A review on design, material selection, mechanism, and modelling of permeable reactive barrier for community-scale groundwater treatment

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ABSTRACT

Over the last thirty years, several techniques of groundwater (GW) remediation based on the principles of physical (air sparging), biological (bioventing), and chemical (e.g., ion exchange) processes have proven to be effective; however, only a handful of them could successfully be implemented at a community or regional scale due to issues like longevity, a requirement of significant investment and operation cost, skilled labours, and others. Therefore, considering the scope of Permeable Reactive Barriers (PRBs) to be implemented on a regional scale and its capability to be a significant replacement for several existing GW treatment methods, this review was prepared with the following objectives: (i) to compare the PRB method with the conventional methods of groundwater treatment along with the possibility and problems associated with the PRB installation in pilot-scale; (ii) to enlist all the probable sets of adsorbents (reactive materials) that can be used for different types of organic and inorganic contaminants; (iii) to understand the key mechanisms of degradation/removal of contaminants involved in PRB design; and (iv) to put forward the future research perspectives of this domain. Review augments that PRBs certainly has a low maintenance cost and a longer life span of ˜30 years that requires very ordinary skills. PRBs promise to be effective in developing countries like India, Bangladesh, and Sri Lanka for the removal of geogenic contaminants like arsenic and fluoride given the appropriate aquifer depth and hydrogeological settings like hydraulic gradient and transmissivity. Furthermore, reactive fillers required in PRBs are readily available, have longer expected life, and operate with no surrounding disturbances. With the advent of several green nanomaterials based adsorbents, PRB's performance can achieve another height, but it needs the experiences from several pilot and larger scale projects. Indeed PRBs are the need of the hour, but a more programming-based investigation would be expected for its superior comprehension.

Keywords:
Adsorbents
Groundwater
Permeable Reactive Barrier (PRB)
Degradation
Reduction
Treatment

1. Introduction

Groundwater (GW) is significantly essential for a varied range of sectors, i.e., irrigation, drinking, and industrial. Close to 2.5 billion people around the globe depend on the GW aquifers for their daily household chores (Thiruvenkatachari et al., 2008). Out of the total 349 billion gallon freshwater extracted in the USA, 26% estimates to be groundwater (USGS, 2009). In India, around 80% of the population depends on GW for irrigation and drinking purposes (World Bank, 2012). In the UK, the total abstraction of groundwater stood at 2747 billion gallons for the year 2017 (DEFRA, 2019). The GRACE analysis has shown the doubling in the groundwater extraction rate globally from 1960 to 2000, i.e., 312 km3/year (1960) to 734 km3/year (2000) (Fienen and Arshad, 2016). It shows our global dependence on GW, which is unlikely to be lowered soon in the upcoming decades. The increased abstraction rate of GW has several adverse effects, such as the lowering of the GW table, subsidence of land, and, most importantly, the GW vulnerability to anthropogenic contaminants, which end up forming contaminated plumes in the aquifers. Groundwater contamination has become a severe problem throughout the world due to the persistent release of various contaminants (geogenic, anthropogenic, emerging) from industrial and non-industrial sectors (Westrick et al., 1984).

The sources of GW contamination divides into two main categories: (a) natural sources, and (b) anthropogenic sources. The latter is divided further into (i) point sources and (ii) non-point sources. Natural sources mostly include mineral-bearing rocks and radioactive substances (NRDC, 2018). Some of them are hydrogen sulphide (H_2S), chromium (Cr), arsenic (As), iron (Fe), fluoride (F), radon (Rn), and uranium (U), as contaminants. Anthropogenic point sources include contamination from leaking chemical tanks, septic storage tanks, municipal sewerage systems, animal wastes from poultry farms, and landfill sites (Whipple et al., 1974). Anthropogenic non-point sources include run-off from a contaminated site, pesticide and fertilizer sprayed agricultural field, forestry practices, acid mine drainage, oil, and toxic substances spill (Whipple et al., 1974; Douglass, 1975).

Anthropogenic GW contamination constitutes pollutants from sources like combustion of fossils fuels, road salts, and other dreadful chemicals leaching down the aquifers (Kumar et al., 2019). The other sources of GW contaminations include leaking septic storage tanks, improperly designed storage systems, corroded/rusted pipe connections, leaching landfills if not shielded from the bottom, road salts, and different types of pest control. These contaminants if gets leached down the aquifer, ends up polluting GW. (Groundwater foundation, 2020). Among all these modes of pollution, the excessive use of the nitrate, DDT (dichloro-diphenyl-trichloroethane) and BHC (Benzene Hexachloride) based fertilizers contaminates the GW at a community scale in developing countries. For example, around 3/4th of India is having more than 45 mg/L of nitrate in its shallow aquifers (CGWB, 2012). Another primary contamination source includes untreated landfill leachates contaminating groundwater with organic matters, ammonium, and metals (Bastiaens et al., 2008). Emerging contaminants like PPCPs (Pharmaceutical and Personal Care Products) are also making their way into the surface water and, to some extent, in GW (Kumar et al., 2017).

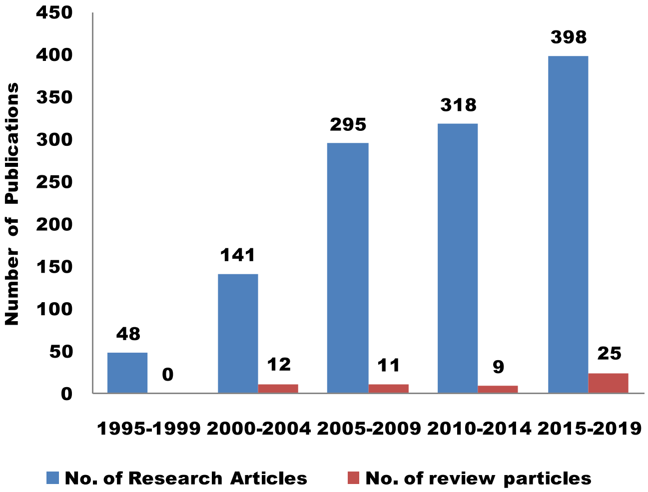


Fig. 1. Number of research and review paper on permeable reactive barriers (PRBs).
Source: Scopus (https://www.scopus.com), March, 2020.

The pollution level of GW due to the factors mentioned above is continuously on the rise, and thus, all the remediation techniques are critically important. The selection of a particular technology depends on several factors characterizing different parameters. An et al. (2016a) analysed four of the technologies pump and treat system, air sparging, natural attenuation and PRB using fuzzy AHP (Analytic Hierarchy Process) and MCDM (Multi-Criteria Decision Making) and then all the technologies were ranked based on ELECTRE (Elimination Et Choix Traduisant la Realite) II method. There have been many technologies for GW remediation like air sparging, bioremediation, but pump and treat (P&T) system was considered to be one of the most profoundly used treatment systems. The last decade has seen a decrease in *ex-situ* remediation technologies (pump & treat) and an increase in *in-situ* remediation methods (PRBs, bioremediation, thermal remediation) (Wilkin et al. 2016). PRBs were introduced as an alternative method for remediating the contaminants from GW, but it has ended up being the most efficient and effective solution (Faisal et al., 2018). This passive remediation method is also a low-cost approach due to (i) removable installation (ii) low energy consumption (iii) targeted remediation (iv) less usage of freshwater and (v) continued efficient treatment till its longevity lasts (Day et al., 1999). The use of PRB started around the year 1995 started taking over the P&T, due to multiple reasons: (a) it degrades and remediates the contaminants below the surface only, thereby, decreasing the need for any expensive technological system to be installed above the surface; (b) it does not require any source of energy and contaminated plume gets treated with the help of natural gradient of GW flow; (c) no advancements needed for the treatment of further effluent as in the case of P&T.

There have already been more than fifty review papers and twelve hundred research papers on PRBs (source: Scopus, March, 2020), as shown in Fig. 1. However, a review that covers all key aspects of PRB design and operation comprehensively seems to be lacking at the moment. In addressing this point, this review paper aims to cover nearly all aspects of PRB technology, namely, (a) design of the PRBs and their modifications over the years, (b) the conducive conditions for the installations of PRBs, (c) mechanisms involved in the remediation, (d) the generic fillers and the new green fillers for PRBs, and, (e) modelling aspects of the PRBs. Also, the review paper aims to discuss the following aspects in detail: (i) the categories of GW contamination sources, (ii) the hydrogeological conditions favourable for PRB installation and (iii) the prominent reactive materials involved and various mechanisms involved. The review is further enhanced with relevant case studies from the developing and developed nations while commenting on the technology's future perspectives. The paper places particular emphasizes on discussing the above issues from the viewpoints of the developing nations, as it seems that there has been little or no progress on PRBs in these countries, and there is a significant gap in translating the theoretical design into practise in these countries (Chandrappa and Das, 2014).

2. Design of PRBs

The very first conceptual idea about PRB was coined by (McMurtry and Elton, 1985) which revolved around three main constituents i.e. (a) treatment methodology (physical or chemical), (b) the hydraulic data and, (c) the geotechnical designs. GW remediation has always proved to be a costly affair. The *in-situ* application of PRB has gained significant interest due to the low operational cost, media longevity and hydraulic performance (Wilkin et al., 2014). PRB uses the hydraulic gradient (natural or induced) for remediating the contaminated GW, the upgradient contaminated water gets decontaminated after reaching down gradient (Starr and Cherry, 1994). A simple set up of PRB requires a series of steps to be followed from the characterization of the site to the economic viability as shown in Fig. 2.

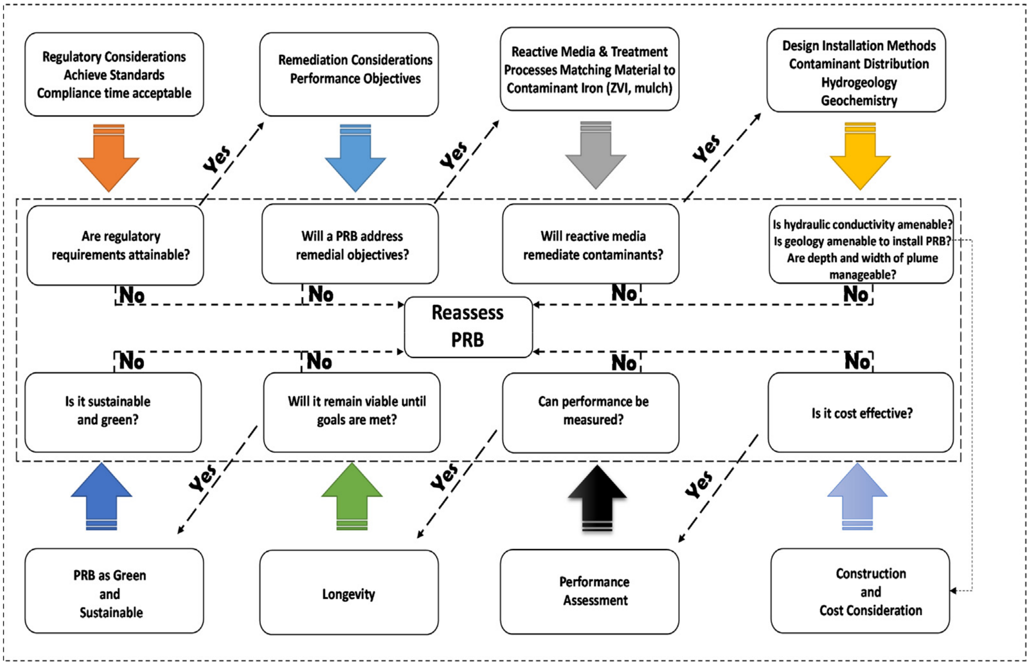


Fig. 2. The assessment diagram of PRB installation.
Source: Adapted and Improvised from Gavaskar et al. (2000).

The foremost thing which should be considered before designing the PRB should be the fact that it should be able to intercept the plume completely. The contaminants should not bypass the barrier. Also, the GW flow should be in the perpendicular direction i.e. across the PRBs, if '*x*' and '*y*' are the height and length of the PRB, then the plume should be flowing through the '*z*' direction, all the three-axis being perpendicular to each other. When a length is should be considered, the PRB should be long enough to treat the entire width of the contaminated plume. The thickness of the PRB should also be enough to remediate the contaminants before they leave the barrier because of the effective degradation of the contaminants. In the case where there is significant fractured flow such as coupled free and porous flow, the PRB must be designed keeping these hydrogeological conditions in mind (Das, 2002, 2005).

2.1. Continuous trench

PRBs are underground structures that are established in the flow of contaminated plume. PRBs are continuously evolving since 1980, the most cost-effective solution to install PRBs are slurry or continuous trench techniques. This kind of technique is favourable in most of the soil types and for depth between 5 to 30 metres (Day and Schindler, 2004). At the site of Somersworth, Nashville, a continuous wall of 280 m long was set up with the depth ranging from 7.9 to 14.3 m (Krug et al.). This design of PRB contained 8 different sections, each of length 30 m. A minimum thickness of 0.7 m was necessary for PRB due to the size of the excavator bucket used. Horizontal wells are extensional continuous trench designs where a PRB facility collects the contaminated GW from within the aquifer and is fed into the treatment area where a series of cylinders filled with ZVI is placed (Korte et al., 1997). There can be further advancements possible in the design to accommodate a higher GW flow rate.

Some of the problems associated with the continuous trench method of PRB construction are problems arising due to the presence of rubble and concrete-like foundations, collapsing of the spoilt contaminant soil, fractured GW flow, diffused contaminant plumes, and other buried structures like rail-road interfering with the construction designs. At Tonolli Superfund site, Nesquehoning, Pennsylvania (RTDF, 2000) many of these problems arose, due to which the wall which was originally designed for 1 ft was later expanded to 3 ft. For the actual construction, the use of biodegradable slurry is preferred over the setting up of the sheets piled up in the dug up trenches to facilitate the construction of the same.

2.2. Funnel and gate

The funnel and gate PRB are systems wherein the cutoff walls, i.e., the funnels give direction to contaminated plume towards the reactive gate. The funnel and gate system is another type of PRB design, where the length of the barrier

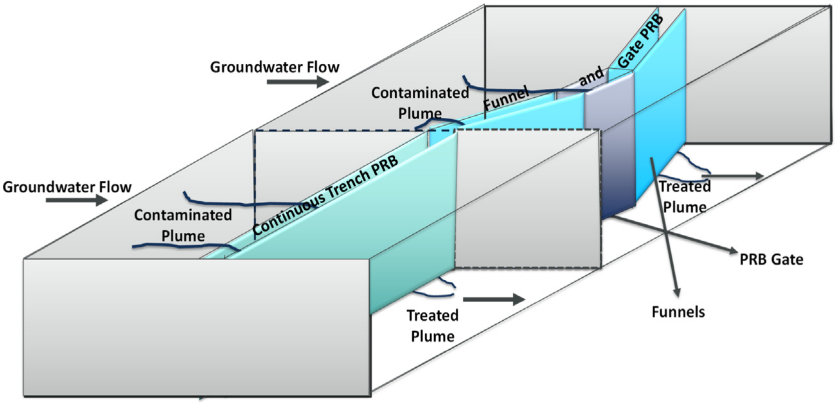


Fig. 3. Configuration of PRB designs (a) Funnel and Gate (b) Continuous Trench.

should be longer than the lateral extent of the plume. The gate material can be made up of bentonite and slurry soil mix (Kreuzer, 2000), and likewise, many other reactive materials. These systems are designed to operate passively so that a natural gradient can be provided to the plume flow towards the reactive barrier. The fundamental design configuration of PRBs are shown in Fig. 3

The continuous trench PRBs are favoured in the developing nations or the countries with lower GDP (Gross Domestic Product) because the installation cost is lesser than the funnel and gate systems, even if, the latter PRBs are easier to decommission than the continuous trench PRBs. Also, the continuous trench is favourable for a wide variety of hydrological and geological conditions; thus, benefitting countries like India with such varying fluvial and aeolian landforms. This scenario becomes exactly the opposite when the reactive material being installed is slightly costly because in the funnel and gate system, the reactive materials are placed in replaceable reactors that are changed after a specific tenure, this being the main reason before installation of PRBs, thus an essential perspective from a country's economic point of view.

2.3. Sequential PRBs

The sequential PRBs, which consist of one iron filler barrier and bio-barrier, could be effectively used for the removal of PAH (Polycyclic Aromatic Hydrocarbon) compounds. Choi et al. (2008) studied the removal of 2,4,6-trichlorophenol using a sequential PRB on a lab scale. The first one was a chemical reactor containing Pd coated Fe, and the second reactor was a biological reactor containing anaerobic microbes seeded sand. Köber et al. (2002) used GACs and ORCs as sequential PRB fillers along with ZVI, being the first filler for the remediation of unevenly contaminated aquifers. The study later concluded the ZVI+GACs better than the ZVI+ORCs for broad applications. Chaturanga et al. (2006) studied the use of 7 sequential barriers namely firewood charcoal, biochar, sawdust, washed quarry dust, dewatered alum sludge, red soil, and washed silica sand (WSS).

2.4. Design modification in recent years

The multiple barriers are the demand for now and are also being popular among the upcoming setups. There are also reaction vessels coming up for remediation installed in the form of reactive gates. The advancement which we can achieve here is that while emplacing the materials as PRB fillers, we need to place forward the idea of a temporary replacement. The barrier can be made in the form of prefabricated units or the filter columns, so that after a while if the reactive materials lose their adsorption capacity, the new ones can be added (Suponik, 2010). Hosseini et al. (2011) has tried rectifying the problem of pore-blocking and permeability loss by designing PRBs in such a way that it contains no porous material and is limited to the ZVI injected at the gate of PRB.

Bio-barrier type of PRBs are the need of the hour. These barrier are designed to get the amended reactive fillers to get into the lithology of the soil. This is done by using one of the passive techniques like varying the alkalinity or by diffusing air into the soil. Even then, a particular type of bio-barrier requires a considerable amount of work to deliver a mixture at an exact lithological depth in the subsurface (ITRC, 2005). A study by Meng et al. (2014) shows the applicability of ANAMMOX (anaerobic ammonium oxidation) for the removal of N_2 This biofilm reactor developed a non-fouling operation state, unlike other biofilm reactors. Deka et al. (2020) studied the application of preoxidation with coagulation in order to control the fouling of membranes. The species that dominated the experiment was *Candidatus Kuenenia*. Table 1 shows the different designs of PRB with different experimental conditions. Nooten et al. (2008) studied the remediation of ammonium, adsorbable organic halogens, chemical oxygen demand and toxicity from landfill leachate in a multifunctional reactive barrier. The first compartment constitutes of diffusive oxygen emitters which were responsible for microbial nitrification of the ammonium to nitrite. The second compartment was filled with the ion exchange *clinoptilolite*. The third compartment was also a denitrification chamber, comprising of sodium butyrate.

Table 1
Design and experimental conditions of PRBs, at lab and *in situ* scale remediating inorganic and organic contaminants.

Reactive materials	Ratio/Scale	Target contaminant	Design of PRBs					Removal results	Reference
			Experimental conditions						
			Design	pH	Dimension	Time/Temp.	Flow Rate		
Hydroxyapatite coated quartz sand	-NA- (Lab Scale)	Uranium U(VI)	4 PVC Column	4.0	D 0.15–0.3 mm, 0.6 mm, 0.6–1.18 mm	–	–	69%–81%	Zhang et al. (2018)
Preheated Rice Husk Biochar and Zeolite	7:3 (Lab Scale)	Ammonium-Nitrogen (NH_4^+-N)	–	–	400 cm x 50 cm x 300 cm	–	–	N – 66%, K – 57%, P – 11%, C – 9%	Kim et al. (2016)
ZVI, Red Sand, Umnegi Sand	3:1 and 1:1	Arsenic (As)	–	–	–	–	–	100% at all flow rates	Trois and Cibati (2015)
$CaCO_3$ based PRB (*In-Situ*)	–	Iron (Fe (II)) and Manganese (Mn (II))	–	6.0	–	–	–	–	Wang et al. (2016)
Quartz, ZVI, Zeolites and Oxygen Releasing Compounds	First Reactor (Q : ZVI = 40 : 60) Second Reactor (Q : ZVI : Zeolites = 34.78 : 43.48 : 21.74)	Zinc, Manganese, Magnesium, Chromium, Strontium, Aluminium	2 Reactors system	6.9	L=90.0 cm, $D_i = 15.0$ cm,	60 days	–	Zn (93%–97%), Mn (90%–99%), Mg (52%–96%), Cr (67-70), Sr (62–95), Al (46–58)	Jun et al. (2009)
Granular Iron	-NA- (*In-Situ*)	Chromium Cr (VI), Trichloroethylene (TCE)	PRB installed at 30 m downstream	–	46 m ×7.3 m ×0.6 m	–	$Q = 0.04 - 40$ L/min	Cr (VI) 99.9%, TCE 99.9%	Wilkin et al. (2014)
Leaves, Compost, ZVI, Silica Sand, Perlite and Sandstone	6 : 9 : 3 : 30 : 30 : 22 (Lab Scale)	Sulphate and Cadmium	Batch Test for diff. comp.	–	D = 0.77 – 1.8	T=80 ° C	–	SO_4 (80%–93%), Cd (94%),	Pagnanelli et al. (2009)
Palladium Coated Iron and Anaerobic microbes	-NA- (Lab Scale)	2, 4, 6 Trichlorophenol	Column Reactor System	4.71–6.07	$C_1 = C2$ ($D_i = 2.6$ cm, L = 30 cm; C_3 ($D_i = 10$ cm, L = 80 cm)	–	–	Cr(VI) 99.9%	Choi et al. (2008)
Cellulose Fibre, Leaf Compost, Bovine Manure, Limestone	43.3 : 27.5 : 16.2 : 13 (Lab Scale)	Aluminium (Al), Copper (Cu) and Zinc (Zn)	Plexiglass Bench Reactor System	2.8	80 cm ×6.5 cm ×30 cm, t = 1 cm	–	–	Al (>99%), Mn (>66%), Cu & Zn (100%)	Torregrosa et al. (2019)
Oxygen Releasing Compounds (Cement, Sand, Water, KH_2PO_4, $NaNO_3$, CaO_2)	100 g of ORC	BTEX (Benzene, Toluene, Ethylene, Xylene)	Column, Batch and Bench Scale	–	10 cm Sand + (5–10) cm + 40 cm Sand	100 days, replacement on 38 & 94 day	–	B (68%), T (56%), E (25%), ×(25%)	Yeh et al. (2010)

3. Hydraulics conditions for PRB installation

The PRBs are not easy to install as it seems that because of the heterogeneous nature of the subsurface and aquifers, one may encounter significant difficulty in the installation process. The site characterization is a must process to achieve decent remediation and also helps in sustaining an extended life PRB. If a proper study is not done before setting up the PRB, we can see the reduction in performance after some time. Benner et al. (2001) state that a decrease in the residence times and an increase in the flux rate will be noticed if the aquifer has heterogeneous hydraulic conductivity. A site-specific study by Duchesneau and Feshbach-Meriney (1999) has resulted in a PRB installed at an ash landfill area, where TCE (Trichloroethylene) and DCE (Dichloroethylene) plume flow net was 365 m ×183 m. Here the geological matrix consisted of the glacial pack (2.1 m) and fractured shale (up to 6 m), depth of GW varied between 1.8 to 2.4 depending on the type of climate season. These layers do have different values of hydraulic conductivities which determine the depth till which PRB should be installed. The hydraulic conditions for the setting up for PRB is shown in Fig. 4.

3.1. Hydrogeology

Installation of PRBs can hit a blowdown due to some of the geological features like too hard lithological feature which is too hard for excavation, sometimes the holding media is not consolidated and disturbs the emplacement of the filler material. The presence of cobbles and pebbles too can hamper the excavation of filling sites and thus pre-requisite knowledge of the stratigraphy of the lithological layers of the aquifers. The testing of the emplacement site is essential and thus geotechnical testing can help to identify the following characteristics (i) Shear Strength and Cohesion properties of clays, sand, silts. (ii) Dryness and Wetness fractions of the materials (iii) The grain size of the various layer found in the site (iv) The density of the materials found (v) Various soil properties in case of deeper PRB emplacement.

3.2. Groundwater hydraulics

The installation of PRBs generally requires its construction to be below the water table and that too on deep and uneasy sites. Thus, having a clear idea of the groundwater hydraulics eases the construction of PRBs and also effects its longevity(Day et al., 1999). GW speed and stream bearing affect the viability of a PRB. Drainage velocity of GW streamflow is generally governed by both of the horizontal and right angle pressure-driven angles. These factors are important for consideration as conductivity and porosity of the aquifers. The residence time of contaminants treated inside a PRB is

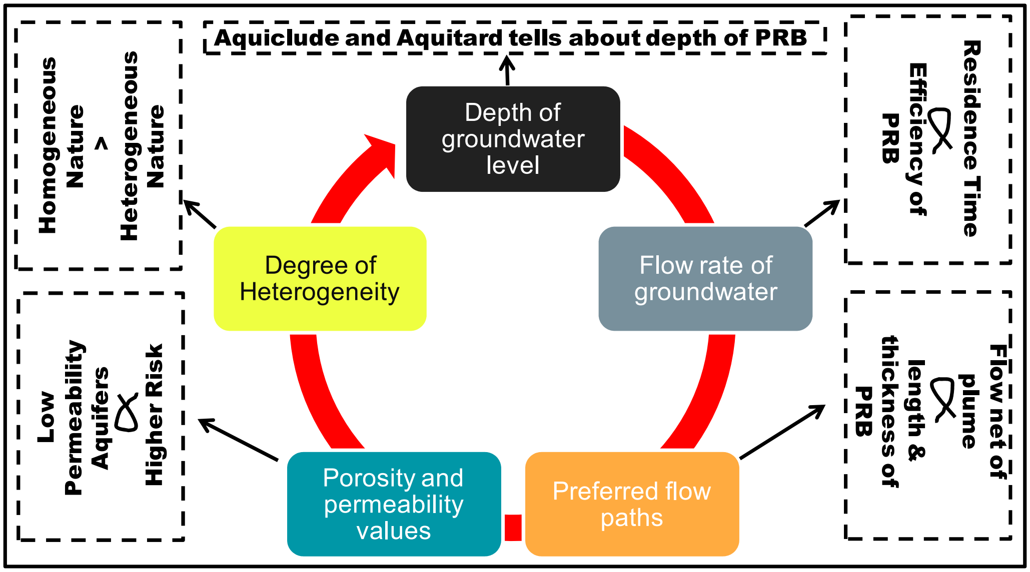


Fig. 4. Hydrogeological conditions for the operation of PRBs at a contaminated specific site.

also affected by the GW stream rates. High paces of GW stream decrease contaminant living arrangement time in the PRB, while low paces of GW stream increment the living arrangement time. Vertical slopes and streams does not play a significant role, in the case of an aquifer with low penetrability layers. Groundwater modelling is important in order to emplace the PRB till aquitard, so that the plume does not go beneath the PRB and goes through it (Smyth et al., 1997). The Funnel and Gate complexes the design even more as the GW velocity increases nearly 5 times the natural one. This effects the quantity of the reactive material used and also the thickness of PRBs (Starr and Cherry, 1994).

The Darcy variables are critical factors that must be taken into account at a particular site, for the notable characteristics of the particular site (Santisukkasaem and Das, 2019). Leakage rates of GW, if less than 0.3 m/d or 109.7 m/year, is the most favourable condition for the installation of PRBs. Higher speed may act as a constraint for the reactivity inside the PRB. Contaminants that are generally broken into further pollutants after getting degraded by the reactive fillers like chlorinated solvents take a lot more time than the contaminants with reducing significance rates. Different arrangements of PRBs are needed for different scenarios.

3.3. Geochemistry

Another vital aspect of PRB setup is aquifer's geochemistry which can have a severe effect on the performance of the PRB. In the case of biological PRBs, an organic substrate is added to gulp down the electron acceptors. It also serves in providing the optimum redox conditions so that a better rate of anaerobic degradation is achieved. The levels of unwanted electron acceptors that are local to the regions may provide a limitation to the effective rate of degradation of actually targeted contaminants. These electron acceptors are species of dissolved oxygen (DO), nitrate (NO_3) and bioavailable iron. Due to an enormous amount of mass available for organic substrates and also due to their reducing capacity, they have become popular over the year as bio wall PRB. It has also helped us in reducing the activities or locally available electron acceptors. The geochemistry conditions of some aquifers are better for PRB emplacement than the others, for example, when DO level and nitrate helps in chemically transforming the chlorinated solvents to less toxic solutions (ITRC, 2005). The geochemical models like MINTEQA2, was used to calculate the sulphide mineral saturation index in order to study the changes in water chemistry up and down gradient (Benner et al., 1999). The comprehensive dataset comprising of pore water chemistry and solid phase data of collected samples were used to confirm to the conceptual model of PRB installation at the given site (Mayer et al., 2006).

Other than these factors, microbiological effects also play a critical role in deciding the life of a PRB i.e. for how long it functions with its topmost efficiency. There are substrate present other in PRB, along with fillers which enhances the metabolism of certain bacteria. Analysis has proven the increase in the population of Sulphate and metal-reducing bacteria (Evaluation of Permeable, 2002). Also noticed was their decreasing concentration along with the thickness of PRBs. Gibert et al. (2019) also state that while studying the performance of a biological PRB for reducing NO_3^-, the denitrification was achieved most preferably at the deepest part of PRB.

The site characterization has always remained one of the critical parameters before the installation of PRB. These characterizations are generally noninvasive, and also it is economical when used along with pits and wells. Electromagnetic and Ground Penetrating Radar are some portable instruments that are used for to detection of debris, contamination (Phillips,

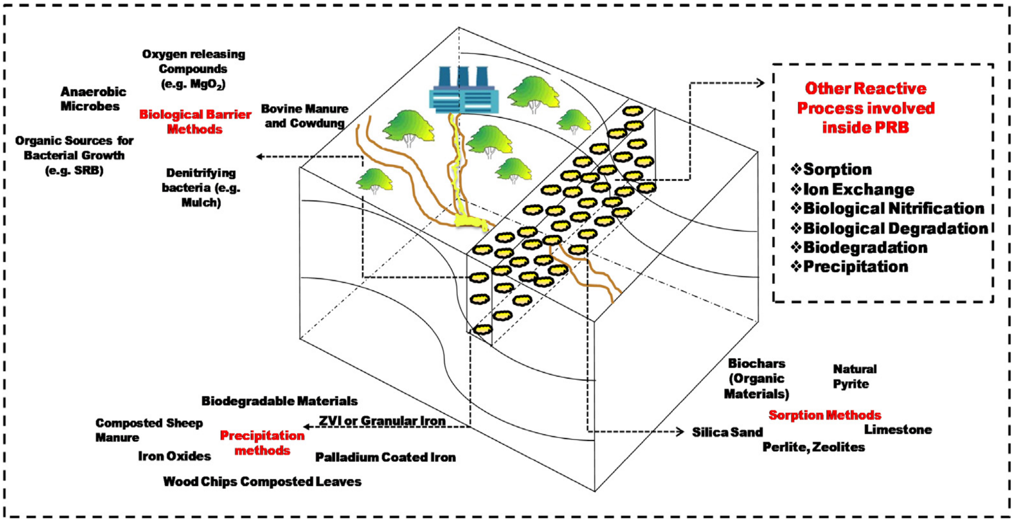


Fig. 5. Different materials, mechanisms and processes involved in contaminant remediation with the help of PRBs.

2009) and thus can help in framework formation. Generally, most of the PRB installations are done by the technique of conventional excavation, which is best suited for the trench of continuous nature (depth < 10 m). Here, the cost of operation varies directly with the depth of PRB installation. These excavations are done with the help of backhoe (US Air force Design, 1997). After trench excavation for the installation PRB, there are also few problems associated with the shallow trenches other than the deterioration of PRB's quality over the years are that the contaminated soil and water are now exposed and can possess a threat if installed in an urban residential setting (Gavaskar et al., 1998).

4. Remediation processes within PRBs

Permeable reactive barrier's one foremost advantage over the pump and treat system is its passive method of working, i.e. without any labour or energy input. The barrier before being set up has to go through (i) preliminary site assessment (types and concentration of contaminants, the velocity of GW) (ii) characterization of site(Aquifer) and distribution of plume (iii) reaction rates and half-lives of contaminants, (iv) barrier location and configuration (Gavaskar, 1999). Modelling in 3D rather than 1D and 2D helps us to simulate the entire flow characteristics of GW in the aquifers and also of a plume (Gupta and Fox, 1999). Bastiaens et al. (2008) studied the use of lab-scale multifunctional permeable reactive barriers to remediate ammonium, halogenated hydrocarbons and CODs (Chemical Oxygen Demand) from a 40-year-old landfill in Belgium. The different materials, mechanisms and processes on which PRBs work are shown in Fig. 5.

Gravel is generally added in between the reactive materials to improve the permeability of PRBs and in the same Limestone is added as Sulphate Reducing Bacteria can have controlled growth (Benner et al., 1999; Jarvis et al., 2006). Pagnanelli et al. (2009) have tested the mixture of organic materials for the removal of sulphate and cadmium ions, the processes they have noticed were Bioreduction and Sorption by SRB and organic matter, respectively.

4.1. Immobilization

This reactive process includes sorption and precipitation of the contaminated plume. Sorption takes place on the filler materials acting as adsorbents and precipitation of the contaminant takes place from its original dissolved state. The former process is generally concerned with the organic contaminants, which are generally hydrophobic;on the other hand, metal generally gets sorbed due to the electrostatic attraction (Scherer et al., 2000). Here the reactive material is electron-donating and thus helps in facilitating electron transfer. Uranium uptake by ZVI was result of two step equation (a) (Morrison et al., 2001). The reaction involves the oxidation state to decrease and thus immobilize U(VI) to U(IV) (Gu et al., 1998).

$$\mathrm{Fe}^0 + \mathrm{UO}_2(\mathrm{CO}_3)_2^{2-} + 2\mathrm{H}^+ = \mathrm{UO}_2 + 2\mathrm{HCO}_3^- + \mathrm{Fe}^{2+} \tag{a}$$

4.2. Transformation

It renders the toxic form of a contaminant into a non-toxic form. The advantage of transformation being that it does not require complete removal of the pollutants. The transformation process includes redox reactions for the treatment of contaminants. Conca and Wright (2006) studied the mechanism for the removal of Zn, Pb and Cd with the help of apatite. The mechanism involved for PB was a 2 step dissolution processes shown in equations (a) and (b).

$$\mathrm{Ca_{10-x}Na_x(PO_4)_{6-x}(CO_3)_x(OH)_2 + 14H^+ \rightarrow (10-}x\mathrm{)Ca^{2+} + xNa^+ + (6-x)[H2(PO4)]^- + xH_2CO_3 + 2H_2O} \tag{a}$$

$$\mathrm{10Pb^{2+} + 6H_2(PO_4)^- + 2OH^- \rightarrow Pb_{10}(PO_4)_6(OH)_2 + 12H^+} \tag{b}$$

The metal concentration and reaction condition determines the precipitation of metal phosphates after homogeneous nucleations (Wright et al., 1995; Lower et al., 1998). This transformation reaction inside PRBs arises concern when due to reducing condition Fe inside reactive wall reduces to FeS and then its further transformation to FeS_2 reduces the effectiveness of PRBs (He et al., 2008). Addition of MnO_2 to ZVI for the treatment of Tetracyline was proven to be effective, as it accelerated the transformation of Fe2+ to Fe3+ and combines with later to remediate the drug at 85% removal efficiency (Dong et al., 2018).

4.3. *Bioremediation*

It includes two main processes as follows. (a) Biostimulation — here, the essential activities of the microorganisms are focused towards the biodegradation of the contaminant by addition of O_2. It is facilitated by the addition of several nutrients (inorganic) which acts as electron donor or receptors (An et al., 2016b). (b) Bioaugmentation — here, simply the microorganisms are added with O_2 and nutrients (Xin et al., 2013). It is used in the places where the pollutants levels are deficient (Samuelsen et al., 2017).

The site-specific study at Shaw Air Force Base in Sumter, showed us the importance of considering the production of daughter products in the design of PRB, as the change in the width and retention time would be required to treat the contaminants till a permissible limit. Wilkin et al. (2005) studied the Chromium removal process with the help of ZVI, and can up with the possibility that there might be an enhancement in the properties of the ZVI by secondary iron-bearing minerals, due to redox reaction at the water-mineral boundary or by the release of Fe(II) in the solution via dissolution/corrosion. Mayer et al. (2006) studied the sulphate removal with the help of organic carbon contained fillers and found out the removal mechanism is the precipitation of the iron monosulphide and siderites and few other reduced mineral phases. (Morrison et al., 2001) studied the precipitation of uranium with the help of Fe(0) PRB and studied the chemical variations in the column experiment and actual installed PRBs. Some notable changes were pH of 7.34 in column effluent than the pH of 9.82 in PRB's effluent and a decrease in the iron concentration of 27.1 mg/L in columns and 0.17 mg/L in actual PRB. This was due to the longer residence time in PRB than the columns. Other process identified in remediating the contaminants are hydrophobic interaction, electrostatic interaction, Hydrogen bonding, exchange of cations & anions and absorption into porous materials. These processes were the main mechanisms noticed in ciprofloxacin removal by Na-alginate and grapheneoxide hydrogel beads (Zhao et al., 2018).

5. Reactive materials

5.1. *Zero Valent Iron (ZVI)*

Zero Valent Iron (ZVI) has shown promising results for several types of GW contaminants. Limitation for PRB having ZVI as its reactive material was incomplete removal of halogenated hydrocarbons as there is no change in their aromatic structures (Choi et al., 2008). Kumari et al. (2018a) used the ZVI and magnetite corn cab silica for the removal of Chromium (VI) ions. Over a period ZVI turns into an agglomerate, thus used with fibrous palygorskite to have an increase surface area (Frost et al., 2010). ZVI Synthesis has seen transition from milling method (Li et al., 2009), to reducing agent method as shown in Eq. (1).

$$\mathrm{Fe^{2+} + 2BH_4^- + 6H_2O \rightarrow Fe^0 + 2B(OH)_3 + 7H_2O\uparrow} \tag{1}$$

ZVI has remained over the years the most efficient PRB filler for non-homogeneous containment of inorganic metals, the organic compounds and also the radioactive nuclides. ZVI, a metal scrap product is easily available in the automotive industry, and can be used as a reactive filler (Morrison et al. 2000). There are several problems also associated with the ZVI are loss of filler's porosity, reduction of permeability and bypass of the contaminated plume. Hosseini et al. (2011) tried to rectify these problems by confining the target zone. The precipitates formed on ZVI after and during the remediation mostly includes lepidocrocite, haematite, magnetite, marcasite, aragonite, brucite, siderite (Wilkin et al., 2002) (Yabusaki et al., 2001). Santisukkasaem and Das (2019) also identified the change in ZVI based PRB and noticed the decline in permeability due to the clogging of the pores within the ZVI PRB by oxidation reaction products within the PRB. The generation of oxidation products was confirmed by XRD, which showed the formation of maghemitye and magnetite. Permeability loss of around 95% was noticed for coarser and 79% for finer ZVI particles for the same water flow rate over a period of three months.

5.2. Granular activated carbon (GAC) and biochars (BC)

The granular activated carbon has been tested for a variety of inorganic contaminants. Suponik (2010) has used the GAC for the removal of phenols and benzene. The most probable process noticed here was of the adsorption due to the hydrophobic bonding shown in Eqs. (2) and (3). The biodegradation rates were achieved at the rate of ƛ (phenol) = 0.0369 1/hr and ƛ (benzene) = 0.0369 1/h. The foremost benefit of using GAC as reactive filler was that no other contaminant was generated as a by product during the degradation process, and thus, there was no need of replacing the fillers until and unless they get blocked.

$$C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O \tag{2}$$

$$\downarrow$$

$$C_6H_5OH + 7O_2 \rightarrow 6CO_2 + 3H_2O \tag{3}$$

Hu et al. (2019) studied the removal of Cr(VI) with the help of peanut shell BC, which was further activated by slow released nutrients which were a mixture of agar yeast extracts and glucose. Here, *morganellamorganii* was used as a species to immobilize BC which was later used in a column experiment to reduce Cr(VI) to Cr(III). Liu et al. (2019) studied the removal of PAHs (Polycyclic Aromatic Hydrocarbon) especially Phenanthrene with the help of two BCs i.e. (a) wheat straw BC (b) coconut shell BC, both of these were further mixed with palygorskite, Diatomaceous Earth and Calcium Peroxide. To protect A and B, its outer shell was made by Portland Cement and later on bounded with Na-Alginate & Water. (Goswami et al., 2016) used the Biochars made from pyrolysis of *Ipomoea fistulosa*for the removal of Cadmium at batch scale. Th application of MnO_2 along with AC to remediate inorganic and organic contaminants was also effective, opening up the future prospect of composite reactive fillers (Shim et al., 2019a,b).

5.3. Sulphate reducing bacteria (SRBs) and oxygen releasing compounds (ORCs)

SRBs are also one of the leading reactive fillers that can be used for the removal of heavy metals. These kinds of bacteria derive their energy from the oxidizing organic compounds and Hydrogen molecules, which helps in reducing SO_4 to sulfides. These sulfides, in turn, reacts with metals to form metals sulphides as shown in Eqs. (4)–(6) (Suponik, 2001).

$$SO_4^{2-} + CH_3COOH + 2H^+ \rightarrow HS^- + 2HCO_3^- + 3H^+ \tag{4}$$

$$\downarrow$$

$$H_2S \rightarrow HS^- + H^+ \rightarrow S^{2-} + 2H^- \tag{5}$$

$$\downarrow$$

$$HS^- + Me^{2+} \rightarrow MeS_{(s)} + H^+ \tag{6}$$

Gholami et al. (2019) studied the bioremediation of the Toluene and Naphthalene with the help of MgO_2 nanoparticles in a sand packed column. This nanoparticle helped in stimulating ORCs, namely P. *putida*, and P. *mendocina* for the contaminant degradation.

5.4. Modification in recent years

There are still a large number of contaminants that are scientifically proven to be the contaminant immobilizer. For example, sawdust, zeolites, limestone, activated alumina, leaf extracts, Indian curry leaves are proven ones at lab and column scales, and, are also one of the most readily available fillers (Borah et al., 2018; Mukherjee et al., 2020). Due to this tendency, they have always remained as one of the most promising PRB Fillers and are used in those contaminants cases which are not susceptible to Eh and pH variations. Some of the features one should look for before going finalizing any reactive filler is its adsorption capacity, selectivity, the degradation nature, its longevity, its reaction kinetics (Roehl et al., 2000). Calcium Peroxide nanoparticles, a type of ORC was used to remediate Nepathalene at a column scale study (Gholami et al., 2019a,b). Nutrient (Nitrate) removal by the concept of alternative latrine was used, where layer of fillers (i) BOF slag (ii) Sawdust were proved to be low cost efficient technology (Suhogusoff et al., 2019).

The green synthesis methods for the fillers should be more boosted and should be pocket-friendly for the developing nations as well. The removal of Cr(VI) with the help of Mn powder from battery waste address concern of 3R approach (Kumari et al., 2018b). The preparation alternatives for the zero-valent iron (nZVI) is also to be looked up for. Fang et al. (2010) has addressed the mechanism of synthesizing the nZVI from the steel pickling waste liquor which was used for the degradation of metronidazole. Gogoi et al. (2015) analysed the effect of vermicomposting on the sewage sludge for the reduction of Zinc and Copper from leaching to the water resources, showing another waste to energy transition. This method of synthesis will help us in decreasing the production cost of our reactive fillers. This was one of the few instances where a nanoscale zero-valent metal was used to treat the antibiotics. The experiments were further repeated with nanoscale Ni^0 and nanoscale ZnO, providing an option to move to other nanoscale metals as well. Table 2 gives a broad idea about a selection of key reactive fillers used till now.

Table 2
Different reactive fillers used in PRBs for geogenic and anthropogenic contaminants in terms of removal percentage.

		Contaminants											
		NO_3	*Cu*	PO_4	Pb	Cr	Ni	SO_4	Zn	F	HCs	NH_4	Cd
Fillers	Sand [a]	25–70	33–76	58–91	11–100	9–49	0–3	–	0–49	–	–	–	–
	Zeolites[a]	35–78	–	70–73	87–89	–	–	–	–	–	–	–	32-99
	Iron Fillings[a]	91–100	80–100	88–94	92–97	37–82	87–89	–	96–99	–	–	–	89-95
	Calcite[a]	28–65	86–99	35–98	98–99	15–60	0–14	–	4–99	–	–	–	88-96
	Clinoptilolite[b]	–	> 80		>80	–	–	–	–	–	–	>80	–
	Sawdust + Sand [c]	77	–	–	–	–	–	–	–	–	–	–	–
	Natural Pyrite[d]	–	–	–	–	27–100	–	–	–	–	–	–	–
	Biochars (Wheat Straw + Coconut shell)[e]	–	–	–	–	–	–	–	–	–	99%(PAH)	–	–
	Red Mud[f]	–	–	–	–	–	–	–	–	87.30	–	–	–
	Volcanic Slug and Pumice[g]	–	85	–	–	–	–	–	–	–	–	–	–
	Sediments (SRBs, Silica Sand, Limestone, Compost)+(chicken manure) + (oak leaf, manure)[h]	–	–	–	–	–	–	25–100	–	–	–	–	–
	Mulch and Gravel[i]	66–99	–	–	–	–	–	–	–	–	–	–	–
	Woodchips[j]	>99	–	–	–	–	–	–	–	–	–	–	–

[a] Reddy et al. (2014).
[b] Park et al. (2002).
[c] Robertson et al. (2000).
[d] Liu et al. (2015).
[e] Liu et al. (2019).
[f] Vinati et al. (2019).
[g] Han et al. (2018).
[h] Waybrant et al. (1998).
[i] Gibert et al. (2019).
[j] Hiller et al. (2015).

Since the first PRB came into place in the decade of the 90s, it has always been a centre of evolving technology, with new and advanced reactive materials being introduced each year, which has significantly increased in recent times. These reactive materials included mulch which was the best-known decontaminator for the chlorinated solvents. Zeolites are best used for the remediation of heavy metals and radioactive nuclides. The advancements are also noticed in the modification of mud and clay-like material. Gibert et al. (2019) used the mixture of mulch and gravel for reducing the nitrate concentration up to 97%. Here, mulch was used as a carbon source for denitrifying bacteria, shown in Eq. (7).

$$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 5HCO_3^- + 2H_2O + H^+ \tag{7}$$

6. Modelling of PRBs

Modelling of PRBs includes a wide range of topics from contaminants transport models to process-based models. Nassehi and Das (2007) have discussed the fundamentals of a range of numerical schemes that may be used for modelling PRBs in conjunction with the aquifer. Herein, we provide a brief synopsis of specific cases, as discussed below.

6.1. *Reactive transport modelling*

The simulations we performed on reactive transport model MIN3P to study the reaction processes controlling the geochemistry within and downgradient of PRB. The determinable parameters within the PRBs were contaminant treatment, electron acceptors reduction, sulphate reduction by microbes, degassing of hydrogen, secondary mineral precipitation. The downgradient involved rock water interactions. The results showed decrease in the porosity of PRBs due to the formation of the secondary mineral. In downgradient, deprotonation and adsorption of cations were the main phenomena behind pH buffering (Mayer et al., 2001). An integrated set of over 3-year dataset containing solid phase data and pore water chemistry. Here, the constraints for the models were alkalinity, pH and amount of dissolved H_2S. The other variations taken into account includes seasonal fluctuation, long term variations of PRB reactivity, further dependent on different fractions of used fillers Mayer et al. (2006). The boundary conditions are well defined for the Ca, Fe, SO_4, CO_3, pH. The conclusion was the confidence factor of 1.5 for Sulphate reduction and Sulphur accumulation after studying the seasonal and spatial variations. Chromium Isotope measurement and 2D Reactive Transport Modelling to assess the Cr(VI) removal efficiency (Wanner et al., 2012).

6.2. Numerical software modelling

Benner et al. (2001) studied the effect of hydraulic conductivity (*K)* variation (spatial scale) on the preferential flow through PRBs. A numerical flow model designed by the author showed an increase in the flow in the localized zone of high *K*. Also, the thickness of the barrier was shown to be inversely proportional to the value of *K*. Moraci et al. (2016) studied the reduction in hydraulic conductivity with the help of numerical modelling in a long term column test. The simulation model also helped in determining the factors responsible for decrease in *K* value which were, corrosion of granular Fe^0, precipitation of reaction products and formation of gas bubbles. Another software CXTFIT 2.1 helped in determination of transport parameters (Huo et al., 2013; Toride et al., 1995). The breakthrough of Ciprofloxacin involved chemical non equilibrium two site model (Zhao et al., 2018) and of KCl involved advection–dispersion equation. Also the lifetime of the PRB installed was defined with Eq. (8)

$$T_L = \frac{120 q_m (1-n) \eta \rho L}{(C - C_a)\, \Delta\epsilon} \tag{8}$$

Here, T_L is lifetime in days, q_m is adsorption capacity, ρ is density, n is porosity, η is volume fraction, C is initial and C_a is target concentration and ?? is Darcy parameter.

6.3. One dimensional multiple reaction model

A pathway model (1D — multiple reactions) is used to characterize the kinetics of degradation of TCE (trichloroethylene) and PCE (tetrachloroethylene) with the help of ZVI PRB. The model is tested with three rate equation including (i) first-order (ii) surface controlled with interspecies competition and (iii) with inter and intraspecies competition. The first-order rate equation predicted the most accurate results when compared. Here, the velocity of water and rate constant were the most essential variables (Ulsamer, 2011). The application of MODFLOW (Modular Three-Dimensional Finite-Difference Groundwater Flow Mode) Eq. (9) and RT3D (Reactive Transport in 3 Dimension) Eq. (10) in modelling PRB was used for the treatment of acidic GW. The model combines geohydraulics and temporal variation of geochemical and biological parameters. Both of these equations are implemented with the help of series of equations i.e. finite difference methods Medawela and Indraratna (2020).

$$\frac{\partial}{\partial x}\left(K_{xx}\frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_{yy}\frac{\partial h}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_{zz}\frac{\partial h}{\partial z}\right) + W = S_s \frac{\partial h}{\partial t} \tag{9}$$

Here, K_{xx}, K_{yy} and K_{zz} are hydraulic conductivities along x, y and z direction respectively, h is hydraulic head, W is volumetric flux/volume and S_s is the specific storage.

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(v_i C) + \frac{q}{\theta} C + R_K \tag{10}$$

Here, C is concentration, D is dispersion coefficient, v is seepage velocity, θ is porosity, q is volumetric flux/volume.

6.4. Artificial neural network (ANN)

Santisukkasaem et al. (2015) applied an ANN to study the permeability loss of PRB fillers. Here, the input parameters taken were residence time, average porosity, pressure drop, flow rate, dynamic fluid viscosity, particle size, reactor's length to calculate the loss in permeability at the output. ANN performed better than the regression models to estimate the permeability loss of the aquifers. The ANN model's results were on par with MRA (Multiple Regression Analysis) and, thus, was presumed as a probable tool for the assessment of decline in permeability of installed PRBs (Maitra, 2019).

7. Case studies of PRBs and scope in developing nations

The case studies are very limited in developing countries than the developed ones. McGovern et al. (2002) designed and built a funnel and gate PRB for remediating petroleum hydrocarbon (toluene, ethylbenzene, xylene, alkanes) in southeastern Australia. After an operation period of 10 months, 'peat' was proved to be an effective reactive material for this PRB with a removal efficiency of 72% overall. Germany was among the first few countries which adopted PRBs as a passive GW remediation technology at a large scale, a total of 9 pioneering PRBs were installed between 1998 to 2002 (Birke et al., 2003). It also includes the world's largest funnel and gate system PRB installed at Edenkoben with 6 gates with the length being approximately 450 m. Krug et al. reported some difficulties in the installation of PRBs, as it was a set of 23 distinctive panels each of, 30 to 50 ft length. Here, the panels are divided into two categories, i.e. primary and

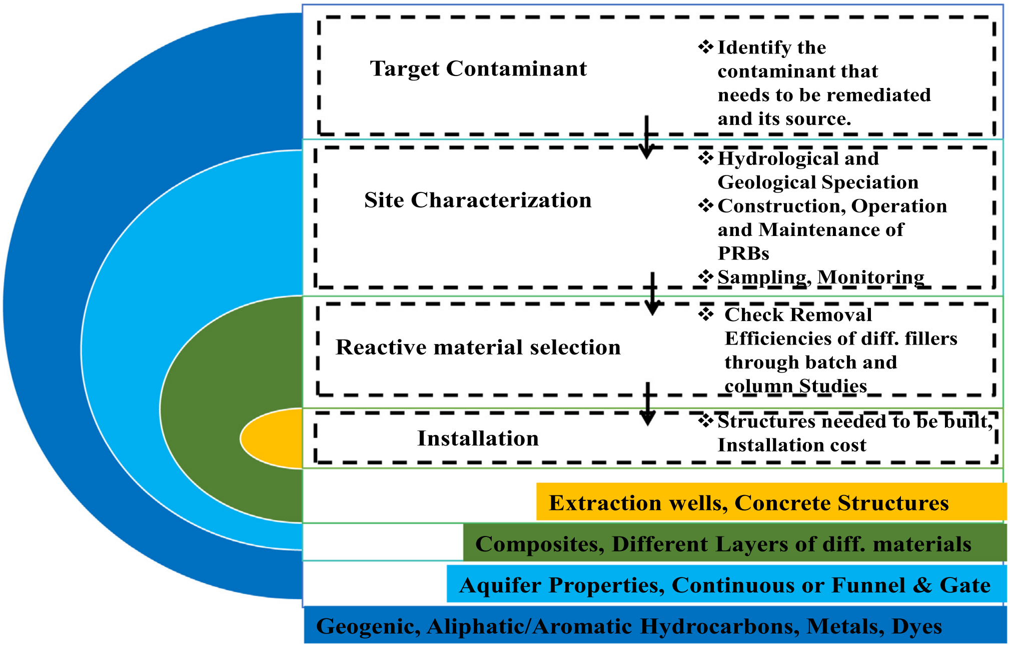


Fig. 6. Standard design protocols for the PRBs, prior to installation at groundwater contaminated site.

secondary, both adjacent to each other. During the installation of primary panels, bio-polymer sufficiently supported the trench, but when the installation of the secondary panel started, some of the sand and silt got settled in the bottom of the trench before emplacing these trenches with ZVI. The effected area remained at less than 1% due to this, and thus there was a negligible effect on the performance of PRB. The standard design protocol before installation of PRB is shown in Fig. 6.

At a site-specific study (Shaw AFB, 1999), the problems faced were the miscalculations of the depth of saturated sand and the value of hydrostatic pressure, due to which there was a shift in the planned design and executed design. Korte et al. (1997) noticed the problems of a decrease in the value of iron medium's hydraulic conductivity, which was due to the precipitation in the form of oxide and sulphide. Thus, a proper consideration of the sulphate concentration of the GW is essential before PRB installation. The Table 3 shows some of the PRB projects around the world with different specifications and their economic viability. Gibert et al. (2019) noticed the emission of greenhouse gases (CH_4, N_2O and CO_2) which are not a major concern but surely a shortcoming. Also, the study was affected by the GW fluctuations due to the varied rainfall.

PRBs, when first installed 25 years back, was seen as a remediation option for developing countries due to its sustainable nature and very little investment in terms of operation and maintenance. The other environmentally friendly feature of PRBs is the possibility to use many solid waste materials such as sawdust, activated carbon, limestone, which are readily available and can be utilized even from a local source (Chandrappa and Das, 2012). PRBs are site-specific remediation, and thus in developing nations with a less adequate amount of water supply, they can help in better management of the available water resources (Chandrappa and Das, 2012; Chandrappa and Das, 2014). The change has already started in some parts of the world. For instance, an international organization IRC (International Water and Sanitation Centre, 2004) launched a wastewater reuse project, where PRBs were devised as a low-cost approach to treat the wastewater to use it again for agricultural purposes in water-stressed nations.

8. Summary

PRB installed everywhere in the contaminated sites do not guarantee the full remediation of the contaminant. From its origin during the '90s, PRBs have made considerable progress regarding its designs, excavation set-ups, fillers used as reactive materials and several other areas. This GW remediation innovation should be more keenly investigated. Although a Permeable responsive boundary has substantiated itself a much-improved option than the conventional pump and treat framework. Issues like manganese precipitation when limestone is utilized as a filler material should be well known beforehand. The significant points of interest of PRB are its lower operational and upkeep cost, yet the sourcing and manufacturing of filler reactive materials and their substitution may add to the expenses. Therefore, a close observation is required for the *in-situ* installed PRBs. The PRBs operating at a large sc has seen a couple of issues related to the PRBs

Table 3
The total cost (set-up and operating) incurred at different scales of PRBs installation around developed nations.

Year	Site	Contaminant	Scale of Implementation	Type of PRB	Dimensions			Reactive Material(Weights in Tons)	Total Cost(USD)	References
					Length	Depth	Thickness			
1995	Sunnyvale, CA	TCE, Freon 113	Full	Funnel & Gate	11 m	6 m	1.8 m	ZVI(220T)	1000	Adapted from RTDF, 2000 and Striegel et al. (2001)
	Ontario Canada	Ni, Fe, SO4	Full	Cut and Fill Method	15 m	4.26 m	3.65 m	Compost-Leaf+Municipal, Wood Chips	30	
1996	Lakewood, CO	TCA, TCE	Full	Funnel & Gate	L(funnel) 317 m L(gate) 12.2 m, 4gates			ZVI	1000	
	Coffeyville, KS	TCA, TCE	Full	Funnel & Gate	Gate (6 m ×0.9 m) Funnel (149.3 m ×9.1 m)			ZVI (70 T)	400	
	Piketo, Ohio	TCE	Full	Horizontal Well	152 m	2.77 m	–	ZVI	NA	Korte et al. (1997)
	Elizabeth City, NC	Cr-VI, TCE	Full	Continuous Trench	45.7 m	2.2 m	0.6 m	ZVI(450 T)	675	Adapted from RTDF, 2000 and Striegel et al. (2001)
1997	Industrial Site, NY	TCE, VC	Full	Continuous Trench	112.7 m	5.5 m	0.3 m	ZVI (742 T)	797	
	Industrial Site, SC	TCE, VC	Full	Continuous Trench	99 m	8.8 m	0.3 m	ZVI	400	
	Hanford Site, WA	Cr-VI	Full	Well and Barrier System	d(5 wells) 30.5 m, barrier (45.7 m vs 15.2 m)			Sodium Dithionate	480	
	National Laboratory, TN	U, Tc, HNO3	Full	Funnel & Gate	67 m	7.6 m	0.6 m (Lgate 7.92 m)	ZVI (80 T)	1000	
1998	Aircraft Mainte-nance Facility, OR	TCE	Full	Funnel & Gate	198.1 m	15.2 m	0.22 m (2 gates)	ZVI	600	
	Caldwell Trucking, NJ	TCE	Full	Continuous Trench	45.7 m 27.4 m	15.2 m	0.07 m	ZVI (250 T)	1120	
	Fairfield, NJ	TCA, PE, TCE, DNAPL	Full	Continuous Trench	38.7 m	7.6 m	1.5 m	ZVI	875	
	Kansas city, MO	1, 2 DCE, VC	Full	Continuous Trench	39.6 m	4.8 m	1.2 m	ZVI	1500	
	Nesque-honig, PA	Pb, Cd, As, Zn, Cu	Full	Continuous Trench	335.3 m	0.9 m	6.1 m	Limestone	NA	
1998	Edenkoben	cVOCs	Pilot	Funnel & Gate	30 m	15 m	1 gate	Granular ZVI	392	
2001			Full		440 m	15 m	6 gates		1964	Birke et al. (2003)
1998	Rheine	cVOCs	Pilot	Continuous (overlap-ping boreholes), Mandrel Method	22.5 m	6 m	dia 0.9 m	ZVI and Iron Sponge	190	Adapted from RTDF, 2000
	Sumter, South Carolina	TCE, DCE, VC	Full	Continuous Wall Trenches	82 m	0.2 m	7 m	Zvi, Iron Fillings	1,065	Shaw AFB (Interim Measure Report) (2001)
	Tubigen	cVOCs	Full	Funnel & Gate	200 m	10 m	3 gates	ZVI	673	Adapted from RTDF, 2000

(*continued on next page*)

including degradation of the reactive materials, longevity issues, precipitation byproducts, fouling of barriers. Batch scale and column scale tests are much important, in order to implement the given PRB design at full scale. Every parameter in these lab scale study should simulate real scale conditions, so that the GW flow is reenacted. The different numerical models helps in determination of these parameters. Some of the models like reactive transfer solute models, preferential flow modelling, MODFLOW and RT3DM are discussed for a better understanding. Also, the applicability of ANN is discussed to analyse the optimum input parameters.

There had been progressively centred approach these days on coupling frameworks, where the PRBs are combined with the electro-kinetic remediation for the treatment of arsenic contaminated soil. A current of 45 mA applied for 7 h at pH 7 coupled with ZVI PRB removed As with an efficiency of 97% (Ruiz et al., 2011). Issues like increasing the life span of PRBs and cutting operational and maintenance cost are also one of the criteria that will help in making PRB economically viable for the developing countries. Some of the advantages and disadvantages of PRBs are enlisted in Fig. 7. The capital investment of PRB is very high then the treatment of its counterpart technologies, which exclusively relies on site qualities (hydrology, geochemistry and geography), the structure of PRBs, method of installation, and cost of reactive fillers that are being utilized. The usage of new age and green reactive materials should be more widely used. Also, the fillers which do not ends up making precipitation products like carbonates and hydroxides can be used. This will increase the longevity issue of PRB by not coagulating the pores of barrier. Nanomaterials assumes a significant job as far as reactive material. There are very few pilot and scale projects right now, which are operational around the world, and that too is limited to the first world countries. PRBs are need of the hour for the developing nations, as there are numerous steps where an organization can cost-cut the overall cost of installation and operation. Likewise, the installation is restricted distinctly to ZVI, when needed to be used in tons as fillers. Therefore, different choices of fillers should be resolved as loss of reactivity is seen in ZVI fillers after a specific period. The more programming based investigation would be expected to do the

Table 3 (*continued*).

Year	Site	Contaminant	Scale of Implementation	Type of PRB	Dimensions			Reactive Material(Weights in Tons)	Total Cost(USD)	References
					Length	Depth	Thickness			
1999	Watervliet, Arsenal	Halogenated VOCs	Full	Continuous Trench	50 m	1 m	3 m	ZVI and Concrete Sand	391	
	Vapokon, Denmark	TCE, DCE, BTEX	Full	Funnel & Gate	15 m	9 m	0.6 m	ZVI (105 yd^3)	940	
	Romulus, New York	TCE, cis-1,2-DCE	Full	Continuous Trench	198 m	3 m	0.35 m	ZVI (5525 ft^3) and Sand	450	Parsons Engineering Science (1999)
	Monticello, Utah	Uranium, Arsenic, Manganese, Selenium, Vanadium	Full	Funnel and Gate	30 m 73 m, 29.5 m	2.4 m –	Gate Funnels	ZVI	800	Kreuzer (2000)
	Golden, Colorado	Nitrate, Uranium	Full	Reaction Vessels (HDPE Panels)	9.7 m, 3.3 m	5.2 m	–	ZVI and Wood Chips	1,300	Adapted from RTDF, 2000
	Bitterfield	Chlorobenzenes	Pilot	Shafts equipped with reactors	d 24 m, 5 shafts with reactors			GAC, ZVI, ORC	673	
2000	Somersworth, NH	TCE, DCE, VC	Full	Continuous Walls	278 m	11 m	30 m (8 sections)	ZVI (3500T) and Sand	2200	
	Reichenbach	cVOCs	Full	Continuous (overlapping boreholes)	20 m	7 m	2 rows	Activated Carbon	224	
2001	Karlsruhe	PAHs	Full	Funnel & Gate	240 m	17 m	8 gates	GAC	4489	
	Denkendorf	cVOCs	Full	Drain & Gate	90 m	6 m	drain	Activated Carbon	673	
	Bernau	cVOCs	Pilot	Funnel & Gate	–	–	Closed Funnel	Granular ZVI	1683	
2002	DenkenDorf	VC	Pilot	Columns inside shaft	–	–	Bypass	Pd on Zeolites	134	
	Oberursel	cVOCs	Full	Funnel & Gate	175 m	4–17 m	1 gate	Granular ZVI	NA	
	British Columbia, Canada	Cu, Cd, Co, Ni, Zn	Pilot	Continuous	10 m	2.5 m	6.5 m	Sulphate Reducing Bacterias(Leaf Compost, Pea Gravel, Limestone)	NA	Ludwig et al. (2002)
2017	Joplin, Missouri, US	Pb, Cd, Zn	Pilot	Column Test	0.01–0.1 m	0.15 m	–	Permeable reactive Concrete	1200	Holmes et al. (2017)

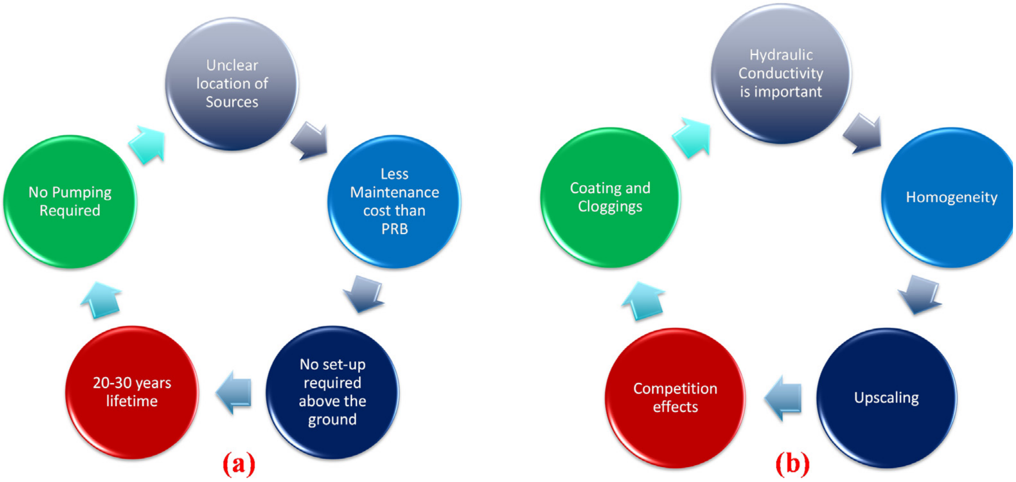
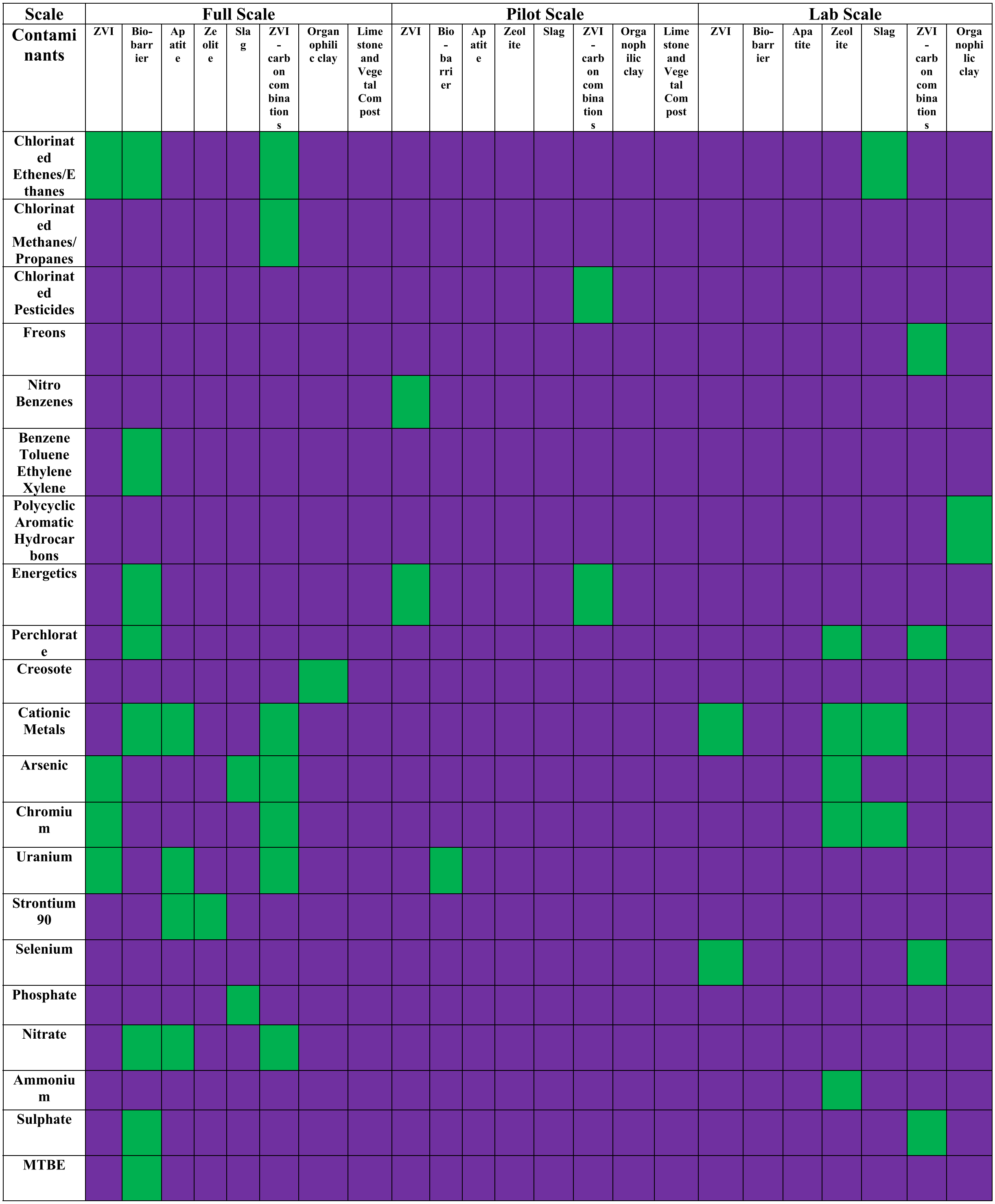


Fig. 7. (a) Advantages and (b) Disadvantages of PRBs.

ongoing recreations of contaminant transport and GW stream to have a superior comprehension of PRBs. Table 4 shows some of the promising reactive materials used around the world.

Table 4
Renowned reactive fillers for PRBs for most persistent contaminants at different scales (Adapted and Improvised, ITRC, 2011).



Scale	Full Scale								Pilot Scale								Lab Scale						
Contaminants	ZVI	Bio-barrier	Apatite	Zeolite	Slag	ZVI-carbon combinations	Organophilic clay	Limestone and Vegetal Compost	ZVI	Bio-barrier	Apatite	Zeolite	Slag	ZVI-carbon combinations	Organophilic clay	Limestone and Vegetal Compost	ZVI	Bio-barrier	Apatite	Zeolite	Slag	ZVI-carbon combinations	Organophilic clay
Chlorinated Ethenes/Ethanes	🟩	🟩	🟪	🟪	🟪	🟩	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟩	🟪	🟪
Chlorinated Methanes/Propanes	🟪	🟪	🟪	🟪	🟪	🟩	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪
Chlorinated Pesticides	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟩	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪
Freons	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟩	🟪
Nitro Benzenes	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟩	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪
Benzene Toluene Ethylene Xylene	🟪	🟩	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪
Polycyclic Aromatic Hydrocarbons	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟩
Energetics	🟪	🟩	🟪	🟪	🟪	🟪	🟪	🟪	🟩	🟪	🟪	🟪	🟪	🟩	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪
Perchlorate	🟪	🟩	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟩	🟪	🟩	🟪
Creosote	🟪	🟪	🟪	🟪	🟪	🟪	🟩	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪
Cationic Metals	🟪	🟩	🟩	🟪	🟪	🟩	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟩	🟪	🟪	🟩	🟩	🟪	🟪
Arsenic	🟩	🟪	🟪	🟪	🟩	🟩	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟩	🟪	🟪	🟪
Chromium	🟩	🟪	🟪	🟪	🟪	🟩	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟩	🟩	🟪	🟪
Uranium	🟩	🟪	🟩	🟪	🟪	🟩	🟪	🟪	🟪	🟩	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪
Strontium 90	🟪	🟪	🟩	🟩	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪
Selenium	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟩	🟪	🟪	🟪	🟪	🟩	🟪
Phosphate	🟪	🟪	🟪	🟪	🟩	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪
Nitrate	🟪	🟩	🟩	🟪	🟪	🟩	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪
Ammonium	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟩	🟪	🟪	🟪
Sulphate	🟪	🟩	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟩	🟪
MTBE	🟪	🟩	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪

Adapted and Improvised (ITRC, 2011) (Green — On-Going Studies) (Violet — Perspective Studies).

9. Conclusions and future perspective

Groundwater remediation technologies need even further technological advancements. Though PRBs have proved to be a much better alternative than the traditional pump and treat system, the issues like precipitation of reactive materials, decrease in longevity of PRB are still some of the issues which needs a bit more focus. Field monitoring and geochemical numerical modelling has been a necessary in calculating the optimum width of PRB which determines the longevity. GW flow rate and reactive filler consumed were the main governing factors for longevity (Pathirage and Indraratna, 2015). The PRBs necessary installation consists of a trench that has been dug inside of an aquifer, consisting of a single material like nZVI or a composite like nZVI + Sand + Limestone. The permeable material should be porous and should have permeability different from that of the aquifer. The problem of Manganese precipitation when limestone is used as a reactive material should be looked upon (Torregrosa et al., 2019). Four technologies based on several parameters considering the social, economical and technological aspects were compared and got the sustainability sequence as Natural Attenuation > Pump & Treat > PRB > Air Sparging (An et al., 2016a). Therefore, future research could be focused more on making PRB more sustainable as GW remediation techniques.

The significant advantages of PRB are its lower operational and maintenance cost, but the periodic removal of the precipitate formed around the reactive material and also the replacement of reactive material from the barriers in some cases may add to the costs, so close monitoring is required for the installed PRB. Day et al. (1999) has noticed a few earlier problems associated with the PRBs, which include degradation of the reactive material. The lessons employed to minimize the errors are, (i) length of the excavated trench is minimized to reduce the risk of slope failure (ii) there should be minimum of stockpiling and equipment activities near the open excavated trenches (iii) at any cost, maintenance of PRBs cannot be ignored (iv) the after-excavation procedure, i.e. the backfilling should be considerably followed (v) when hilly contours are there, gravitational forces can be used to provide the respective gradient and thus a specific flow rate (RMRS, 1996). Column studies are required as much as batch studies so that the GW velocities and aquifer residence time can be simulated. Site-specific study at Seneca Army Depot, Romulus, New York suggested that walls of PRB need to be thicker as well as it should be comprised of 100% of the reactive fillers to ensure complete treatment of contaminants. This can be ensured by installing more monitoring wells to continuously monitor concentrations and velocities of the plume.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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