources that are involved in degradation and thus accelerating pH. Precipitation of heavy metals as metal sulfides can occur under quite elevated pH conditions, as the reaction of sulfides can take place subsequently with heavy metals. Sulfate reduction by microbes was achieved by H_2 production (FeO oxidation) and the presence of bacterial species like *Desulfosporosinus*, that uses H_2 production as an energy source. One of the results showed the advantage of Fe^0 + SRB integrated systems over conventional Fe^0

based system regarding precipitate stability. The combination of Fe^0 and microbial activities could enhance the treatment capability of PRBs and produce stable precipitates of Zn (Kumar *et al.*, 2015). Zn removal in integrated system Fe^0 + SRB system can be succeeded by two ways i.e. initially Zn can be removed via Ferrite-Zn formation reflecting adsorption of Zn on Fe^0 surface and later on activation of microbial sulfate reduction by possible interaction of Zn-Fe-S. The result obtained showed the overall activity of Fe^0 and SRB by removing the dissolved contaminants, and SRB thus fix metals as stable metal sulfides meanwhile Fe^0 provides H_2 as an electron donor which stimulates growth of SRB.

4.3 Chlorinated Solvents

Ozturk *et al.*, (2012) investigated by batch and column experiments to degrade Trichloroethylene (TCE) in groundwater with the use of commercial compost and eucalyptus mulch and the result showed that the decomposition rates were 0.23 and 1.2 d^{-1} in mulch and compost respectively and this shows that highly organic natural media developed a bioactive zone which allows the anaerobic decomposition of TCE. Mondal *et al.*, (2016) did an experiment to evaluate the degradation efficiency of peat and sawdust as reactive media in PRB for TCE. The experiment was conducted in a laboratory batch microcosm and flow through the column and the result showed that peat was quite capable in biodegradation of TCE to ethene in a contaminated soil than sawdust. The findings concluded that peat completely supports reductive dechlorination of TCE and can slowly release electron donor source. Another is that peat can have lower biological growth and methane production compared to sawdust.

4.4 Hexavalent chromium

Liu *et al.*, (2015) conducted an experiment to treat Cr (VI) contaminated groundwater with immobilization of Cr (VI). The results of the experiment showed that pH had a significant influence on the removal of Cr (VI). The removal efficiency decreased with increase in pH from 5.5 to 9.0. An experiment was conducted in a column reactor by (Boni and Scaffoni, 2009) for the removal of Cr (VI) from contaminated groundwater by compost based biobarrier comprising of green compost and siliceous gravel as a reactive media. Almost 99% of Cr (VI) removed during the whole activity. The removal mechanism involved in this process was adsorption on the organic-based matrix and reduction of Cr (VI) into Cr (III) by anaerobic bacteria present in green compost. The involvement of siliceous gravel in removal process was negligible as only used as the structure matrix. Cr (III) was entrapped in the solid matrix as is not detected in the outlet. A contaminated water was containing Cr (VI) as a contaminant was treated by (Pagnanelli *et al.* 2012) with sulfate reducing bacteria fed with ethanol. This biological treatment performed in a fixed bed reactor with sulfate reducing bacteria as reactive media. Two fixed bed column reactors used in which one supplied with SRB and other used as a blank. Both the reactors continuously fed with a synthetic solution

containing ethanol, Cr (VI) and sulfate. The result obtained showed that inoculated column removes $65 \pm 5\%$ of sulfate and $95 \pm 5\%$ of chromium removed due to a biological mechanism. Ethanol serves to be a better alternative to common electron donors and carbon source for SRB growth.

4.5 Hydrocarbons

Among various microorganisms used for the treatment of contaminants, *Arthrobacter* species are of particular interest because they are highly efficient for bioremediation. These bacteria can detoxify metal wastewater by two mechanisms: either by reduction or accumulation inside the cells and/or adsorption on their surface (Blazquez *et al.*, 2009). Furthermore, several strains of this genus have been identified in degradation of aromatic compounds which include 4-fluorophenol, 4-chlorobenzoate, phenol, p-hydroxybenzoic acid and mono- and dichlorinated biphenyls (Ferreira *et al.* 2008; Karigar *et al.* 2006). Amongst various identified strains, the species *Arthrobacter viscosus* have high potential as bioreactive medium in the PRBBs for many of the organic compounds such as diethylketone, phenol, chlorophenol, o-cresol (Costa *et al.*, 2012; Quintelas *et al.*, 2010) as well as metals (Lameiras *et al.*, 2008; Pazos *et al.*, 2010). Besides their degradation potential, *A. viscosus*, a non-pathogenic bacterium releases a high amount of viscous extracellular polysaccharides (Lopez *et al.*, 2003). The more the release of viscous extracellular polysaccharides the more is the holding capacity of different support structures favoring its use as a bioreactive medium. Some of the microorganisms belonging to the genus *Acidovorax* were also identified as degraders of polycyclic aromatic hydrocarbon (PAH) and were also used in treatment of contaminated soil at laboratory scale (Singleton *et al.*, 2013). Other abundant

bacteria enriched were *Pseudoxanthomonas*, *Bdellovibrio*, and *Serpens* in which *Pseudoxanthomonas* genus was able to degrade PAH also, and several other strains were isolated from contaminated soil and sediment (Klankeo *et al.*, 2009; Patel *et al.*, 2012). Hydrocarbons have been widely degraded by a variety of microorganisms in both conditions whether aerobic or anaerobic having different electron acceptors (Kleinstauber *et al.*, 2012; Hyman, 2013). *Hydrogenophaga flava* ENV735 was identified to degrade both TBA and MTBE in pure culture as well as enriched both in bioreactors and in microcosms (Raynal and Pruden, 2008; Bastida *et al.*, 2010). It has observed by many researchers that *Hydrogenophaga* was able to degrade PAH with a mixture of toluene and benzene as a carbon source and BTEX contaminated groundwater as a source of inoculum (Aburto and Peimbert, 2011, Martin *et al.*, 2012). Another species *Pseudoxanthomonas spadix* BD-a59 discovered which was able to degrade all the BTEXs (Kim *et al.* 2008). A BTEX fed reactor was enriched with another type of species namely *Bdellovibrio* for water treatment (Li and Goel, 2012), and for the first time, *Serpens* genus has been used for hydrocarbon degradation. *Thauera aromatica* K 172, a member of *Serpens* genus has the better ability to degrade aromatic hydrocarbons under aerobic and denitrifying conditions (Anders *et al.*, 1995). It has also found that *Thauera* with toluene as carbon source best suited under denitrifying conditions. (Li *et al.*, 2012). Some of the work carried out by some researchers in BTEX contaminated groundwater and the result found was that *Mycobacterium sp.* C3 was able to degrade both toluene and m-xylene, (Cavalca *et al.*, 2004). Some of the other microorganisms belonging to the genus *Azoarcus* were reported to degrade hydrocarbons in nitrate-reducing conditions. Table 3 summarizes various micro-organism utilized for remediation of contaminants in PRBBs.

Table 3. Microorganisms used in PRBBs for removal of contaminants

| PRB with reactive | Installation in different country | Types of contaminants removed | Configuration | References |
|------------------------------|-----------------------------------|-------------------------------|--------------------------|---------------------------------|
| GAC, Zeolite | Casey station Antarctica | Petroleum hydrocarbon | Funnel & Gate | Mumford <i>et al.</i> , 2014 |
| Limestone & Crushed concrete | Florida | Fe(II) & Mn(II) | - | Wang <i>et al.</i> , 2016 |
| Granular iron | California | Carbonate | Gate and Continuous wall | Jeen <i>et al.</i> , 2011 |
| Granular iron | Elizabeth city, North Carolina | Cr(VI) & TCE | - | Wilkin <i>et al.</i> , 2014 |
| Activated carbon | Italy | PCE & TCE | - | Erto <i>et al.</i> , 2014 |
| Grey cast-Fe with gravel | Willisau, Switzerland | Chromate | - | Flury <i>et al.</i> , 2009 |
| GAC | Canadian arctic | PCB | - | Kalinovich <i>et al.</i> , 2012 |

5. Modifications in the PRB technology

The treatment of chlorinated solvents such as trichloroethylene (TCE), the three isomers of DCE (1,2-cis-, 1,2-trans- and 1,1-DCE) and vinyl chloride (VC) contaminated groundwater first conducted within PRB. The PRB technology being effective for the treatment of compounds like TCE, DCE, and VC, its use was further elaborated to remediate other contaminants also. The types of PRBs mainly used for field application are the

funnel-and-gate and the continuous gate designs (Thiruvengkatachari *et al.*, 2008). The funnel-and-gate design consists of two structures: the funnel, comprising of cut-off walls used to join the contaminant to the zone of treatment, and the reactive gate used for the treatment process. However, the funnel-and-gate PRB system is quite expensive to construct; it treats some of extensively dispersed plumes.

On the other hand, the continuous gate PRB system consists of transverse treatment barriers to the path of contamination. The advantage of this PRB system is that it is cost effective; simple to construct and possess modest effect on the flow of groundwater. But the limitation with this type of system is that only plumes with narrow widths are suited for treatment and bypass of contaminated water may pose problems. Earlier the use of zero-valent iron (ZVI) in the PRB system was limited for some of the contaminants. For avoiding this problem, the concept of biobarrier introduced which uses organic materials for the remediation of contaminants that has not removed by the use of reactive materials like ZVI in the PRBs. With the use of biobarriers in PRBs, the growth and activities of microorganisms for degrading contaminants gets enhanced as it became easier to use cost-effective substrates/organic materials as filling materials (Vesela *et al.*, 2006).

Earlier the PRBs were seen to have a single barrier (with a single reactive material) (ITRC, 2011). The single barrier system treats only one type of contaminants or contaminants of comparable characteristics (e.g. heavy-metals). The major disadvantage with single barrier system was that the system was quite inefficient to treat contaminants of different properties having different physical, chemical and thermodynamic properties (e.g. heavy-metals, BTEX and TCE) (Kober *et al.*, 2002). Besides the incapability of such barriers to treating multi-contaminants, research has been going on to deal with the problem of pollutant mixing, which is the headless generation of new potentially hazardous contaminants while removing other contaminants (Stevens and Quinton, 2009; Healy *et al.*, 2012). However, in the path of increased global environmental concern and use of sustainability approach for remediation, pollutant swapping has become a major concern. For such problem, a concept of the multi-barrier system (Figure 1) has set up which make PRBs a more suitable and sustainable approach and which broadens their applicability to a larger extent. A multi-barrier PRBs consists of two or more than two barriers with similar or different types of reactive materials (sequenced multi-barrier). However, it can also be defined as a single barrier filled with different types of reactive materials (a mixture of reactive materials or multi-treatment barrier) (Obiri *et al.*, 2014).

Some multi-barriers have been limited to treat mainly organic contaminants. A study conducted by (Teerakun *et al.*, 2011) to address TCE with conjugation of ZVI and biobarrier in synthetic groundwater. The three-barrier system installed in which the first column filled with iron fillings, the second column with sugarcane baggase mixed with anaerobic sludge as an anaerobic barrier and the third one with biofilm coated on oxygen carbon inducer releasing material as an aerobic barrier. The fourth column installed with sand to evaluate the performance of TCE and its metabolites down gradient of the system. The removal mechanism includes chemical and biological processes in which the overall removal was 84% and the removal by individual column was iron fillings 42%, anaerobic barrier

16% and aerobic barrier 25% respectively. The breakdown of TCE into different metabolites showed the degradation of the column system. Morkin *et al.*, (2000) reported the use of two barriers for the treatment of a mixture of chlorinated ethenes (DCE and VC) and BTEX within a funnel-and-gate system. The first barrier was filled with granular iron for reductive dechlorination, whereas the second was a biobarrier which allows for degradation of the contaminants by biological means, mainly BTEX and the by-products of the chlorinated ethenes. Lee *et al.*, (2007) also used a multibarrier PRB system filled with iron and a biobarrier filled with the biologically active tire to remove PCE, TCE, and organic matter. Kober *et al.*, (2002) used Fe0 and granular activated carbon (GAC) as reactive materials for the treatment of multifaceted contaminant mixtures in groundwater.

Van-Nooten *et al.*, (2010) also combined different reactive materials and for removing a composite mixture of organic and inorganic contaminants consisting of, adsorbable organic halogens (AOX), chemical oxygen demand (COD), ammonium and the by-products of nitrification and denitrification. Apart from costs, the multi-treatment system has various complexities in design and also has difficulties in monitoring them holistically. To address such type of issues, some approaches and innovation in technology are being used to make the system more suitable and sustainable. Various studies have often been carried out to get information about different microbiological and geochemical treatment facts in such treatment systems to make it more efficient.

To analyze and predict variations in an assortment of parameters such as changes in pH and Eh of groundwater from the reactions between the reactive materials, the contaminants and the groundwater elements, sequencing of barriers, type of reactive materials, tools like MINTEQA2 (Allison *et al.*, 1991) and PHREEQC (Parkhurst and Appelo, 1999) are also being used. Healy *et al.*, (2012) reported that certain factors need to assess for pollution swapping problem and the risk associated with the release of greenhouse gases (GHG) and generation of dissolved contaminants in bioreactors.

Recently, Fenton *et al.*, (2014) recommended that using microbial and molecular fingerprinting as an in-situ cost-effective tool can assess balancing of nutrient and gas in PRBs. Some researchers have reported that while treating contaminants or the usefulness of PRBs with respect to time has shown to be ineffective because of the interaction between reactive media, contaminant and aquifer properties inside or up-gradient of the barriers. The reason behind PRB failure is an accumulation of precipitates of carbonates and sulfates, failure in reactivity and decline in hydraulic residence time, production of gas following a reduction in permeability, and competition for or loss of reactive sites due to corrosion, fouling or precipitation. Henderson and Demond, (2007) did a critical review to know the long-term performance of PRBs filled with ZVI using statistical and graphical methods and tools to recognize the most significant factors that affect the prolonged existence of barriers. Their study discovered

that indecent hydraulic depiction was the prime factor that led to failure of most PRB.

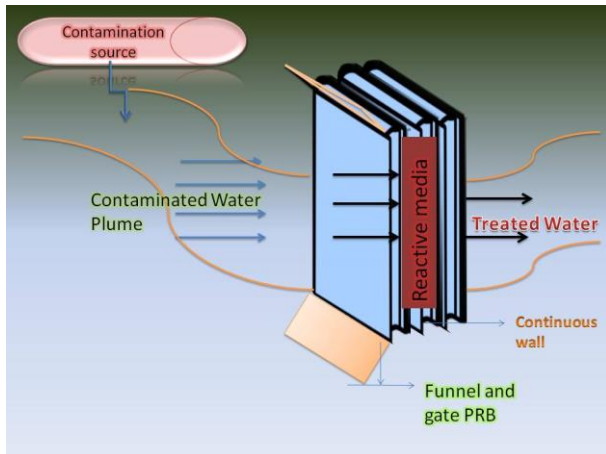


Figure 1. Schematic diagram of Multibarrier PRB

A concept of an enricher reactor (ER) – PRBB in the batch process has been successfully applied to treat contaminated groundwater (Kasi *et al.*, 2013). ER is an offline reactor in which bacterial culture is inoculated to target compound(s) and is used to supplement the main treatment system, such as PRBB. Appropriate growth conditions maintained for culture enrichment, such as availability of nutrients and target compounds, and suitable environmental conditions (pH and temperature) monitored in the ER in order to get the desired degradation capability.

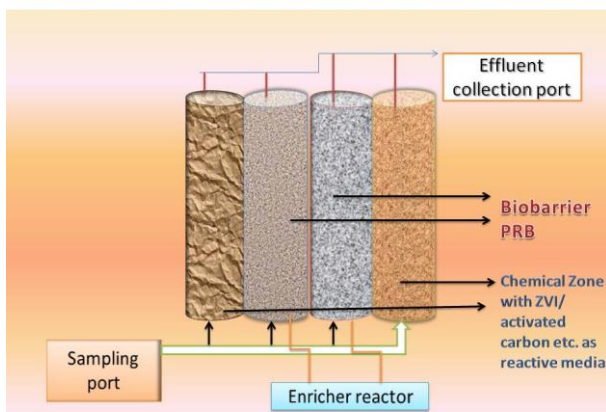


Figure 2. Concept of ChemBio-PRBB/BS with Enricher reactor

A treatment system designed in combination with chemical–biological hybrid PRB and bio-sparging (ChemBio-PRB/BS) reactive zones with a series of different media in the reactive wells and indigenous bacteria belonging to *Delftia* species and *Pseudomonas* species for the treatment of nitrobenzene and aniline contaminated groundwater (Wen *et al.*, 2015). The two strains were able to degrade 98% organic within 72 h at 10 °C which shows that the present strains can degrade even at low temperature. The chemical-biological hybrid PRB shows

degradation of 91% aniline and 85% nitrobenzene respectively up to 40 days, and after 40 days of treatment, the reactive media were further replaced so maintain the efficiency (Figure 2).

6. Long-term performance of PRB

PRB containing different types of reactive media have been gaining a lot of attention for treatment of a variety of contaminants for different time intervals. The most common reactive media used in PRB is iron, which is studied by many researchers that it may experience stabilization and reduction in permeability due to inflation of precipitates (Agrawal *et al.*, 2002; Klausen *et al.*, 2003). An experiment was conducted by (Suk *et al.*, 2009) to evaluate the long-term performance of iron PRB through column experiments and numerical simulation. The research carried out with four types of iron materials having a different configuration for the degradation of cis-DCE and performance of Column bearing iron materials. The result showed that one of the iron material namely ISPAT having higher corrosion rate was showing reduced degradation of cis-DCE and earliest breakthrough and poor performance in comparison with other iron material namely, Connelly iron having lower corrosion rate. The reduction in porosity was observed at five years due to the accumulation of precipitates because of higher corrosion rate than with those having lower corrosion rate. This type of study was also suggested by (Jeen *et al.*, 2007a) that iron material bearing high corrosion rate are not so much beneficial for long term use in PRB as the performance may get hindered by precipitates. Yang *et al.*, (2010) did an experiment to remove 2,4-dichlorophenol with the help of modified GAC and original GAC through PRB system and found that removal efficiency was quite higher with modified GAC than original GAC which could consistently improve the performance of PRB system. A calcium carbonate based PRB was installed for iron and manganese groundwater remediation at landfills by Wang *et al.*, (2016), and they found that total iron removal was 91% during the first year of installation. But the performance of PRB began to decrease during the third year. Another column experiment was performed by Wang *et al.*, (2013c) which showed that removal efficiency of Fe and Mn decreased with an increase in pH over the year because of mineral precipitates accumulated over the surface of walls of PRBs. At the end of the third year, iron-rich soil/mud coating observed on the surface of the calcium-carbonate-based material (CCBM). Yin *et al.*, (2015) performed the removal of nitrobenzene (NB) in two columns i.e. abiotic column having a mixture of sand and iron and biotic column having a mixture of sand and iron along with NB reducing culture. They also demonstrated the longevity of the two columns used and found that biotic columns are having 60% longer life span than the abiotic column and significant amount of physical NB removal because particular iron reducing bacteria could diminish the ferric oxide formation by reducing Fe^{3+} to Fe^{2+} . Hana *et al.*, (2016) performed an experiment using acid washed zero valent iron and aluminum mixture in PRB for the removal of various heavy metals and found out that ZVAI and ZVI together have

better removal efficiency than used alone with the removal efficiency of 99.5 % at 300 hr. Also, fewer oxides were formed on the surface of acid washed ZVAI and ZVI than unacid-washed ZVAI and ZVI. Also, there was an effect of pH on the performance of PRB as in this while increasing the initial pH from 3.0 to 7.0 the removal efficiency of PRB increased because of formation of hydroxide precipitates which favors the abolition of heavy metals along with reduction and adsorption. The long-term performance of PRB was also investigated by (Moraci and Calabro, 2010) having heavy metal contamination and ZVI and pumice as reactive media. The test performed for columns having aqueous nickel and copper solutions of varying concentration. The three sets of columns comprise of ZVI alone, a granular mixture of ZVI and pumice and pumice in series with ZVI and also in later case the pumice was placed downstream of ZVI so that pumice efficiency could also be analyzed. The results demonstrated that copper removal efficiency was high among all the set-ups, but the best performance came out of ZVI-pumice mixture and the concentration of copper was below detection limit, but the performance of ZVI alone ceases at the end. The reason behind ZVI-pumice best performance may be that pumice is not inert with heavy metal, and it enhances the reactivity of ZVI. The reaction products stored in pumice pores from where they remove the pollutants by reduction, adsorption or co-precipitation. The removal of nickel was maximum at 30:70 ZVI-pumice mixture. The overall result indicated that ZVI-pumice mixture was better in the removal of contaminant and also has long-term performance throughout.

7. Symbiotic relationship between microorganisms and reactive media

Reactive media used along with microorganisms exerts symbiotic relationship, and various experimental results showed their interaction in PRB. Parra *et al.*, (2016) performed another experiment to look for the effect of reactive media on microorganism in the degradation rate. The study was conducted to treat acid rock drainage containing sulfuric acid and heavy metals (copper, cadmium, and lead) using sulfate-reducing bioreactor with ZVI by flow-through column in a laboratory-based test. The continuous-flow bioreactor comprises of ZVI, limestone or a mixture of limestone and ZVI. The sulfate reduction by ZVI column was 40 to 50% which was slightly less as compared to ZVI-limestone column which may be due to improved inorganic carbon supply in ZVI-limestone column. The initial degradation by limestone column was only 10% which gradually decreases, and at the end, it ceased. The removal of copper in all the three columns was up to 99.8% to 99.9%. In ZVI based column the degradation was maybe due to metal sulfide precipitation. The concentration of cadmium and lead was very little in the column, so the reduction was negligible. It confirmed from the study that ZVI the slow exogenous electron donor to enhance sulfate reduction. The generation of low amount of hydrogen sulfide in the effluent is due to using of ZVI. However, limestone alone is not so much useful as compared to ZVI. Baric *et al.*, (2012) investigated the relationship between

reactive media and microorganism in PRB for the removal of contaminants. They performed an experiment to treat chlorinated ethanes in PRB by Coupling of polyhydroxybutyrate (PHB) and ZVI. PHB has used a carbon source for enhancing microbial degradation mechanism, increasing iron reactivity and longevity. With the formation of Volatile fatty acids (VFAs), fermentation of PHB has carried out anaerobically and thus can donate electrons for reductive dechlorination by microorganisms. Two columns designed in which the first column filled with mixture of silica sand and granulated iron and the second with Fe and PHB. The result obtained from experiment revealed that the column with Fe and PHB significantly reduced chlorinated ethanes on 199 days of operation and the degradation continues after 199 days, and the contaminant completely removed from the column. But in the case of the column without PHB was lower at 199 days and after this, the column completely lost its removal efficiency. The Fe-PHB column operated under acidic condition compared to Fe-column and it observed from earlier findings that reactivity of ZVI is strongly affected by pH and the degradation rate increases with increase in acidic condition (Chen *et al.*, 2001). A microbial and mineral progress in a zero-valent iron based permeable reactive barrier operated for a long time was carried out by (Kumar *et al.*, 2016). A laboratory-based four column study was performed using granular zero-valent iron and micro-zero valent iron in which one was filled with a small quantity of glycerol to enhance indigenous microbial activity and another one was exposed to gamma radiation for metals and sulfate reduction. It was found out that dissolved sulfate concentration at the outlet of both the biotic column ($m\text{Fe}^0$ and $g\text{Fe}^0$) decreased to nearly a non-detectable concentration of less than 2 mg/l having initial sulfate concentration of 380 mgL^{-1} in almost 30 days. However, the concentration of dissolved sulfate concentration remains unchanged in an abiotic column in which gamma radiation was constantly exposed to the column all through the experiment. Dissolved metal concentration dropped to a nondetectable concentration in both biotic and abiotic column. The Concentration of Zn was to some extent higher in the biotic column because of microbial participation in the column. The Presence of anaerobic microorganism trigger exalted Fe concentration in the biotic column and afterward reduced Fe^{2+} concentration in the columns. The microbial species identified as *A. ferrooxidans* before incubation consistent with acidic pH and metal load. It was an earlier observation that these microbial populations can tolerate metal load and well adapted to reducing environment of Fe^0 . These can grow autotrophically using H_2 , CO_2 , and SO_4 and the experimental observation showed the presence of H_2 produced by Fe^0 oxidation and CO_2 in column headspace. It was evident from results that these are primarily responsible for sulfate reduction. Mineral formation observed in columns. In biotic column formation of mackinawite (FeS) and lepidocrocite ($\gamma\text{-FeOOH}$) (also known as metal scavengers) was found which was consistent with microbial sulfate reduction in columns. The presence of Fe^0 detected in all the columns even at the end

of the experiment that showed that reactivity of Fe^0 was not exhausted and completely oxidized. The clogging was not observed in the biotic column because the iron grains were comprehensively mixed with microbial population thereby increasing the porosity of the column. However, field application might be less precise because of the changes in characteristics of groundwater. Another kind of relation between iron and microbes has been shown by (Fang *et al.*, 2015) in which the growth and feasibility (protein mass) of *S. decolorationis* S12 observed with and without application of iron. The result showed that the protein mass was twice more in culture with iron support than without iron supplement which clearly indicated that iron favors the culture growth. Due to corrosion of iron H_2 so produced favors the growth and also the live/dead ratio was more in iron supplemented culture. Various analysis like SEM, TEM, CLSM, EDS indicated that direct interaction took place between iron and S12 and the strain also get attached to the surface of iron which promoted removal of contaminants. Several other species were identified like *Shewanella spp.*, such as *S. alga*, *S. putrefaciens* and *S. oneidensis*, which showed attaching ability on the surface of iron minerals (Shin *et al.*, 2007, Neal *et al.*, 2005). It was observed that the toxicity of iron particles on microorganisms occur mainly through three pathways which includes altered organization of biological membranes and its associated parts leading to damage to DNA, increased membrane permeability, production of reactive oxygen species leading to oxidative stress. The production of more reactive oxygen species occurs under aerobic condition when Fe^0 reacts with oxygen to produce hydrogen peroxide. It was observed that ROS production increases with increase in iron concentration.

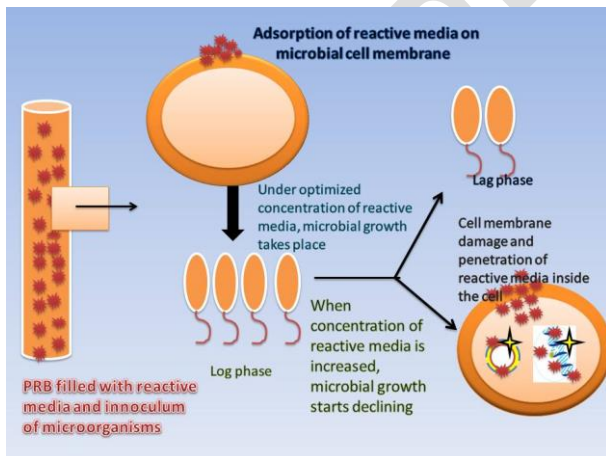


Figure 3. Interaction of reactive media and microorganism

8. Discussion

Since the invention of PRB from the beginning of 90's, it has proved as a creative idea behind the in-situ treatment of contaminants in groundwater at large scale. This review paper apparently deals with advancement in PRB technology, types of reactive media used with their efficiencies and limitations too, different biobarriers for the treatment, different types of microorganisms used for the biodegradation purpose, long-term performance of PRB,

symbiotic relationship between microorganisms and reactive media used in PRB. The overall study states that different reactive media have different efficiencies depending on the type of contaminant. The results also revealed that reactive media, when combined with microorganisms shows increased degradation efficiency but also exert some effect on the life cycle of microorganisms which include generation of ROS leading to oxidative stress on the cell, DNA damage, poor permeability, etc. as a result, the degradation efficiency gets slower with time. The increased types of contaminants need much more attention towards further improved treatment mechanism. However, further research may be undertaken to improve the efficiencies of bio-barriers in treating emerging pollutants and to establish various combinations of microbes and reactive media for better environmental clean-up strategies.

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