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Funnel and Gate Permeable Reactive Barrier Permeable Reactive Barrier Configuration for Contaminated Groundwater Remediation – Designing, Installation, and Modeling: A Review

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ABSTRACT

Groundwater is a valuable resource whose purity is necessary for human survival. It serves as a significant source of water for household, industrial, and agricultural purposes. Traditional groundwater pollution remediation technologies include pump & treat, phase extraction, aeration gas of groundwater, bioremediation, and chemical oxidation. Permeable reactive barrier (PRB) is one of the most key technology being developed as alternatives to the pump and manage method for the remedying contaminated groundwater. An overview on the groundwater significant as important sources for water, sources of groundwater contamination, transport of contaminants, and groundwater remediation technologies have been discussed in this paper. In addition to reactive media, the design and installation of PRBs of funnel-gate configurations and their application as a remediation technique have been covered in this review. Finally reaction mechanisms in groundwater, contaminant transport governing equation, isotherms sorption models, kinetic sorption models, breakthrough curves modeling have been presented in this review. PRB technique provides financial benefits while also encouraging waste material reuse, so contributing to environmental sustainability. Funnel and gate PRB can offer one or more dense treatment areas for maximizing groundwater pollution plume capture. Funnel-gate PRB is characterized by smaller reaction area, ease in replacement and removal during the blocking of the reactive barrier by fine soil particles and reactive sediments.

Keywords: permeable reactive barrier, funnel and gate, groundwater, remediation, sorption isotherm, COMSOL, ANN, kinetics models.

INTRODUCTION

Sustainable management of water represents a continual challenge especially due to a number of parameters including an expanding global population, depletion of water resources, and, last but not least, an expanding global demand for clean water, bioenergy, and food. Hence, the removal of pollutants and decontamination of the pollutant source require rapid and efficient actions [1–4]. The deterioration of freshwater ecosystems has led to legislative demands to protect and manage surfacewater, while ecosystems dependent on groundwater have received less attention [5]. In dry and semi-arid areas, groundwater is one of the most important sources of water. Due the expanding worldwide population and growing demands for water for both urban and agriculture uses [6]. For millions of people in poor nations, groundwater is considered as a unique source of safe drinking water [7, 8]. It provides water for drinking as well as other domestic, agricultural, and industrial uses [9, 10]. Groundwater is used by about 2.5 billion people in all over the world in their daily lives [11]. Groundwater is used to meet the demands of diverse industries when fresh surface water resources are scarce. Contamination of groundwater owing to waste materials has become a major concern due to large-scale industrial expansion [12, 13].

Assuring a secure and sustainable supply of groundwater for home use is one of the key factors in a country's sustainable development. However, agricultural practices, urbanization, industrial activity, and climate changes all represent threats to the ground water quality. Health, the ecological services, and long-term socioeconomic development are all under risk from toxic metals, pesticides, hydrocarbons, trace organic compounds, and other apparent pollutants [14].

Globally, the quality of groundwater is a significant environmental concern, necessitating the ongoing monitoring of a variety of physicochemical characteristics, such as cations and anions. [15]. Groundwater quality is improved by eliminating human activities. Controlling industrial and agricultural pollution inputs can improve the quality of groundwater and the whole environment. Natural cleaning techniques for the contaminated groundwater might require decades or hundreds of years, even after the contamination source is eliminated [16]. Despite the fact that there are numerous contaminants being discovered in groundwater on a regular basis, they may be categorized into three groups: chemical contaminants, radioactive contaminants, and biological contaminants. These toxins can result from both natural and artificial sources [17, 18]. In order to comprehend physical processes, characterize a specific system, or develop predictive modalities for estimating feasible solutions for water distribution, interaction of surface water and groundwater, landscape management, or effects the withdrawals of new groundwater, numerical or conceptual models are applied to hydrological modeling [19].

The pump-and-treat approach has been the standard method for treating groundwater polluted with organic and inorganic toxins for many years. However, this technology disregarded the sustainability in addition to the new concept employing renewable energy. Due to their efficiency and simplicity, permeable reactive barriers (PRBs) had been used as an alternative one to traditional pump-and-treat methods for cleaning up polluted groundwater [20]. Numerous researchers have examined at the utilization of reactive media produced from waste or byproducts of natural resources. Waste from natural resources is an essential resource for the recovery and extraction of precious materials. To transform these waste products into useful resources, specific techniques and approaches must be used [21]. The main objectives of this review are discussing the following aspects (i) the funnel-gate PRB system principals, (ii) the configuration of funnel-gate PRB and (iii) the funnel-gate PRB configuration design and installation. PRB technology is passive and efficient alternative treatment approach for remediation of the contaminated groundwater. Funnel-gate PRB is most relevant configuration which introduced as passive and cost effective approach for treating polluted groundwater when contaminated plume is huge and expensive reactive media.

RESEARCH METHODOLOGY

This review was design to focus on the funnel-gate PRB technology which used in groundwater remediation, as there are not many studies available on this topic. PRB technology provided efficient technique as passive method for groundwater remediation. To discuss funnel-gate PRB, there are many topics related to it that must also be focused on in order to reach a complete and comprehensive explanation of this technology. In this paper an overview on the groundwater significant as important sources for several purposes, sources of groundwater contamination, transport of contaminants, fate of contaminants, contaminants transport governing and groundwater remediation technologies have been discussed. In addition to reactive media, impermeable wall materials, the design and installation of PRBs of funnel-gate configurations have been discussed. Reaction mechanisms in groundwater, isotherms sorption models, kinetic sorption models, breakthrough curves models have been presented Figure 1.

SOURCES OF GROUNDWATER CONTAMINATION

The contamination of groundwater is a global problem which significantly affects both the ecological system and human health. Natural sources of the contamination of groundwater include mineral deposits, brackish water, low-quality surface water, and saltwater. Such natural sources can develop into significant sources of contamination if the activities of the human disturb the balance of the natural environment like aquifers depletion leading to the intrusion of saltwater, acid mine drainage resulting from mineral resources exploitation, and the leaching of the hazardous chemicals

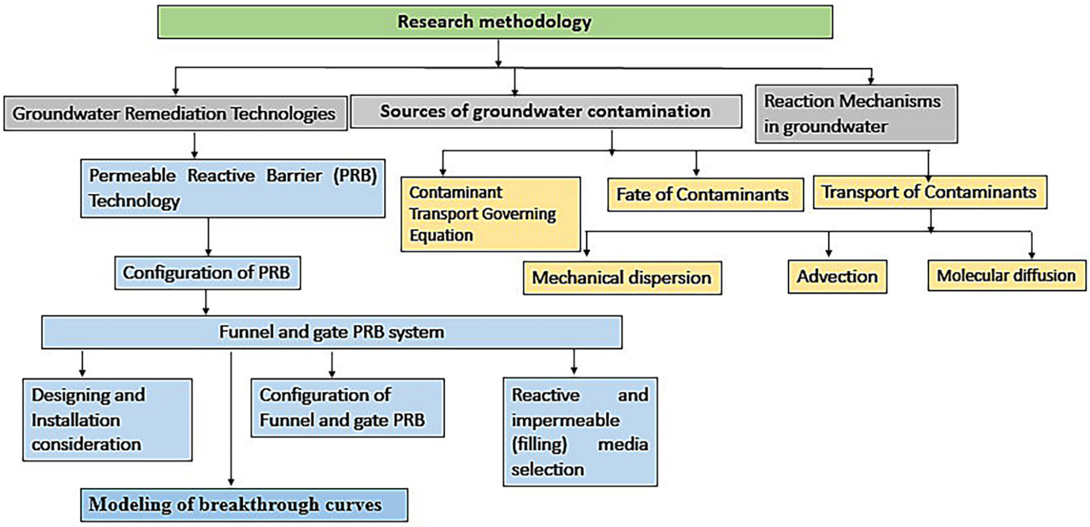

Figure 1. Research methodology

resulting from excessive irrigation [22]. Groundwater resources have recently been contaminated by a variety of activities, including agriculture, treatment systems of decentralized wastewater, livestock, and acid rain. The groundwater can be harmed by seepage from industrial waste lagoons, landfill leachate, mine tailings, sewage, non-engineered deep well liquid waste disposal, and mine tailings [23]. Pollutants from sources like as fossil fuel combustion, road salts, and other terrible compounds leaching into aquifers are examples of anthropogenic groundwater contamination [24]. Leaking of septic storage tanks, incorrectly built storage system, corroded or rusted pipe connections, and leaching landfills are additional sources of groundwater pollution [25]. The movement of organic matter from the vadose zone to the subsurface by rainwater recharge is the primary source of dissolved organic matters in groundwater [26].

The presence of toxins due to industrial activities in the water can impair crop output and plant growth, harm aquatic living animals, and change the quality of surface and groundwater. Industrial pollution is a key contributor to environmental degradation [4]. Surface aquifers, which are polluted in many locations and shallow wells yield poor water quality, which causes an increase in water-related diseases and poverty [27] . Groundwater contaminants are mostly related to two types of sources:

1) Point sources,
2) Distributed, or non-point sources.

Point sources of contamination are localized contamination sources. The contamination reacting with moving groundwater and soil spreads out for producing a plume that follows the groundwater's path. The ensuing contamination plume in groundwater could spread hundreds of meters or even further away from sourced pollution. Groundwater can further be contaminated via diffused sources that extend over a large region, such as widespread fertilizer uses in gardens and fields. Because of a considerably larger volume of water affected by diffuse of contamination, it may have a higher environmental impact than contamination from point sources. Pollutants from point sources are typically associated with urbanization, whereas diffuse sources are typically found in rural areas [28].

Advection, dispersion, and diffusion are three mechanisms that can be used to move contaminants that have been dissolved in the soil matrix. Advection entails movement in the flow direction and is related to the mean fluid velocity. Due to the fact that the contaminant is traveling with the conveying fluid, it is a passive mode of transfer. Pollutants move through the diffusion process when they are propelled by kinetic energy in the direction of concentration gradient [29]. The level of urbanization has a positive correlation with groundwater contamination in permeable aquifers. contaminated groundwater proportions in urbanized and semi-urban areas were almost two times higher than non-urbanized areas [30]. Heavy metals, cosmetics ,pesticides, waste of by-products, pharmaceutics, and biological agents are among the contaminants present in groundwater from natural and anthropogenic activities [31]. Solid waste is a significant contributor to groundwater pollution. These wastes can be gathered into landfills or dumpsites, and the chemicals and byproducts of the decomposition percolated into the groundwater through precipitation and surface runoff. Manure, trash, and industrial waste are some examples. Waste from industry may contain heavy metals including arsenic, cadmium (Cd), lead (Pb), zinc (Zn), copper (Cu), and nickel (Ni), which are found in dumpsites. Depending on the source of the waste that makes up the dump and the area's natural soil composition, the concentration of these heavy metals differs from dump to dump [32]. Nitrate and fluoride are among the fastest contaminants that percolate into aquifer systems because they come from a variety of geogenic and non-geological activities [33]. There is a huge risk to human health if pathogenic bacteria enter groundwater sources. *Escherichia coli, Clostridium, Campylobacter, Rhodococcus coprophilus, Enterococci, Arcobacte*r (an emerging bacterial disease), *Fecal streptococci*, and *sulfite-reducing Clostridia* are the most common bacteria detected in groundwater. The main source of pathogenic microorganisms in surface and groundwater systems is cited as the application of animal waste to agricultural areas [34]. Emerging contaminants like pharmaceuticals and products of personal care are forming their ways to surface water and to a lesser extent into groundwater [35].

Recently pharmaceuticals are one of many anthropogenic organic compounds that have been recognized as growing threat to groundwater resources. Despite the fact that their presence and subsequent fate in the environment are mostly unregulated and poorly understood, numerous studies have proven the growing problem of their existence in both groundwater and surface water [36]. Sulfonamides, quinolones, tetracycline, fluoroquinolones, and nitroimidazoles are the most frequently discovered antibiotics in wastewater. Different antibiotics have different overall concentrations depending on the body of water. Surfacewater and groundwater include pharmaceutical chemicals that come from various sources. Urban wastewater is the first of these sources; due to a lack of management monitoring, it improperly disposes of old or expired prescriptions and has a high content of pharmaceuticals from human waste. Pharmaceuticals are primarily obtained from animal waste, particularly that from agriculture and animals. Large, intensive livestock farms regularly add medications to the meals of their animals and frequently modify the soil with animal excrement, which seeps into the groundwater. Pharmaceutical sector effluents are a significant source of pharmaceuticals contamination as high levels of pharmaceuticals have been detected in discharges from businesses in Asia, Europe, and America [37].

Transport of contaminants

The soil is a dynamic system because it is used as a pathway or a sink for dangerous chemicals. After polluting the surface soil, some of these pollutants will sink beneath the water table and create a plume of contaminants. Chemical reactions can change a compound's state, transform it into another substance, or cause it to mix with other chemicals. Sorption is the chemical process that is most beneficial for the transportation of organic and inorganic pollutants in the subsurface environment. Sorption occurs when a solute adheres to the surfaces of solid particles, prolonging the time of arrival. Isotherm or kinetic ideas are frequently used to describe chemical reactions in the context of how the pace is changed by reactant concentrations. There are three main mechanisms that govern whether pollutants travel in the subsurface environment [38].

- Molecular diffusion: refers to the movement of a solute from regions with a high to low concentration. Fick's first Law may be used to describe how the transported mass of a solute is proportional to its concentration in one dimension:

$$F = -Dd * \left(\frac{dc}{dx}\right) \quad (1)$$

where: F (mg/cm^2-sec) – mass flux of solute per unit area, Dd – the diffusion coefficient (m^2/s), C is concentration of solute (mg/L), dC/dx – represents the concentration gradient per unit length. The negative sign indicates the movement of a solute from a higher to a lower concentration.

Fick's second law applies to the solute concentration with time [39] :

$$\frac{\partial c}{\partial t} = Dd * \left(\frac{\partial 2c}{\partial x2}\right) \quad (2)$$

Solute ion diffusion occurs slower rate in porous media. This is to ensure that ions can only diffuse through pore openings and avoid mineral grains by traveling farther. It is necessary to use an effective coefficient of diffusion to account for these two variables.

$$D^* = \tau Dd \quad (3)$$

where: τ – a tortuosity factor and its values ranged 0.01 to 0.5.

- Advection: is the process that moves contaminants through the groundwater. The rate of advection and the flow rate of groundwater are same. The media's actual velocity (*Va*) and the Darcy velocity (*V*) are connected by porosity (*n*). This formula is used to determine the advective flux (*Fa*):

$$Fa = VaC = \frac{v}{n}C \quad (4)$$

- Mechanical dispersion: is the contaminants with water combination as a result of spreading around solid structures in the aquifer media. Actually, there are three reasons that groundwater travels either more quickly or more slowly than at linear speed, (1) fluids often move through pores' centers more quickly than their margins; (2) some fluid parts may move over shorter, random paths; (3) larger holes enable faster distribution. Because no two fluid particles move at the same speed, mechanical mixing occurs throughout the flow path. Such dispersion causes the solute particles near the border of the flowing flow through to be diluted:

a) Longitudinal dispersion: is the case when the combined fluid flows in the stream's direction.
b) Transverse dispersion: is the movement of the fluid in the direction of the stream's sides.

In groundwater, the processes of mechanical dispersion and molecular diffusion are inextricably linked. The two processes are considered collectively as hydrodynamic dispersion, a single process.

$$D_L = \alpha_L V_L + D^* \quad (5)$$

$$D_T = \alpha_T V_T + D^* \quad (6)$$

One of the most important processes involved in the transport, mobility, accumulation, bioavailability, and the toxicity of the organic contaminants in the soil matrix is sorption/desorption. The concentration, structure, and physical and chemical characteristics of the contaminants and soil constituents have an impact on the mechanisms and amount of sorption [40].

Fate of contaminants

Chemical reactions often entail the change of molecules, such as pollutants, into other compounds, altering the states of compounds, or combining with other metallic or organic chemicals. Modeling the movement pattern of these compounds is made easier by the fact that reactions between contaminants result in differences in mass distribution in a certain volume. Chemical reaction kinetics, which is often referred to as zero-order, first-order, or equilibrium, is based on how the concentrations of the reactants are affecting the rate of the reaction. The most significant chemical change that influences the transportation of metallic and organic pollutants within the subsurface zone is known as sorption. Soluble particles are stuck to solid surfaces by this process, which is a type of surface reaction. Under the conditions of linear equilibrium partitioning, sorption is represented as a factor of retardation (*R*) in the transportation (advection-dispersion) equation of pollutants. If the factor R = 1.0, the solute is inert and moves with groundwater. It has been demonstrated that pollutants with lower R values move farther than those with higher R values during a given period of time.

Contaminant transport governing equation

The "Advection-dispersion" equation is the primary differential equation exploited to depict the solute transport in the aqueous solution passing across a porous bed. Equations (7 and 8) represent the basic formulas for the "Advection-dispersion" Equation in one and two dimensions, respectively. Equation (7) has two terms on left hand side; the first refers to the "Dispersion" that means movement of contaminants (solute) as a result of the concentration gradient and the changed pathways, whereas the second one refers to "Advection" which describes the solute transport via the flowing velocity. On right hand side of Equation (7), *R* refers to "Retardation factor" that is exploited to compute the contaminant quantity retarding on solid particles, while the reaction associating solute transport is determined as sorption. Such a factor can be estimated from Equation 9 where *n* and ρ_b are the porosity and bulk density corresponding to the porous medium.

$$D_x \frac{\partial^2 C}{\partial x^2} - V_x \frac{\partial C}{\partial x} = R \frac{\partial C}{\partial t} \quad (7)$$

$$D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} - V_x \frac{\partial C}{\partial x} = R \frac{\partial C}{\partial t} \quad (8)$$

$$R = 1 + \frac{\rho b}{n} \frac{\partial q}{\partial C} \quad (9)$$

Equation 9 may be solved numerically or analytically; however, the process of employing such methods to solve problems is typically associated with several problems and demands strict assumptions. The q value in Equation (9) may be estimated either from kinetic models for non-equilibrium transport or isotherm models for the equilibrium transport.

GROUNDWATER REMEDIATION TECHNOLOGIES

Traditional techniques for removing groundwater pollution are included pump-treat (P&T), groundwater aeration gas, bioremediation, phase extraction, and in-situ chemical oxidation [41].

A variety of groundwater remediation methods have been used over the past thirty years and have shown to be effective when based on the fundamentals of biological (bioventing), chemical (ion exchange), and physical (air sparging) processes. Nevertheless, only a small number of these methods had been successfully used at a level of field scale due to problems with longevity, the need for the significant initial investment, skilled labor, and operational costs. Air sparging and soil vapor extraction (SVE) is regarded as one of the most widely used techniques for treating groundwater, which is contaminated by the volatile organic contaminants (VOCs). Here, it is anticipated to be effective, fast, and inexpensive.

This process purify the groundwater via injection pressurized air at groundwater's lowest point to turn volatile chemicals into vapor. Air is injected beneath the saturation zone, pollutants are removing from aquifer and supplying oxygen for biodegradation of toxins. To remove any dangerous substances from the extracted air, vacuum extraction machines must be employed. The high cost of working on hard surfaces is one of this method's disadvantages [42].

Bioventing is the most popular bioremediation technique. This method uses controlled airflow stimulation to increase the activity of indigenous microorganisms and enhance bioremediation by supplying oxygen to the unsaturated (vadose) zone. The microbial transformation of pollutants into a harmless condition is the ultimate goal of bioventing. Amendments are made through the addition of nutrients and moisture to promote bioremediation. This method has become more prevalent than other in situ bioremediation methods, particularly for cleaning up areas where light petroleum compounds have been spilled [43]. The pump-treat (P&T) approach includes the extraction of polluted groundwater out of the earth and treating it with well-known techniques such as air flotation, precipitation, ion exchange, and others before its back reinjection into aquifer, or mixing it with the surface water [44].

One of the major technologies that have been developed as alternatives to the pump and treat approach for the treatment of the polluted groundwater is permeable reactive barriers. PRB is a novel in-situ approach commonly used to treat polluted groundwater [45]. Permeable reactive barriers had been signified as the most appropriate remediation technology that can be utilized to remove the contaminants such as heavy metals, the chlorinated solvents, the aromatic hydrocarbons and carbonates. The reactive media used to remove pollutants is the most important criterion for a successful PRB [46].

In comparison to traditional technologies used in contaminated groundwater treatment, PRB is a significant in the situ remediation technology for contaminated groundwater that has been used for decades. The benefits of PRB include inexpensive operating costs, limited requirements for ground area, and no external power [47, 48]. PRB is a revolutionary groundwater cleanup technology that is employed all over the world. To facilitate waste disposal, this method combines adsorption, chemical precipitation, and degradation processes to induce physical, chemical, or biological reactions between contaminants and reactive compounds included in barriers [11, 49]. Because of the cheap operation cost, longevity of media, and hydraulic performance, the in-situ application of PRB has sparked a lot of attention [50–52]. Permeable reactive barriers are a flexible containment method since they are a passive way to remove pollutants from groundwater. They can apply the reactive media to a range of locations and pollutants by making the right choice. The capacity of reactive media to remove site-specific contaminants determines how well they work with PRBs. Several materials can be served as reactive media (adsorbent) in PRB technology.

Permeable reactive barrier technology

Permeable reactive barriers were initially reported by [53]. The idea underlying a PRB is very simple. A passive treatment system develops by placing reactive material in the subsurface where a plume of the contaminated ground water must pass through it while it flows, often under its natural gradient Figure 2. The treated water exits the other side. The PRB acts as a barrier to the contaminant but not as a barrier to the water. PRBs are able to remediate a variety of pollutants to regulatory concentration goals when correctly developed and deployed. It is now anticipated that these systems will require very little, if any, maintenance after installation for a minimum of five to 10 years. Only routine compliance and performance monitoring should incur operational expenditures [54].

USEPA (1989) defined PRB as “an emplacement of reactive media in the sub-surface designed to intercept a contaminated plume, provide a flow path through the reactive media and transform the contaminant(s) into environmentally acceptable forms to attain remediation concentration goals down gradient of the barrier”. The operating idea of PRBs is basing on the placement of a reactive medium across the flow the path of the contaminated plume, which is then driven to migrate within the reactive medium in the subsurface by the natural groundwater gradient. Chemical, physical, and/or biological reactions between the reactive medium and contaminants cause the contaminants to degrade and/or deposit as they pass through the reactive media, completing the process of remediation before the groundwater returns to the natural aquifer (Shabalala, 2013).

The porous material used for making PRBs reacts when toxins in the groundwater seep through it. If contaminants remain in the reactive medium long enough for the rate-limited reactions to take place, PRBs offer containment. PRBs are currently developed with the assumption that the PRB and aquifer are homogeneous and isotropic. The specific type of reactive material employed affects PRBs’ capability to remove pollutants. While some reactive media function by physically removing contaminants, others alter the biogeochemical processes throughout the treatment zone, creating favorable circumstances for contaminant immobilization or (bio) decomposition. To eliminate pollutants such heavy metals, the chlorinated solvents, the aromatic hydrocarbons, and the pesticides, a number of materials have been used [57].

The PRBs are filled with reactive media and have typical dimensions of 5 m as a width (parallel to flow), 10m as a depth, and 50 m as a length (transverse to flow). To optimize the hydraulic behavior of this barrier, inert media like sand can be combined with the reactive materials .In order to calculate the appropriate width of PRB, determining the longevity, field monitoring, and geochemical numerical modeling are required. The key regulating elements for longevity are the groundwater flow rate and the amount of reactive media consumed [58]. The reactive materials either immobilize or transform the pollutants (biologically or abiotically), such that treated groundwater flowing down the PRB’s hydraulic gradient shouldn’t endanger water resources or other receptors [59]. Some reactive mediums remove contaminants via physical contact, while others

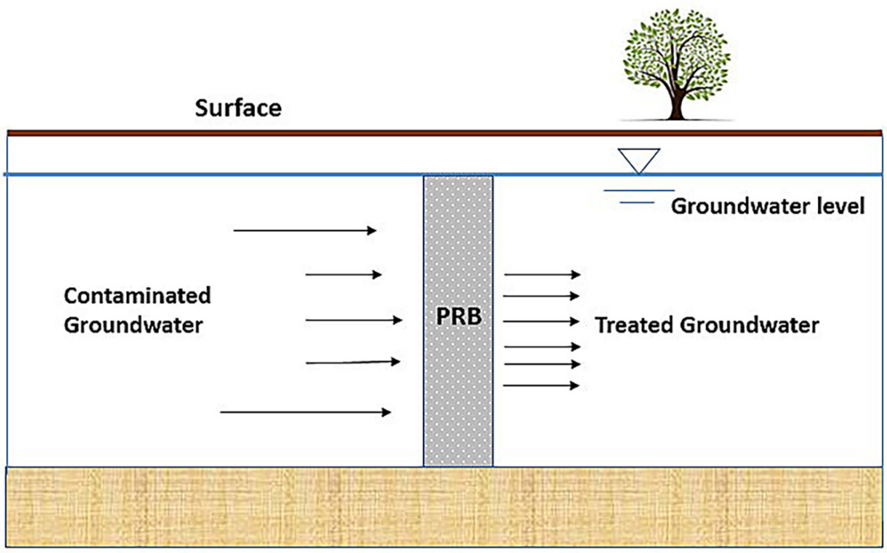

Figure 2. Permeable reactive barrier technology

modify biogeochemical processes in the treatment zone, allowing chemicals to be immobilized or degraded. A number of materials have been used as reactive media for removing pollutants including pesticides, the heavy metals, the chlorinated solvents, and the aromatic hydrocarbons [60]. In addition to groundwater reclamation, using less virgin resources and other inexpensive reactive media that are made from industrial waste or byproducts can help reduce the effects of PRBs on the ecosystem [61]

Configuration of PRB

Two most configurations of PRB, the first one is continuous PRB and the other one is funnel and grate PRB Figure 3. The funnel and grate system comprises permeable gate (as a reactive media) located between 2 impermeable walls, which direct the polluted plume towards reactive media. The continuous configuration of PRB comprises a single reactive zone placed across the contaminated plume. The decision between the two configuration is depending on hydrogeological parameters of site as and the reactive materials cost [62]. The funnel and gate configuration is recommended when design of PRB due to zone requires less reactive [63].

As a result, balance must be established between the reactive material cost and cost of barrier construction based on the contaminants to be removed and the removal level required. Both configuration have required some excavation and have only reached relatively modest depths of 50 to 70 feet. Some of these emplacement restrictions may be addressed by newer means for inserting reactive media, such as injecting slurries, hydro fracturing, driving mandrels, etc.[54]. Additionally, when the contaminant distribution is not uniform, the configuration of radial filtration/caisson, in which the filter is positioned in a cylindrical shape of the reactive media surrounded by the coarse material within a core of course materials, can better homogenize the pollutant concentration when entering the PRB gate. By using a hydraulic gradient, there must also be a radial centripetal flow. By increasing the contact duration between pollutant and reactive barrier, the third kind of the PRB has a lengthy lifespan and a superior treatment effectiveness [64].

Funnel and gate PRB system

Starr & Cherry (1994) proposed the term "funnel and gate", which was initially discussed by [53]. A funnel and gate system is a passive remediation technique that changes flow patterns so that groundwater mostly flows via high conductivity gaps (the gates) by using cutoff barriers (the funnel). The system would need to go down between 60 and 70 feet, at least 25 feet of which would be in the zone of extremely dense weathered rock. Additionally, it can be placed directly below contamination source zones to stop contaminants from flowing into plumes or at the front of plumes to stop further plume moving. The funnel and gate system's key benefit is its ability to perform without any need for pumping, extensive contaminated soil excavation above subsurface treatment stations, or offsite disposal. Additionally, polluted groundwater may be guided through a regulated reactive zone in the soil by the present natural groundwater flow and isolation barriers (funnel). Depending on the site-specific circumstances, funnel-and-gate technology has long-term cost savings of roughly 50%. It also requires little to no maintenance. Additionally, because the system does not require aboveground structures, there are no restrictions on how the property may

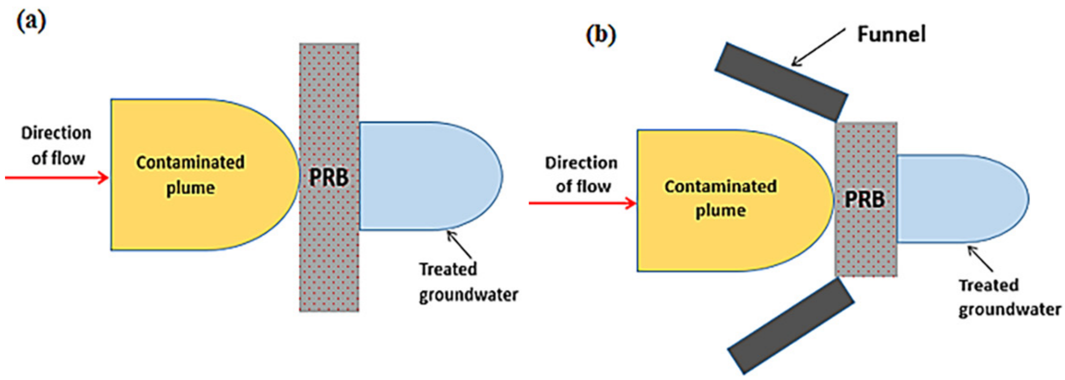

Figure 3. (a) Continuous PRB, (b) funnel and gate PRB

be used. The funnel must be defect-free and have a lower hydraulic conductivity than the aquifer, but the gate must possess a greater hydraulic conductivity than the aquifer (Starr & Cherry, 1994).

Configuration of funnel and gate PRB

The funnel and gate PRB can be adapted to have numerous gates in an exceedingly large contaminated plume or highly heterogeneous aquifer [67]. Under site-specific conditions, different funnel extensions in Figure 4 (a, b, c, and d) are occasionally used to capture plumes. In the funnel and gate system, the barrier length must be greater than the lateral extent of the plume. Bentonite and slurry soil mix, as well as a variety of other reactive ingredients, can be used to make the gate material. These systems are passively operated in order to provide a natural gradient for plume flow toward the reactive barrier. Due to some specific contamination characteristics, funnel gate PRB may offer one or more extensive treating areas to maximize groundwater pollution plume capture. The funnel and gate PRB has a smaller reaction zone and easier to remove and replace when reactive PRB is blocked by means of sediments and particles of fine soil. Furthermore, numerous funnel-gate PRB systems can be set up concurrently in parallel or series, depending on the site requirements [63]. The funnel-and-gate design alters the ground-water flow more than the continuous PRB does because of the funnels. To prevent diverting the flowing waters around the reactive zone, it is important in both designs to maintain the permeability of the reactive zone at a level that is equivalent to or higher than the permeability of the aquifer [54].

Reactive and impermeable (filling) media selection

Industrial pollution of geologic media has been a severe issue, posing a threat to the reliable supply of groundwater resources and human safety. Because of the difficulty in recognizing and remediating contaminated deep subterranean environments, pollution of hard rock aquifers is a particularly critical concern. The performance of PRB for contaminant removal in groundwater is determined by the reactive material, barrier structure and design, and aquifer conditions. In underground conditions, the reactive material must be physically stable, chemically reactive, not soluble, remain reactive, available with acceptable cost, and hydraulically permeable for extended periods of time [68, 69]. The permeable material ought to be porous and possess a different permeability than the aquifer [70].

The bed of the reactive media in a PRB accomplishes chemical and physical processes in addition to biological transformations of the pollutants. Sorption is a physical process in which contaminants are immobilized by adsorption without changing their chemical state. Permeable barriers should be constructed with a reactive media which is appropriate for the subsurface environment. When reactive medium reacting with components in the contaminated plume, the medium should not cause any potentially hazardous

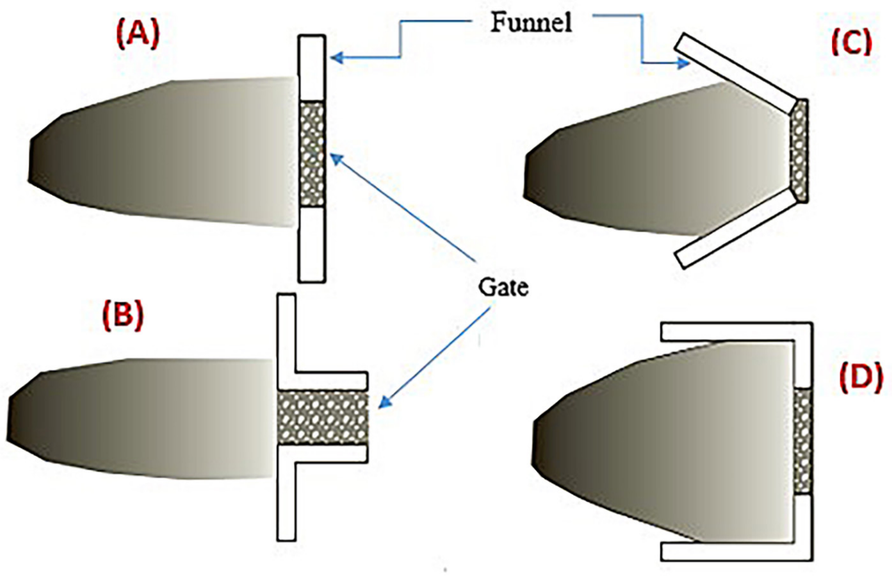

Figure 4. Different configuration of funnel and gate PRB

chemical reactions or byproducts, nor should it act as a potential source of the contaminants. To keep PRB in low cost, the reactive materials must last for a long time (i.e., it must not be depleted in reactivity or easily soluble) and it must be easily accessible at a low to a moderate cost. This material must not possess an overly small particle size, and it must not include a large range varying size particles that could cause groundwater flow limitations [68]. Reactive and adsorptive materials are placed in the course of migrating and contaminated groundwater using the PRB approach. Contaminants are either adsorbed onto the reactive material surface or converted into less hazardous molecules as groundwater passes through the barrier before being discharged into the surrounding environment [71]. The impermeable funnel of the funnel-and-gate PRB is typically built via slurry wall installation. One of the most popular wall types are soil/bentonite, cement/bentonite, and composite slurry walls with soil/ bentonite. Depending on the required depth, a backhoe, a modified backhoe, or a clamshell digger are typically used to dig a slurry trench. The trench is filled with the proper slurry to keep it stable. Depending on the slurry used, a completely hydrated filter cake of bentonite or composite forms along the sidewalls as it seeps into the excavation's sides. The trench is filled with soil and bentonite. Slurry wall building takes longer and costs more money than sheet piling [72]. Clay deposits, Carboniferous rocks, and steel sheet piling are used as an impermeable funnel in the funnel and gate PRB [73,74].

Designing and installation consideration

Several factors should be taken into account when designing funnel-gate PRB configurations. The hydrogeological features of the aquifer, such as hydraulic conductivity, hydraulic gradient, and aquifer heterogeneity, are essential elements that influence PRB performance among the field circumstances. Many reliable data from the site is essential while designing of PRB. Typically, work begins with a review of historical or other existing data as well as observations from the location. The configuration design methodology is based on how long pollutants remain in the reactive media. In contrast, there are not many useful resources in literatures for designing funnel-and-gate PRBs, and those that are accessible tend to be heavily hydraulic in nature [6–8]. Design of such PRBs, however, is dependent on 3 technical considerations: (a) the reactive media should be suitable for the pollutants, (b) Filter's sizes must be sufficient to allow a satisfactory residence period, and (c) the reactive material should have a satisfactory hydraulic conductivity to avoid any bypass of the system . The first factor is a crucial consideration in the design of PRBs, and when installing any PRB system, special attention must be paid for selecting reactive or sorbent materials. As a result, having a good understanding of the site's history aids in the right design of PRB [77]. Dimensions are the most significant parameters in PRB design. The barrier should be long enough for treating the plume entire width (dimension perpendicular to the flow of groundwater) and be keyed into an impermeable layer. The goal is to identify the best thickness of a PRB that will allow impurities to be reduced to the required effluent concentration in a reasonable amount of time. This is required for deciding where PRBs should be placed as well as calculating PRB dimensions and lifetime. The suitability of a location for PRB treatment is determined by factors such as hydraulic conductivity, soil porosity, hydraulic gradient, and the chemical make-up of the groundwater [78]. The performance of PRBs can improve, but it needs recommendations obtained from various larger-scale and pilot operations. PRBs are undoubtedly necessary at the moment, but for better comprehension, a more programming-based approach is preferred [79].

The need that the entire contamination plume flows through the reactive gate of specified thickness (b) at a specific velocity (v) is a crucial condition of successful remediation. That is, the contaminant will come into touch with the reactive medium within a certain time frame (residential time). It is critical to build a reactive gate with suitable thickness. The following equation can be used to calculate the thickness of the PRB wall. Design of reactive gate width B and PRB form (length of impermeable walls L and its connection angle) should also be considered [80].

$$b = v * tres * SF \quad (10)$$

where: b – reactive gate thickness, v – the groundwater velocity in the reactive media, the factor tres is time residence required, SF – a certain safety factor.

PRBs are mainly limited to depths of less than 20 m, and so are not viable for contamination at deeper depths [81]. Right angle used between all funnels and side walls was based on the literatures of they discovered that in isotropic aquifers with little variation in groundwater flow direction, this was the most efficient configuration [65] . The design of PRBs is carried out using numerical methods or simulators, which are effective for predicting scenarios and evaluating the resulting groundwater flow systems in relation to specific site characteristics. In the search for the best PRB designs, numerical models can be extremely useful. The hydrogeologic (groundwater movement), geochemical (chemical reactions), and economic components of the system all require modeling (construction and operational costs). Numerical approaches, on the other hand, are complex and can result in considerable mistakes if the discretization is too coarse or the alignment is incorrect [82].

Designing a sorption based PRB necessitates an awareness of the site's main characteristics as well as the medium that will be used to construct the barrier. Installation of PRBs can be affected by geological features such as too hard lithological structures that are difficult to excavate, and sometimes the holding media is not cemented, causing filler material emplacement to be disrupted. The existence of pebbles and cobbles can also make excavation of filling sites difficult, necessitating prior knowledge of the lithological layers corresponding to aquifers' stratigraphy. The emplacement location must be tested, and geotechnical testing can assist in identifying the following qualities, which are (i) clays, sand, and silts having different shear strength and cohesion qualities, (ii) the materials' dryness and wetness fractions, (iii) the size of grain in the different layers discovered in the site, and (iv) the density of the discovered materials [79]. The Darcy variables are key parameters that must be considered in a specific location in order to understand the unique properties of that location. The most favorable condition for PRBs installation is GW leakage rates (<0.3 m/d or 109.7 m/year). Higher speeds may operate as a constraint on the PRB's response. Pollutants that are typically broken down into additional contaminants after being degraded by reactive media, such as chlorinated solvents, take much longer to degrade than contaminants with lower significance rates. For various cases, different PRB layouts are required [83]. Although a few solutions for deeper installations have been found, the majority of experience with permeable treatment wall installation is with relatively shallow emplacements (10 m) utilizing typical geotechnical design and construction approaches. In the simplest situation, a trench of the required width can be excavated and backfilled with reactive material to intercept the contaminated layer. Normally, this approach would be limited to modest depths in geologic materials that are stable [53].

The cost consideration of installing a PRB is determined by geology, hydrogeological factors (such as aquifer depth and thickness), PRB configuration, and installation methods. In general, the cost of a PRB application is determined by the depth and length of the PRB. The higher the prices, the longer the PRB and the deeper the aquifer. Trenching wall can cost up to 70% of the entire building cost since it necessitates the use of specialized equipment. Material prices are low, accounting for just around 5–10% of overall installation expenses; however, delivery to the job site must be factored in [73]. Consequently, the researchers came at the following conclusions for PRB design after simulating many scenarios:

- The width of funnel-gate PRB catch zone is proportionate to the discharge flow passing through the gate.
- The 180 degree (straight) funnel provides greatest capture zone for any single direction of flow, but not the largest composite capture zone when flow directions change.
- Achieve balance between the size of the gate's capture of zone and the amount of time polluted groundwater is retained in the gate.
- As Kgate/Kaquifer increases to Kgate/Kaquifer = 10, discharge via the gate (of a particular design) increases exponentially.
- High hydraulic conductivity reactive materials usually have large grain sizes and thus low surface area-to-mass ratios. As a result, reaction rates are often lower and residence times are shorter. Making the gates longer in the direction of groundwater flow could readily lengthen the residence duration (without significantly impacting the capture zone) to correct this condition. The establishing of the funnel and gate PRB will alter the hydrodynamics of groundwater and slow down how quickly contaminants react in the monitoring well. using of funnel and gate permeable reactive barrier (FGPRB) for treating groundwater pollution is a successful strategy [84]. Important elements including the hydraulic capture zone and residence time must be considered when establishing a funnel and gate. The hydraulic capture zone is the length of the groundwater

zone that will pass through the gate as opposed to under, over, or around the barrier [73] .

REACTION MECHANISMS IN GROUNDWATER

Permeable reactive barriers are representing a flexible containment method since they are a passive way to remove pollutants from groundwater. They can apply the reactive media to a range of locations and pollutants by making the right choice. The capacity of reactive media to remove site-specific contaminants determines how well they work with PRBs.

- Precipitation, an immobilization technique, can remove heavy metals from groundwater. Using PRBs consisting of medium containing mildly sulfate-reducing bacteria or soluble salts, heavy metals can be removed from groundwater. Groundwater dissolves barrier salts or bacterial salts, which then form compounds with heavy metals in the aqueous phase. Heavy metal complexes precipitate out of the groundwater within or downstream of the PRB because they are less soluble than metal ions.
- Volatilization and biodegradation – through volatilization and biodegradation, respectively, it is possible to remove septic waste (i.e. phosphorus and nitrogen) or petroleum chemicals (i.e. nitrogen and phosphorus) from groundwater. Barriers that depend on biodegradation and volatilization are made of permeable media containing oxygen release chemicals (ORCs) or coarse-grained media that has been injected with air. Contaminants injected through PRBs into the air volatilize in the stream and are carried to the surface where they are recovered or released into the atmosphere. Additionally, oxygen generated by ORC or pumped into groundwater increases its dissolved oxygen content, which encourages the aerobic biodegradation of contaminants within and downstream of PRB [85].
- Oxidation-reduction – utilizing oxidation-reduction techniques, inorganic contaminants and halogenated organic compounds can be eliminated from groundwater. Some inorganic contaminants will precipitate if their valence state is altered [86].
- Sorption – it is a retardation or immobilization mechanism which can be utilized in groundwater to decrease the mobility of the organic compounds and metals. Wood chips, activated carbon, straw, peat, coal, paper sludge, shale, and tire chips are all possible mediums. Because pollutants sorb to the media, mobility of the organic compounds or metals entering a PRB made of these materials is decreased. Natural or increased breakdown (rate-limited reactions, decay, or biodegradation) within the barrier, or the excavation of contaminant-laden sorbent is planned for the final disposal of the sorbed chemicals over time [87].

Sorption process modelling

Two basic models were used for sorption process modeling

- Freundlich model: for the sorption isotherm model, Equation 11 solves the nonlinear regression principle. The Freundlich constants (K_f and n) are corresponding to adsorption capacity and adsorption intensity, respectively [88].

$$q_e = K_f C_e^{1/n} \tag{11}$$

- Langmuir model: Equation (12) describes sorption data, especially for the consistent adsorption energies on the sorbent surface. It also justifies why adsorbed chemical species on unoccupied sites do not interact. The Langmuir model is used to determine the greatest sorption capacity (qmax, mg/g) of sorbent [89].

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \tag{12}$$

where: b – the adsorbent particles – contaminant molecules affinity measured in (L/mg).

Sorption kinetic models

Two conventional models are listed in Equations (13 and 14) for formulation of kinetic data. These models are applied in a wide range of adsorption process, involving nanomaterials and biomass as sorbents, as well as medicines and heavy metals as contaminants. Pseudo first order model: is popular formula Equation 13 used to describe the rate of solute adsorption :

$$q_t = q_e(1 - e^{-k_1 t}) \tag{13}$$

where: k_1 – rate constant for the model (1/min).; the quantities q_t and q_e (mg/g) are the amounts of solute retained on the sorbent particles at a time *t* and equilibrium, respectively.

Pseudo second order model: assumes that single layer of the solute adheres to the adsorbent particles, that the sorption energy cannot vary for each sorbent, and that there is no interaction between the sorbed chemicals. It is written as in Equation 8. [90]

$$q_t = \frac{k_2 q_e^2 t}{(1+k_2 q_e t)} \tag{14}$$

where: k_2 – the rate constant for 2nd order model (g/mg min).

Intra-particle diffusion model: is developed by Weber and Morris as follows :

$$q_t = k_{int} t^{0.5} + C \tag{15}$$

where: k_{int} – rate constant for the diffusion model (mg/g min$^{0.5}$), and the intercept value can be illustrated by *C* [91].

MODELING OF BREAKTHROUGH CURVES

Optimizing and modeling have become essential to modern environmental management. Growing concerns about balanced development prompted several agencies responsible for environmental quality to seek new methods to save energy and operating expenses. For environmental study and data comparison, numerical and statistical methods are most typically used [92]. Analytical models are useful for addressing relatively easy and generalized contamination transport problems, whereas numerical models are used to simulate real-world contamination transfer [93]. Various models and software programs may be a good choice to explain the contaminant front propagation by drawing the measurement of normalized concentration (C/C_o) against travel time. Where, *C* and C_o (mg/L) are outlet and inlet concentrations, respectively:

- Thomas-BDST model – it can be employed to anticipate the spread of breakthrough curve and the sorbent's maximal solute sorption. It is presumed that the column has no axial dispersion and that rate of sorption follows the Langmuir isotherm with the pseudo-2nd order kinetics. In contrast to the Adams-Bohart model, the Thomas model is appropriate for presenting the whole breakthrough curve. The below equation can be exploited to explain this model [94]:

$$\frac{C}{C_o} = \frac{1}{1+\exp\left(\frac{K_T}{Q}qM - K_T C_o t\right)} \tag{16}$$

where, *M* is defined as the mass of the packed sorbent (g), *t* (min) is corresponding to the time that has been elapsed, and *Q* (mL/min) represents the pumped discharge, and K_T (mL/mg/min) represents the Thomas rate constant.

- Belter-Cussler-Hu model – it is a model proposed by Chu (2004) for breakthrough curves as follows [95]:

$$\frac{C}{C_o} = 1 + \text{erf}\left[\frac{(t-t_o)\exp\left(-\sigma\left(\frac{t}{t_o}\right)\right)}{\sqrt{2}\sigma t_o}\right] \tag{17}$$

where: erf[*x*] – refers to the *x* error function, *t* represents the residence time within a column, t_o – denotes the instant of time at which the effluent concentration equals half the influent concentration, and *σ* represents the standard deviation stands for a direct measurement of the straight part slope of breakthrough curve [96].

- Yan model: [97]describes a statistical basis model of Yan with great precision of measurements of the continuous experiments.

$$\frac{C}{C_o} = \frac{1}{1+\left(\left(\frac{0.001\times Q\times C}{q_o M}\right)\times t\right)^a} \tag{18}$$

where: *M* – represents the dry weight of adsorbents (g), q_o – the greatest sorption capacity for sorbent (mg/g), and (*a*) estimates the regression curve slope. This model also indicates the Dose-Response (DR) model extensively applied in the scientific literature.

- Artificial neural network (ANN) model – ANN is used in a variety of applications, including water quality modeling [98], management of water quality [99], and nitrate concentration in groundwater [100]. The ANN model represents a data-driven model which mimics the operations of the biological neural networks in the brain of the human. ANN is made up of a variable number of units called neurons that can be joined together via connections. In general, an ANN is made up of three distinct layers: the input, hidden, and the output. Each layer incudes neurons with comparable characteristics [101, 102]. ANNs' parallel distributed processors process data information from the input to the output via a network topology of the interconnected nodes. The computed input data in input and output layers corresponds to the network response of the current database or known as input pattern, while the hidden or intermediate layer plays an essential turn in representing and estimating complicated relationships between patterns [103]. ANNs offer a wide range of applications in the research of groundwater quality. An ANN model was developed previously to determine the extent of a polluted zone in an aquifer following an unanticipated leak. The use of ANNs has grown in a variety of scientific and engineering domains. Many difficulties in groundwater investigations have been effectively solved utilizing ANNs [104]. The ANN models, being "black box" models with unique attributes, are well suited to simulating dynamic nonlinear systems [105]. The neural network has been programmed to solve a given problem by a process of learning that includes typical stimulation and response with the appropriate reaction; this varies from the classic modeling method, which requires the definition of an algorithm and the creation of a program [106]. An effective Levenberg-Marquardt algorithm-based artificial neural network (LMA-BANN) model represents one of fastest backpropagation strategies for addressing least-squares of nonlinear problems [107]. The Levenberg-Marquardt algorithm, assembled independently by Kenneth Levenberg and Donald Marquardt, may be used to solve the problem of minimizing a nonlinear function numerically. This method is suitable for training small and medium-sized problems in artificial neural networks.

- COMSOL Multiphysics Program – Version 3.5a of COMSOL Multiphysics (2008), which was based on the older version of FEMLAB, was used to solve the boundary value issue previously described. This version may be used to analyze flow problems through porous media. Graduate students at Stockholm, Sweden's Royal Institute of Technology provided codes for the COMSOL software (2005). Using PDE, this interactive tool is typically used to simulate and solve all engineering and scientific problems. It works out the finite element, adaptive/refinement meshing, and error control analysis procedures employing a variety of numerical solver packages. Solver and simulation software were employed to solve different systems of time-dependent or stationary second-order partial differential equations in space. Both 2D (quadrilateral/triangular) and 3D (hexahedral/tetrahedral/prism) meshes can be supported. Building models can be accomplished more effectively by defining the physical parameters (such as loads, material properties, constraints, fluxes, and sources) and directly correlating these expressions, variables, or numbers with solid boundaries, edges, domains, and points, regardless of the calculated mesh, rather than by defining the fundamental equations. In COMSOL, the most fundamental focus is on how to generate a grid or a large mesh by manipulating a spatial domain in a discretized pattern into small cells and then applying an efficient method to solve the equations. Then, using either a flexible graphical user interface or by writing a script in the COMSOL language, COMSOL may create a variety of PDE that internally reflects the whole model. The script is created in the computer language C++, ensuring that all compliance and authority offered by this language are fully utilized. This opens the door to other useful benefits including active memory supply, efficient data design, and a configurable solver (COMSOL User's Manual, 2008). The base Multiphysics of COMSOL program's eight add-on modules are crucial in extending the software's capabilities to cover fields of use including Heat Transfer, Earth Science, Chemical Engineering, and others.

CONCLUSIONS

Permeable reactive barriers represent a flexible containment method since they are a passive way to remove pollutants from groundwater. PRB technique provides financial benefits while also encouraging waste material reuse, so contributing to environmental sustainability. Funnel and gate PRB can offer one or more dense treatment areas for maximizing groundwater pollution plume capture. Funnel-gate PRB is characterized by smaller reaction area, ease in replacement and removal during the blocking of the reactive barrier by fine soil particles and reactive sediments. As a result, in every sense, PRB has the potential to be a very practical application. Analytical models are applicable for solving simple and idealized contamination transport problems, while numerical models deal with real world contamination transport simulations. Various models and programs software by graphing the measurement normalized concentration vs travel time, can be used to describe the propagation of contaminants fronts in groundwater.

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