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Review

Permeable Reactive Barriers in Groundwater Remediation: A Review of Efficiency in Removing Pharmaceuticals and Heavy Metals

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Abstract

Global water pollution driven by industrial and agricultural expansion has resulted in the widespread occurrence of persistent contaminants, particularly pharmaceuticals and heavy metals, in groundwater systems. Conventional treatment methods often prove inefficient, costly, and environmentally unsustainable, highlighting the need for innovative in situ remediation technologies. Permeable Reactive Barriers (PRBs) have emerged as a promising and energy-efficient solution for the long-term purification of contaminated aquifers. Their efficiency arises from passive operation, relying on natural groundwater flow to promote pollutant removal through adsorption, ion exchange, precipitation, and redox-driven transformations. This review emphasizes the superior performance of materials such as Activated Carbon, Biochar, Zeolites, and Zero-Valent Iron (ZVI) in the immobilization and reduction in pharmaceuticals and metal ions. Key challenges to PRB longevity include permeability loss and reactive media depletion due to mineral precipitation and biofouling. Advances in hybrid PRB configurations, coupled with electrokinetic (EK) and bioreactor systems, and predictive modeling, particularly Artificial Neural Networks (ANNs), offer pathways to enhance performance, optimize design, and ensure sustainable operation. Overall, PRBs represent a scalable and environmentally sound approach to groundwater remediation, with future progress relying on the development of multifunctional, regenerable materials and integrated design strategies.

Keywords: permeable reactive barriers; groundwater remediation; heavy metals; pharmaceuticals; adsorption; zero-valent iron (ZVI); biochar; zeolites

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1. Introduction

Water pollution remains one of the most pressing environmental challenges associated with rapid industrialization, urbanization, and agricultural intensification [1,2]. The continuous release of contaminants into aquatic environments leads to the deterioration of both surface and groundwater quality, posing significant risks to ecosystems and human health [3]. Aquifer systems are particularly vulnerable due to their slow renewal rate and limited natural attenuation capacity, which promotes the long-term persistence of pollutants once contamination occurs.

Anthropogenic activities are the primary drivers of subsurface contamination. Industrial effluents introduce complex mixtures of organic compounds, heavy metals, and toxic by-products into aquatic systems [4].

Agricultural practices further contribute through nitrate leaching and agrochemical infiltration into subsurface environments [5]. Urban runoff represents an additional pathway for contamination, transporting heavy metals and other pollutants into water bodies [6]. These combined sources result in heterogeneous hydrochemical conditions that complicate monitoring and remediation processes [7].

In recent years, increasing attention has been paid to emerging contaminants, particularly pharmaceuticals and microplastics, due to their persistence, bioactivity, and widespread occurrence in aquatic environments [8–10]. Pharmaceutical compounds are frequently detected in water systems as a result of incomplete removal during wastewater treatment processes, while microplastics are widely reported in both surface and drinking water [11,12]. Notably, these pollutants often coexist and interact. Microplastics can adsorb pharmaceutical compounds and facilitate their transport through porous media, thereby altering contaminant mobility and distribution in subsurface environments [9]. Such interactions alter contaminant fate and reduce the efficiency of conventional treatment approaches [8,9].

In addition to emerging contaminants, heavy metals remain among the most hazardous pollutants in water systems due to their persistence, toxicity, and bioaccumulation potential [13–15]. Their presence is mainly associated with industrial discharge and wastewater effluents, and long-term exposure may lead to severe environmental and human health impacts [14,15]. Therefore, the development of effective remediation strategies capable of addressing both inorganic and organic target compounds is essential.

Various conventional water treatment technologies, including adsorption, chemical precipitation, membrane filtration, and advanced oxidation processes, have been widely applied for contaminant removal [16].

Despite their widespread application, these technologies often exhibit significant limitations, including high energy consumption, operational costs, and the generation of secondary waste streams. In addition, their efficiency strongly depends on contaminant properties and environmental conditions, which restricts their applicability for long-term groundwater remediation. A summary of the advantages and limitations of conventional treatment methods is presented in Table 1.

Table 1. Advantages and limitations of water treatment methods.

Method	Advantages	Limitations	References
Adsorption (activated carbon (AC), natural sorbents, biochar)	Reducing concentrations of heavy metals, organic pollutants, pharmaceuticals, and emerging contaminants in water	Sorbent saturation; regeneration or replacement required; efficiency depends on water chemistry	[10,14,15]
Advanced oxidation processes (AOPs)	Effective degradation of persistent and emerging organic contaminants	High energy and operational demands; possible formation of transformation by-products	[4,10]
Conventional wastewater treatment	Effective for reducing organic load and microbial contamination	Limited removal of pharmaceuticals, microplastics, and trace metals	[3,10]
Disinfection (chlorination, UV)	Proven microbial inactivation and public health protection	Does not remove chemical contaminants; potential disinfection by-products	[10]
Membrane-based processes	High removal efficiency for dissolved contaminants, pathogens, and microplastics	Membrane fouling, high cost; concentrate disposal issues	[12]

In situ remediation technologies are increasingly recognized as sustainable alternatives. Among them, permeable reactive barriers (PRBs) are widely recognized as passive systems installed along the natural groundwater flow path [17,18]. As contaminated groundwater flows through a reactive medium, pollutants are removed via adsorption, ion exchange, precipitation, and redox reactions. The operating principle of PRBs is illustrated in Figure 1.

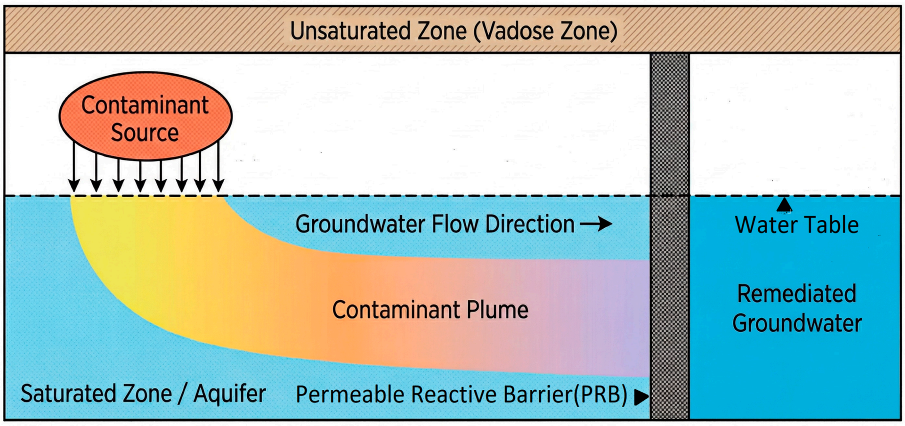

Figure 1. Schematic representation of the functioning of a Permeable Reactive Barrier (PRB).

The performance of PRBs depends on the selection of reactive materials and site-specific hydrogeological conditions [19,20]. Field-scale studies have demonstrated the successful application of PRBs for the remediation of nitrate-, ammonium-, and metal-contaminated water systems under real environmental conditions [21–23]. However, long-term operation is often limited by permeability reduction, clogging, and passivation of reactive media, which significantly reduce treatment efficiency over time [20].

Although the number of studies on subsurface remediation and PRB technology continues to increase, existing research remains fragmented. Most studies focus on individual contaminant groups or simplified system conditions, while emerging contaminants such as pharmaceuticals and microplastics are often considered separately, despite their frequent co-occurrence in real groundwater systems [8,9].

However, in natural environments, pharmaceuticals, heavy metals, and microplastics coexist and interact, leading to complex processes such as competitive adsorption, surface interactions, and redox transformations. These coupled effects remain insufficiently addressed, particularly in the context of PRB systems and their long-term stability.

This review provides an integrated assessment of PRB applications for the simultaneous removal of pharmaceuticals and heavy metals from aquifer systems. This study systematically links contaminant characteristics, removal mechanisms, and reactive material performance under mixed-contaminant conditions, with particular emphasis on long-term efficiency and stability.

Therefore, this review aims to evaluate PRB-based remediation strategies for groundwater treatment, focusing on removal mechanisms, reactive materials, key factors governing system performance under realistic environmental conditions.

2. Overview of Permeable Reactive Barriers

PRBs are advanced systems employed in groundwater remediation of contaminated sites, with sustainable solutions to environmental cleanup. They allow the natural flow of subsurface water to pass through reactive materials that actively facilitate the degradation or immobilization of designated pollutants. Serving as a multifaceted and cost-effective approach, PRBs have been accepted within environmental engineering and among regulators, making them the focal point of studies of the domain of groundwater management [24,25].

The performance of PRBs primarily depends on their design, which can involve configurations of continuous reactive barriers or funnel-and-gate systems (Figure 2), and selection of reacting agents such as granular activated carbon (AC) and ZVI. Such components interact to enhance contact between contaminated groundwater and reactive media, improving pollutant removal efficiency [26,27].

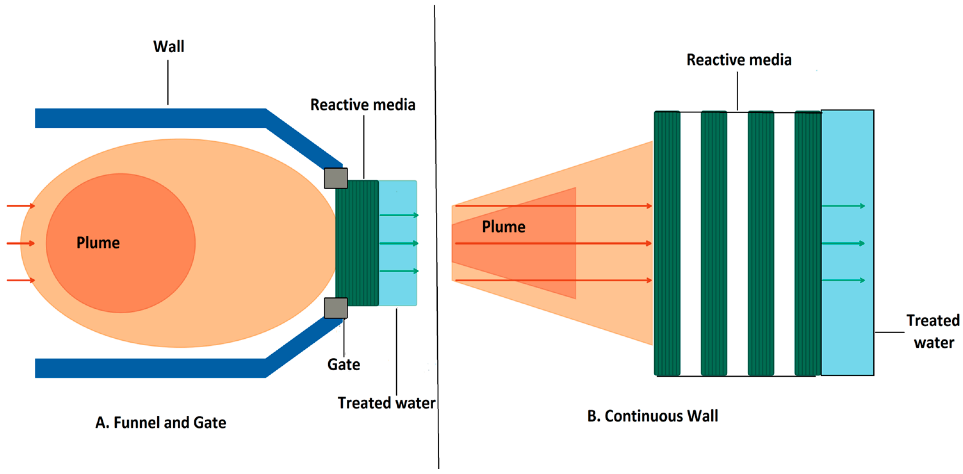

Figure 2. Examples of PRBs.

PRBs are passive remediation systems with low maintenance requirements, offering a sustainable and cost-effective alternative for long-term environmental rehabilitation [28,29]. Despite their advantages, PRBs also have their disadvantages, including differing effectiveness depending on site conditions, types of contaminants, and possible need for complementary remediation technologies. Hydromechanical conditions governing groundwater flow may pose challenges that govern groundwater flow, and the persistence of reactive media requires focusing on careful design and construction to ensure continuing effectiveness [30,31]. Hence, PRB execution is subject to careful site characterization and continuing monitoring. Continuous monitoring is critical to manage these complexities and to verify the sustained effectiveness of remediation measures over time [32]. While they present numerous opportunities for sustainable environmental restoration, ongoing research and case studies are essential to optimize their application and address inherent challenges in various contaminated sites.

2.1. Types of Permeable Reactive Barriers

PRB technology encompasses several structural configurations that are selected based on site-specific characteristics, contaminant type and distribution, hydrogeological conditions, and economic considerations such as the cost of reactive materials. The most commonly described configurations in the literature include the Continuous Reactive Barrier (CRB), the Funnel-and-Gate (F&G) system, and a range of advanced or modified designs such as Sequential PRBs, Injection PRBs, radial filtration systems, bio-barriers, and modular or prefabricated barrier systems [33]. The CRB, also known as a continuous trench or continuous wall, represents one of the most widely adopted and straightforward PRB configurations (Figure 3). It consists of a single, permeable reactive zone installed underground across the flow path of the contaminated groundwater plume. For effective treatment, the CRB must capture the entire width and depth of the plume, thereby ensuring that groundwater flow, perpendicular to the barrier, passes fully through the reactive zone. The most common construction techniques for CRBs include slurry walls and continuous trenching, with conventional excavation being cost-effective at depths less than 10 m. CRBs are typically suitable for installation at depths ranging from 5 to 30 m and can be applied across a wide range of soil types. Owing to their simplicity, lower construction cost, and applicability to various hydrogeological conditions, continuous trenches are particularly favored in developing countries. Certain design variations include the use of horizontal wells, which function as an extended form of continuous trenches, collecting contaminated groundwater from within the aquifer and directing it into treatment units containing reactive materials such as ZVI. However, despite their advantages, CRBs become economically unfavorable when groundwater plumes are significantly deep or wide, as construction costs rise significantly. Furthermore, continuous trench PRBs are generally more difficult to decommission compared to Funnel-and-Gate systems [18,33].

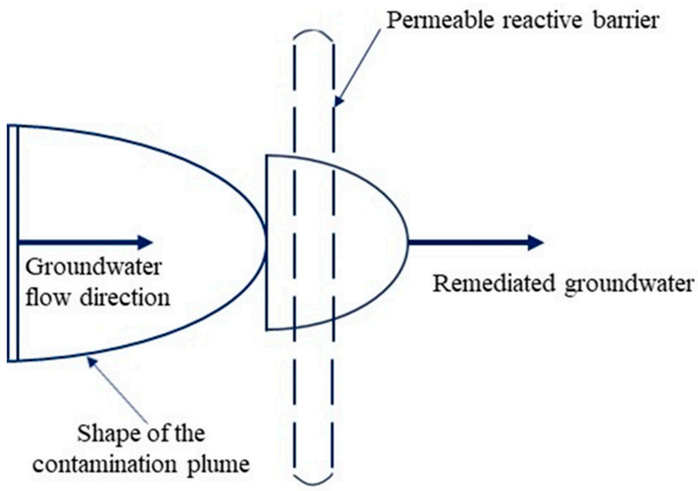

Figure 3. Continuous reactive barrier.

To overcome some of the limitations associated with CRBs, the Funnel-and-Gate (F&G) system was developed, offering enhanced efficiency and reduced use of expensive reactive materials. This configuration employs impermeable cut-off walls, referred to as funnels, to direct the contaminated plume toward a reactive gate (Figure 4). The funnels are embedded into impermeable layers to prevent contaminants from bypassing the system. The F&G system operates passively, relying on the natural hydraulic gradient to transport groundwater through the gate. Since the reactive zone in an F&G system occupies only a portion of the plume's cross-section, the volume of reactive material required is significantly lower than in continuous barriers, making this design particularly cost-effective when using high-cost materials such as AC or metal oxides. Additionally, the reactive media within the gate are often installed in substitute-ready reactors, enabling straightforward replacement once the material's reactivity diminishes. Due to this design, F&G systems are easier to maintain and decommission than continuous trenches. This configuration is highly suitable for sites characterized by heterogeneous soils or non-uniform contaminant distribution because the funnels channel the plume, promoting more uniform pollutant concentration before treatment. One critical hydraulic consideration is that channeling the plume through a narrow gate significantly increases groundwater velocity, often by a factor of five compared to the natural rate, necessitating careful calculation of reactive material thickness and quantity [17,33].

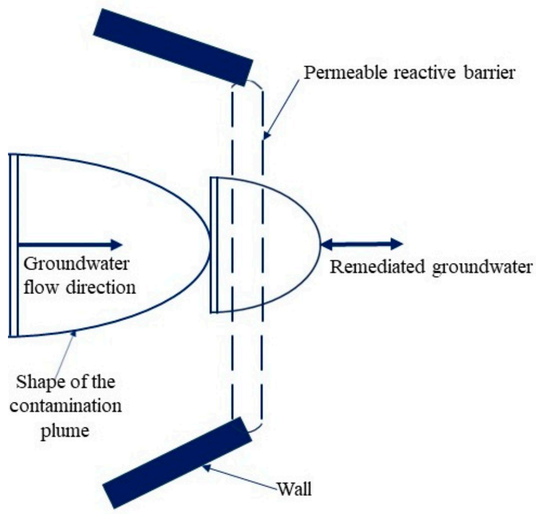

Figure 4. Funnel-water gate.

Beyond these two primary structures, several advanced and specialized PRB configurations have been developed to address complex contamination scenarios, mixed pollutants, deep groundwater plumes, and long-term operation and maintenance challenges. Sequential (or multi-barrier) PRBs incorporate multiple reactive zones arranged in series to treat contaminants with differing physicochemical or thermodynamic properties. These systems also help prevent pollution swapping, where the removal of one contaminant inadvertently generates another. Sequential barriers may combine chemical and biological processes; for example, an iron-based reactive zone may be followed by a bio-barrier for the degradation of polycyclic aromatic hydrocarbons (PAHs). Research has demonstrated the effectiveness of systems such as palladium-coated iron, followed by anaerobic microbe-seeded sand for the removal of 2,4,6-trichlorophenol, or ZVI, followed by granular AC or oxygen-releasing compounds. Injection-based PRBs are employed where excavation is challenging, particularly for deep groundwater contamination. In such systems, reactive materials are injected directly into the subsurface to create overlapping in situ treatment zones. These barriers offer lower installation costs and a simpler structure but require high subsurface permeability. Their primary limitation lies in the complex interactions between the reactive agents and subsurface conditions, including adsorption, clogging, and aggregation, which restrict the effective radius of influence [16,17,33,34].

2.2. Working Principle of PRBs

Permeable Reactive Barriers function as passive, in situ groundwater remediation systems that harness natural subsurface hydrodynamics rather than external energy input. A PRB is installed as a subsurface wall of reactive material positioned perpendicularly across the path of a contaminated groundwater plume, so that the entire plume is intercepted and forced to pass through the reactive zone under the natural hydraulic gradient of the aquifer. This eliminates the need for mechanical pumping or continuous energy supply, which distinguishes PRBs from active pump-and-treat technologies and underpins their cost-effectiveness over long operational lifespans [16,33].

For the system to function without impeding groundwater movement or causing upstream mounding, the hydraulic conductivity of the reactive medium must be at least two to ten times greater than that of the surrounding aquifer material [16,33]. As contaminated groundwater migrates through the barrier under this hydraulic pressure, target contaminants interact with the reactive medium and are removed or transformed through one of two broad categories of mechanisms: non-destructive immobilization or destructive transformation, as summarized in Table 2.

Table 2. Classification of contaminant removal mechanisms within PRBs: non-destructive and destructive processes.

Process Category	Advantages	Limitations
I. Non-Destructive Processes (Immobilization)	Adsorption/Sorption	Pollutants attach to the large specific surface area of the active materials. This can involve mechanisms such as hydrophobic interaction, electrostatic interaction, and adsorption into porous materials. Activated carbon (AC) is frequently uses this process for organic contaminants [16,17,33].
	Precipitation	Contaminants are converted from their original dissolved state into low-soluble solid precipitates (e.g., metal hydroxides or carbonates). This typically occurs due to chemical reactions, such as those caused by changes in pH [16,17,33].
	Ion Exchange	Pollutant ions are removed from the liquid phase by exchanging places with identical ions present on the solid surface of the reactive material (e.g., zeolite). This process is reversible [16,17,33].
	Redox Reactions (Abiotic Reduction)	The toxic form of a contaminant is converted into a non-toxic form. ZVI is a commonly used material that releases electrons, resulting in the precipitation or degradation of contaminants via a reductive mechanism [33,34].
II. Destructive Processes (Transformation)	Bioremediation/Biochemical Degradation (Biotic Reduction or Oxidation)	Microorganisms use the pollutants as a source of energy and materials for cell synthesis, breaking them down into less harmful compounds such as carbon dioxide (CO_2), water (H_2O), or inorganic compounds. This mechanism includes Biostimulation (adding nutrients/O_2 to enhance microbial activity) and Bioaugmentation (adding specific microorganisms along with nutrients) [33,34].

Non-destructive mechanisms retain contaminants within the reactive medium without chemically altering them. These include physical adsorption, in which pollutant molecules accumulate on the surface of porous media such as GAC or zeolites; ion exchange, whereby charged contaminant species are displaced by ions on the reactive surface; and precipitation, in which dissolved pollutants form insoluble mineral phases that become immobilized within the barrier matrix. While effective, immobilization mechanisms have a finite capacity and eventually require media regeneration or replacement [34].

Destructive mechanisms, by contrast, convert contaminants into less harmful or entirely benign products. Redox reactions are among the most widely exploited, particularly in ZVI-based PRBs, where reductive dechlorination of halogenated organic compounds and oxidative degradation of antibiotics proceed through sequential electron transfer pathways [16,17]. Microbial degradation represents a biological variant of destructive treatment, in which communities of microorganisms colonizing the reactive medium metabolize organic contaminants, ultimately mineralizing them to carbon dioxide, water, and inorganic ions. In practice, many PRB systems rely on a combination of both categories—for example, initial adsorption concentrates contaminants at the reactive surface, where subsequent chemical or biological transformation completes their removal [18,33].

The treated groundwater that emerges on the downstream side of the barrier typically exhibits contaminant concentrations well below influent levels, frequently meeting applicable regulatory discharge standards [16–18]. The dominant removal pathway in any given installation depends on both the physicochemical properties of the target contaminant and the characteristics of the reactive medium selected, which is why reactive material selection is the central design decision in PRB engineering and is discussed in detail in the following section.

PRBs represent an energy-efficient and sustainable approach to groundwater remediation, combining natural subsurface flow with engineered reactive materials. Their hybrid treatment capability, encompassing both physicochemical and biological reactions, enables the effective removal of a wide range of contaminants, including heavy metals, chlorinated solvents, and emerging organic pollutants. The continued optimization of PRB design, reactive media composition, and long-term stability remains a critical focus for advancing this environmentally friendly remediation technology.

2.3. Types of Reactive Materials

The effectiveness and longevity of Permeable Reactive Barriers fundamentally rely on the proper selection of reactive materials (also referred to as active materials or reactive media) used to fill the barrier zone. These materials serve as the core functional component of the PRB, directly controlling the removal efficiency, reaction mechanisms, hydraulic performance, and durability of the system over time. Therefore, the selection process must be carefully aligned with the specific site conditions and treatment objectives. Reactive media are chosen primarily based on the type and concentration of the target contaminants, as different pollutants (e.g., heavy metals, chlorinated solvents, pharmaceuticals, nitrates) require distinct remediation mechanisms [17]. In addition, factors such as the desired rate of reaction, the persistence of contaminants, and the required treatment endpoints play a critical role in determining the most suitable material.

Beyond contaminant characteristics, several practical considerations also influence media selection. Cost-effectiveness is essential, as PRBs are designed to operate over long periods with minimal maintenance; therefore, materials must provide sustained performance without excessive replacement. Availability and ease of sourcing are equally important, especially for large-scale installations. Moreover, the chemical and physical stability of the media under subsurface conditions must be ensured to prevent structural breakdown, dissolution, or secondary pollution. Compatibility with local groundwater chemistry, pH, redox potential, and geochemical interactions is also crucial, as unfavorable conditions may reduce reactivity or accelerate passivation. Furthermore, the media must maintain sufficient hydraulic conductivity to allow natural groundwater flow without causing clogging or bypassing [17,18,35].

Reactive media in PRBs generally function through two major categories of processes to remove contaminants from groundwater: destructive and non-destructive mechanisms. Destructive processes involve the transformation of pollutants into less harmful or non-toxic forms, often through chemical reduction, oxidation, or microbial biodegradation. These processes are particularly beneficial because they achieve permanent removal rather than temporary immobilization. Non-destructive processes, on the other hand, include adsorption, precipitation, ion exchange, and surface complexation, which immobilize contaminants by binding them to the media or converting them into insoluble forms. While non-destructive mechanisms are often simpler, they may lead to eventual saturation of the media, requiring regeneration or replacement. In practice, many reactive materials exhibit multiple mechanisms simultaneously, and composite materials are increasingly designed to combine both destructive and non-destructive pathways to enhance overall treatment efficiency and extend PRB lifespan [18,36]. Table 3 presents different types of reactive materials along with their respective characteristics.

Table 3. Reactive materials used in PRBs.

Reactive Material	Description and Mechanism	Advantages	Limitations/Challenges	References
Zero-Valent Iron (ZVI)	Strong reductive material used in >60% of PRBs; reduces chlorinated hydrocarbons (TCE, PCE, VC), Cr(VI), U(VI), NO_3^-. Acts through redox reactions (electron transfer, precipitation).	High removal efficiency (exceeding 90–95% for Cr(VI) and U(VI)); low cost; non-toxic; easily synthesized.	Pore loss, reduced permeability, and clogging due to secondary precipitates (lepidocrocite, magnetite, etc.). Mixed with sand or zeolite to mitigate.	[16,18,33,36]
Activated Carbon/Granular Activated carbon (AC/GAC)	Adsorptive material with high surface area (~1000 m^2/g). Removes hydrophobic organics and metal cations (Zn^{2+}, etc.) by adsorption and ion exchange.	Microwave regeneration yields 79–110% relative to fresh GAC; yields > 100% reflect surface reactivation and new micropore formation induced by MW irradiation.	Competition for adsorption sites by other ions; potential early saturation.	[16,18,33,36–39]
Zeolites	Aluminosilicate minerals with high ion exchange and adsorption capacity; chemically stable.	High removal capacity for heavy metals and radionuclides; low fouling and clogging.	Lower reactivity compared to ZVI; often used in composites.	[17,33,37]
Sulphate Reducing Bacteria (SRBs)	Biological reactive medium; reduces sulphates to sulphides, forming insoluble metal sulphides.	Effective for heavy metal removal; supports anaerobic biodegradation.	Requires organic substrates; sensitive to redox and pH conditions.	[33,36]
Limestone (Calcite)	Used to improve permeability and support SRB growth; removes fluoride by adsorption/precipitation.	Enhances pH control; inexpensive.	Limited adsorption capacity.	[18,33]
Agricultural/ Lignocellulosic Waste (Biochar, Corn Stalks, Mulch, Straw, Pine Bark, Sawdust)	Bio-based reactive media provide a carbon source and an adsorptive surface. Biochar from peanut shells, wheat/coconut shells, shows 99% PAH removal. Corn stalks, mulch, straw, and bark retain permeability and promote bioremediation.	Renewable, low-cost, dual adsorption + biological activity, high surface area.	Variability in properties requires modification for optimal reactivity.	[16,18,33,36,40,41]

2.4. PRB Design Considerations

The design and long-term operation of PRBs fundamentally depend on several interrelated key parameters, including permeability (hydraulic conductivity), thickness (barrier dimensions), and reactivity (reaction rate and longevity) [12]. These parameters must be carefully balanced and determined through thorough site characterization and numerical modeling to ensure that the PRB effectively intercepts and remediates the contaminated groundwater plume over the required operational period [16,18,33,34].

2.4.1. Hydraulic Conductivity and Clogging

Maintaining high hydraulic conductivity is one of the most critical physical design requirements for PRBs, as groundwater remediation relies on the contaminated plume flowing through the barrier rather than bypassing it [33,34,36,40]. To achieve this, the reactive material within the PRB must exhibit a permeability coefficient equal to or greater than that of the surrounding aquifer soil [16,41]. In practice, the permeability of the PRB is typically required to be two to ten times higher than that of the aquifer to ensure optimal interception and treatment efficiency [34]. The permeability of the reactive barrier is positively correlated with the particle size of the reactive media; larger particles promote higher hydraulic conductivity. Nevertheless, an increase in particle size may decrease specific surface area, thereby reducing reaction performance and potentially increasing material cost [18]. Therefore, a balance between hydraulic performance and material reactivity must be achieved to ensure effective contaminant removal without causing excessive construction and operational expenses [16].

Despite initial design optimization, permeability frequently decreases over time, representing a major factor that limits PRB longevity [33]. Several mechanisms contribute to this permeability loss. Precipitation of secondary minerals and reaction products, such as carbonates (e.g., calcium and magnesium carbonates), iron oxides, iron hydroxides, and ferrous carbonates, accumulate within pore spaces and lead to clogging. In particular, ZVI-based PRBs often experience permeability reduction due to oxidation reaction products like magnetite and maghemite [33]. Bioclogging is another significant issue, as the uncontrolled growth of microorganisms results in biofilm formation that blocks pores and reduces hydraulic conductivity [34,35]. Additionally, the migration and deposition of fine soil particles into the barrier matrix can decrease pore volume and restrict flow [34]. Conversely, in some composite media such as biochar-iron materials, initial operation may cause fine particles to migrate or diffuse outward, temporarily enlarging pore spaces and increasing permeability [42]. Understanding and mitigating these clogging mechanisms are essential for prolonging the effective lifespan of PRBs.

2.4.2. Barrier Geometry and Flow Path

The physical dimensions of PRB play a critical role in its overall efficiency and long-term performance. In particular, two key parameters, length (i.e., the extent of plume interception) and thickness (i.e., the flow path length through the reactive zone), directly influence the barrier's capture efficiency, hydraulic behavior, residence time of contaminants within the media, and installation cost [17]. Therefore, the proper design of these dimensions is critical to ensure that the PRB can fully intercept the contaminant plume and provide sufficient contact time for contaminant removal before the treated groundwater exits the system.

One of the primary considerations in PRB design is the length of the barrier, which must be sufficient to cover the entire horizontal width of the contaminant plume. If the PRB is shorter than the plume, part of the contaminated groundwater may flow around the barrier, leading to incomplete remediation and downgradient contamination [16,33]. Hence, the length is often defined by the capture zone, which represents the total width required to fully intercept the plume under specific hydrogeological conditions, considering groundwater flow direction, dispersion, and seasonal variations [17]. In many cases, site characterization and groundwater flow modeling are used to accurately determine this capture zone.

While the length ensures lateral interception, the thickness of the barrier determines the residence time of contaminants within the reactive media. The thickness must be adequate to allow complete degradation, transformation, or adsorption of pollutants before the treated water exits the PRB [33]. Several factors influence the required thickness, including groundwater velocity, contaminant concentration, pollutant degradation kinetics, and the reactivity and longevity of the reactive materials used. When groundwater flow is fast, thinner barriers provide insufficient contact time, resulting in incomplete treatment. Therefore, a thicker PRB may be required to maintain removal efficiency; however, increasing thickness also leads to higher construction and material costs [18].

To optimize thickness without compromising performance, numerical models are frequently used to evaluate the relationship between barrier dimensions, hydraulic conditions, and media reactivity. These models can simulate long-term performance and predict barrier lifespan under different scenarios. For example, simulation results demonstrated that increasing the thickness of a mixed reactive material (MRM) PRB from 2.5 m to 10 m significantly extended its predicted operational life—from 1000 days to 2600 days—based on Class III water quality standards for zinc (Zn) [35]. This example illustrates that while thicker barriers may be more expensive initially, they can offer substantial long-term benefits in terms of treatment durability and reduced maintenance.

2.4.3. Reactive Media Performance and Longevity

Reactivity refers to the capacity of the reactive media within a PRB to remove or degrade contaminants, whereas longevity describes the ability of the barrier to maintain its treatment performance over long operational periods, often spanning years or even decades [20]. These two parameters are closely interconnected, as sustained reactivity is essential to ensure long-term functionality and cost-effectiveness of PRBs. To achieve high reactivity, the reactive media must be carefully selected to match the physicochemical characteristics and concentrations of the target contaminants, ensuring sufficient degradation or immobilization within the available residence time in the reactive zone [18].

Residence time (t_R) is a critical factor that governs the interaction between contaminants and reactive media, directly affecting treatment efficiency. It represents the time required for pollutants to remain in contact with the reactive material to achieve remediation goals [17]. Since residence time is inversely proportional to groundwater flow rate, high flow velocities reduce contact time and may lead to incomplete treatment, whereas lower flow velocities enhance reaction time and overall removal capability [33]. Therefore, maintaining a sufficiently long residence time is vital for effective treatment performance [32]. Residence time can also be incorporated into predictive models and longevity equations, such as Equation (1), where $\Delta\epsilon$ represents the Darcy parameter related to velocity:

$$T_L = \frac{120qm(1-n)\eta\rho L}{(C-Ca)\Delta\epsilon} \quad (1)$$

In this equation, T_L represents the lifetime in days, qm is the adsorption capacity, ρ is the density, n is porosity, η is volume fraction, C is the initial concentration, and Ca is the target concentration, illustrating how media properties and hydraulic conditions collectively affect PRB lifespan [33]. Longevity is a critical design consideration because PRBs involve high initial installation costs and are expected to operate passively over extended periods with minimal maintenance [18]. The long-term effectiveness of PRBs depends heavily on the durability and sustained reactivity of the reactive materials, which must resist degradation, passivation, or exhaustion over time [20]. Nevertheless, longevity is not solely dependent on material properties; it is also strongly influenced by local environmental conditions. Elevated contaminant concentrations and high groundwater velocities can accelerate media exhaustion or inhibit the performance of materials such as nanoscale zero-valent iron (nZVI), ultimately reducing PRB efficiency. Longevity prediction models incorporate these factors and consistently demonstrate that increasing contaminant loading and pore water velocity lead to shorter operational lifetimes. Advanced longevity prediction functions, which include parameters such as the retardation factor, partitioning coefficient, and mass transfer coefficient, can be developed using site-specific contaminant concentrations and groundwater velocities to more accurately estimate PRB service life [43]. Furthermore, longevity is inherently limited by the depletion, passivation, or saturation of the reactive media. Over time, reactive sites become occupied or consumed, reducing treatment capacity. Structural changes, such as mineral precipitation or biofilm development, may further impact performance. Numerical simulations are commonly employed to estimate PRB longevity by determining the point at which the reactive material becomes depleted or when contaminant concentrations at the effluent side exceed regulatory thresholds (e.g., Class III water quality standards) [35]. Overall, the interplay between reactivity, residence time, environmental conditions, and material durability determines the long-term success of PRBs, highlighting the importance of careful material selection, accurate modeling, and proactive design to ensure sustained remediation performance.

3. Removal of Pharmaceuticals in PRBs

3.1. Common Pharmaceutical Pollutants

Pharmaceutical pollutants, including sulfamethoxazole, paracetamol, amoxicillin, ciprofloxacin, and other antibiotics, are increasingly detected in groundwater and subsurface water worldwide over the past decades. These compounds are categorized as "emerging contaminants," since they were not previously monitored under standard environmental programs but are now recognized as a significant threat to aquatic ecosystems and human health [44].

The main pathways for the entry of pharmaceuticals into aquifers include the discharge of treated and untreated wastewater, leakage from sewage systems, infiltration from municipal solid waste landfills, and percolation of wastewater containing residual concentrations of pharmaceuticals [44–46]. An additional source of contamination is the use of treated wastewater for agricultural irrigation, which promotes the migration of pharmaceutical compounds into the soil and subsurface environment and their subsequent infiltration into groundwater. Conventional wastewater treatment methods (biological, aerobic, and anaerobic processes) provide insufficient removal efficiency for antibiotics and analgesics. The concentrations of sulfamethoxazole, trimethoprim, diclofenac, and paracetamol in treated effluents often exceed 100 ng/L, which necessitates the implementation of additional purification stages [44–46].

Among the antibiotics most frequently detected in groundwater, particular attention is given to sulfamethoxazole (SMX). The concentrations of this compound range from several to hundreds of nanograms per liter. For example, in a study conducted in Minnesota (USA), SMX was detected in all samples downstream of wastewater discharge points at concentrations ranging from 7 to 965 ng/L [45]. Similar results were reported in Kenya, where this compound was found in 14.3% of groundwater samples with a maximum concentration of 258.2 ng/L [47]. In the Cape Cod region (USA), it was shown that even trace concentrations of SMX (~0.005 μM) can inhibit bacterial growth and reduce nitrate reduction activity. At a concentration of 1 μM, alterations in microbial communities were observed, including a decrease in Pseudomonas populations [48]. These findings demonstrate that the presence of antibiotics in groundwater can disrupt microbial and biogeochemical cycles, thereby reducing the natural self-purification capacity of ecosystems.

According to review data, the concentrations of sulfonamides in North American groundwater range from approximately 0.0099 to 1.1100 μg/L [49]. In Germany, sulfamethoxazole was among the antibiotics detected in both surface and groundwater, including in water abstraction zones for drinking water supply [41]. Similar results were observed in Switzerland, where SMX was identified among the most widespread pharmaceutical contaminants, particularly in areas of river water infiltration containing treated effluents. In most cases, its concentrations did not exceed 0.1 μg/L [50].

Alongside antibiotics, paracetamol and other non-steroidal anti-inflammatory drugs (NSAIDs), including diclofenac and ibuprofen, are also regularly detected in surface and groundwater [51,52]. The main reasons for their presence are the low efficiency of biological treatment stages in wastewater treatment plants (WTP) and the improper disposal of unused medications by the population. The concentration of paracetamol in drinking water after standard filtration and chlorination stages can reach 0.42 μg/L, indicating its persistence against conventional treatment methods [53]. Under unfavorable conditions, such as low temperatures or anaerobic layers, acetaminophen can persist for extended periods and migrate into deeper aquifer zones.

Transformation products of paracetamol, including p-aminophenol and quinone-imines, exhibit increased toxicity and can induce oxidative stress in aquatic organisms, alter antioxidant enzyme activity, disrupt the expression of detoxification-related genes, and cause tissue damage in the liver and gills of fish and invertebrates [54,55]. Therefore, when assessing the ecological risk of pharmaceutical compounds, it is essential to consider not only the parent compounds but also their metabolites, which often possess more pronounced toxic properties.

The occurrence of pharmaceutical compounds in wastewater treatment plant (WTP) effluents has been widely reported across different regions of the world, confirming their global distribution. However, the reported concentrations vary considerably depending on the level of wastewater treatment infrastructure, monitoring practices, and regional socio-economic conditions.

In developed regions, such as the United States and European countries (e.g., Germany), pharmaceutical concentrations in treated effluents are generally reported within the range of several hundred to a few thousand ng/L. For example, concentrations of commonly detected compounds such as metformin and caffeine in the United States have been reported up to approximately 13,500 ng/L and 677 ng/L, respectively, while in Germany values up to about 1270 ng/L have been observed.

In industrialized regions such as China, concentrations of pharmaceuticals in wastewater effluents may reach approximately 2000 ng/L, whereas in developing regions such as India, reported values are typically around 743 ng/L, although local variability remains significant.

Higher concentrations are often reported in regions with less efficient wastewater treatment systems. In Brazil, pharmaceutical concentrations in effluents have been reported up to approximately 560 ng/L, while in Kenya values up to about 7500 ng/L (e.g., metformin) have been observed, along with detectable levels of antibiotics such as sulfamethoxazole.

Even higher concentrations have been reported in Africa. In South Africa, pharmaceutical levels exceeding 12,100 ng/L have been observed, indicating significant contamination associated with wastewater discharge. The most extreme case was reported in Nigeria, where amoxicillin concentrations reached up to 272,156 ng/L, highlighting the critical impact of insufficient wastewater treatment infrastructure [56].

A comparison of pharmaceutical concentrations in WTP effluents across these countries is presented in Figure 5.

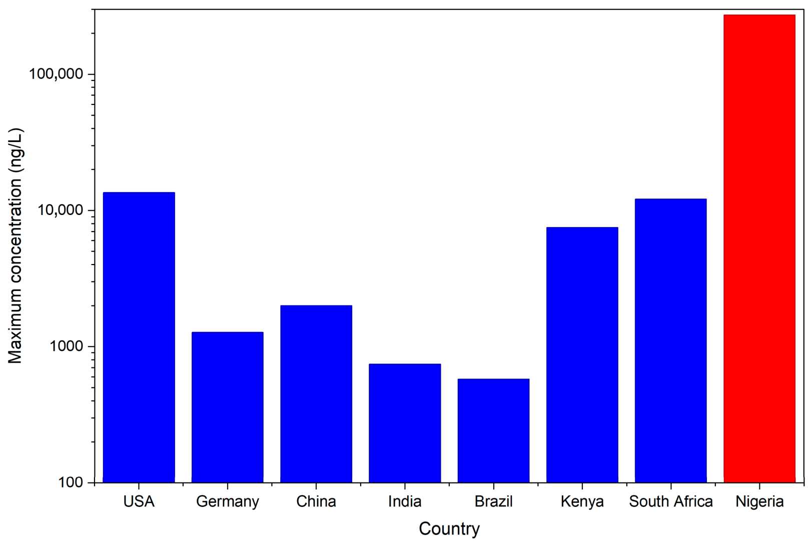

Figure 5. Comparison of pharmaceutical concentrations in wastewater treatment plant (WTP) effluents worldwide.

3.2. Mechanisms of Pharmaceutical Removal

The removal of pharmaceutical contaminants in conventional wastewater treatment systems remains limited and highly variable. In activated sludge processes, biodegradation efficiency is strongly influenced by the chemical structure and physicochemical properties of the compounds. Certain pharmaceuticals, particularly those containing aromatic structures, halogen substituents, or complex side chains, exhibit significant resistance to biodegradation. For example, X-ray contrast media such as iopromide and iopamidol undergo negligible degradation in wastewater treatment plants. Process conditions such as sludge retention time critically determine treatment efficiency, with insufficient retention leading to incomplete degradation of pharmaceutical compounds [43].

Constructed wetlands represent an efficient and sustainable approach for wastewater treatment, offering considerable removal efficiency and a cost-effective solution for a wide range of contaminants, including pharmaceuticals. However, these systems require long hydraulic retention times and large surface areas, which limit their use in densely populated urban areas where pharmaceutical pollution is most prevalent. Chlorination is an essential step in the treatment of drinking water. Nevertheless, many pharmaceuticals containing reactive hydroxy-substituted aromatic groups can react with residual chlorine, leading to degradation and the formation of byproducts. The generation of such chlorination and degradation products poses a major concern, as they are often highly toxic and potentially carcinogenic [43].

Advanced filtration methods, including nano-, micro-, and ultrafiltration, have demonstrated high removal efficiencies (ranging from 90% to 99.9%). Despite their effectiveness, the practical application of these technologies is constrained by membrane fouling, high operational costs, and significant energy demands [43].

The most promising technologies include ozonation, photocatalytic oxidation, adsorption on activated carbon, and bioremediation using specialized microorganisms [43]. Their application, combined with comprehensive environmental monitoring and increased public awareness regarding the proper disposal of pharmaceuticals, can significantly reduce the risks of groundwater contamination [56].

Conventional water treatment plants were not originally designed for the complete removal of pharmaceutical compounds, which explains the limited performance of many existing systems [57]. Among the methods, adsorption offers several advantages, including simple system design and low capital investment [58].

Adsorption is among the most widely applied mechanisms in PRB systems targeting pharmaceutical contaminants. GAC has long served as the reactive medium of choice owing to its porous structure and high specific surface area. The incorporation of magnetic iron oxides onto GAC surfaces—yielding magnetic granular activated carbon (MGAC)—substantially enhances pharmaceutical uptake by increasing the number of accessible active adsorption sites and introducing iron-based surface complexation as an additional removal pathway. In studies targeting azithromycin, MGAC demonstrated maximum adsorption capacities of 192.1 mg/g, with the adsorption process governed by pseudo-second-order kinetics and Freundlich isotherm behavior, indicating multilayer, heterogeneous adsorption on a surface of varying energy. The dominant mechanisms at low pH include pore filling, hydrogen bonding, and surface complexation with Fe^{2+} and Fe^{3+} species, with iron ions capable of forming stable coordination complexes with amino groups present in macrolide antibiotic structures. The MGAC-based PRB achieved up to 99.96% removal efficiency in batch conditions and maintained 67% efficiency under continuous flow. Its integration as a pretreatment step significantly reduced membrane fouling and improved operational performance, increasing permeate flux and extending membrane lifespan [58].

Biochar is considered an environmentally safe and economically viable adsorbent. Its performance is attributed to a well-developed porous structure and the presence of surface functional groups capable of forming hydrogen bonds and π–π interactions with the aromatic rings of pharmaceutical molecules [59]. The adsorption mechanism involves physical sorption, surface complexation, ionic interactions, micropore filling, and hydrophobic bonding [60]. The adsorption efficiency depends on the sorbent's chemical structure, solution pH, temperature, and the presence of competing ions. For example, the adsorption of sulfamethoxazole, tetracycline, and paracetamol onto biochar is enhanced under neutral and slightly alkaline conditions, due to stronger π–π interactions between the aromatic structures of the pollutants and the adsorbent surface [61].

Natural and modified mineral adsorbents, such as montmorillonite and its organically modified forms (MMT-STA), show high removal efficiencies (95–97%) for ibuprofen and carbamazepine, while surface modification further increases sorption capacity [62]. Similarly, the addition of chitosan or magnetic iron oxides to fly ash increases the number of active sites and strengthens interactions with the functional groups of pharmaceutical molecules [63].

The key mechanisms of pharmaceutical adsorption include electrostatic interactions, π–π electron donor–acceptor (EDA) interactions, hydrophobic forces, hydrogen bonding, and pore filling [64]. π–π EDA interactions are particularly important for aromatic compounds, as the aromatic rings of pollutants interact with the π-system of carbonaceous adsorbents, thereby enhancing affinity and sorption efficiency [64]. This method is energy-efficient, provides up to 90% pollutant removal, and operates under mild conditions (ambient temperature of 20–30 °C, near-neutral pH of 5–8, and atmospheric pressure), without requiring UV irradiation, elevated pressure, or chemical oxidant dosing.

Redox-driven degradation constitutes another critical mechanism in PRB systems, particularly in ZVI-based barriers. In the ZVI-MnO_2 PRB configuration developed for tetracycline removal, the coupling of ZVI with manganese dioxide generates a sustained oxidative environment through sequential electron transfer reactions. ZVI corrodes under weakly acidic groundwater conditions to release Fe^{2+}, which is subsequently oxidized to Fe^{3+} by MnO_2—a process that simultaneously generates hydroxyl radicals (-OH). These radicals contribute approximately 58.3% of observed tetracycline degradation, attacking the A-ring of the tetracycline molecule, while MnO_2 itself coordinates preferentially with the BCD ring system. This synergistic coupling overcomes a key limitation of ZVI-only PRBs, in which progressive passivation of the iron surface diminishes long-term reactivity; the presence of MnO_2 regenerates reactive iron species, maintaining removal efficiencies of approximately 85% over 30 days compared to around 65% for ZVI alone. The degradation products identified by LC-ESI-MS confirm that ring opening occurs, yielding low-molecular-weight intermediates that can be further mineralized to CO_2, H_2O, and inorganic ions [65].

Ultrasound-assisted PRB systems using iron shavings have shown promising results. Cavitation effects generate reactive radicals and provide continuous surface cleaning of the reactive media, preventing clogging and maintaining reactivity. Such systems achieved up to 90% tetracycline degradation within 30 min, significantly higher than non-assisted systems, while also producing less toxic by-products [66].

These case studies demonstrate that integrating advanced materials (e.g., MGAC), redox-coupled systems (ZVI–MnO_2), and physical enhancement techniques (ultrasound) can substantially improve PRB performance, ensuring higher removal efficiencies, reduced fouling, and enhanced long-term stability in pharmaceutical-contaminated groundwater treatment.

In engineered systems, the efficiency of redox mechanisms is determined by controlling parameters such as pH, reagent concentrations, catalyst surface state, and contact time. As noted in recent studies, the adsorbent not only concentrates the pollutant but also catalyzes redox transformations, making combined adsorption–Fenton oxidation processes possible [67].

The Fenton method allows the treatment of large volumes of wastewater and effectively degrades organic pollutants. A significant advantage of photocatalysis lies in the use of the semiconductor TiO_2, which is non-toxic, environmentally friendly, cost-effective, and stable. High levels of organic matter degradation can be achieved under solar irradiation and through in situ cathodic production of H_2O_2 [68]. However, the main limitation of most of these technologies remains their high operational cost associated with energy consumption [57].

Despite recent advances in PRB-based systems, a comprehensive evaluation of existing treatment technologies continues to reveal several inherent limitations. A comparative evaluation of the most applied treatment technologies indicates that the removal of pharmaceutical compounds remains a persistent challenge due to their complex molecular structures, high stability, and occurrence at trace concentrations. As a result, the performance of existing treatment approaches is highly variable and strongly dependent on both physicochemical conditions and process design parameters [43,57].

Conventional biological treatment systems are inherently limited in their ability to eliminate recalcitrant pharmaceutical compounds. Their removal efficiency is largely governed by biodegradability and sludge retention time, which makes them insufficient for the reliable attenuation of micropollutants under real environmental conditions [43].

Adsorption-based technologies, particularly those employing carbonaceous materials, have demonstrated robust performance due to their high surface area and affinity toward a wide range of pharmaceutical molecules. However, such systems are constrained by finite sorption capacity, competitive adsorption in multi-contaminant matrices, and the gradual loss of efficiency associated with sorbent saturation and aging effects [57,58].

Advanced treatment processes, including membrane filtration and advanced oxidation processes (AOPs), provide superior removal efficiencies and are often capable of achieving near-complete degradation of target compounds. Nevertheless, their large-scale implementation is limited by high energy demand, membrane fouling, and the formation of transformation products, some of which may exhibit greater toxicity than the parent compounds. These limitations raise important concerns regarding the long-term sustainability and environmental safety of such technologies [43,57].

Nature-based solutions, such as constructed wetlands and biologically driven systems, offer an environmentally sustainable alternative with low operational requirements. However, their performance is often constrained by slow kinetics, sensitivity to environmental fluctuations, and substantial land requirements, which restrict their applicability in densely populated or industrialized regions.

The advantages and limitations of the applied treatment technologies are summarized in Table 4, indicating that each method exhibits certain constraints related to operational conditions, efficiency, and economic considerations [43,57,58].

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Table 4. Advantages and limitations of commonly applied treatment technologies for pharmaceutical removal from water.

Treatment Technology	Main Mechanism	Advantages	Limitations	Reference
Conventional biological treatment (activated sludge)	Biodegradation	Well-established process; effective for removal of bulk organic matter	Limited removal of pharmaceuticals at low concentrations; depends on biodegradability	[43,57]
Adsorption (activated carbon, biochar)	Surface adsorption	Simple operation; relatively low cost; applicable to a wide range of compounds	Sorbent exhaustion; reduced efficiency in the presence of competing substances	[57,58]
Membrane filtration	Physical separation (size exclusion)	High removal efficiency; suitable for various contaminants	Membrane fouling; high operational cost; concentrate handling required	[43,57]
Advanced oxidation processes (AOPs)	Oxidation by reactive radicals	Effective for degradation of persistent compounds	High energy demand; possible formation of intermediate products	[43,57]
Photocatalysis	Light-induced catalytic oxidation	Environmentally friendly catalyst systems; potential use of solar energy	Limited efficiency under real conditions; catalyst recovery issues	[57,58]
Chlorination	Chemical oxidation	Widely applied; easy to implement	Formation of by-products; not effective for complete removal	
Constructed wetlands	Biological and physicochemical processes	Low energy demand; environmentally sustainable	Large area required; slow treatment rates	[43,57]
Bioremediation	Microbial degradation	Natural and low-cost approach	Process instability; strongly dependent on environmental conditions	[56,57]

Combined treatment processes that integrate adsorption, ozonation, and photochemical oxidation exhibit superior performance in the removal of pharmaceutical contaminants from aqueous systems (Table 4). The simultaneous application of ozonation and adsorption ensures almost complete degradation of target compounds, accompanied by a significant reduction in the toxicity of transformation products. Hybrid ozone–adsorption systems based on cross-linked chitosan and bentonite achieve over 80% removal of pharmaceutical compounds such as acetaminophen and amoxicillin (Table 5). Photo-Fenton and biological processes demonstrate efficiencies exceeding 95%, while catalytic ozonation coupled with adsorption on Fe_2O_3/CeO_2-modified activated carbon enables nearly complete elimination of sulfamethoxazole within 50 min. Sequential ultraviolet–ozonation and electrooxidation–ozonation approaches provide comparable removal rates, reaching 89 and 90%, respectively. Among the investigated technologies, the combination of photocatalysis and adsorption is recognized as the most promising strategy, enabling comprehensive degradation of pharmaceutical pollutants and effective removal of their transformation byproducts [57].

Table 5. Removal of different drugs by combined processes.

Treatment Approach	Drugs	Combining Process	Reaction Time (min)	Significant Findings	Reference
UV + Ozone + Adsorption	Multiple pharmaceuticals	UV irradiation + Ozone	40 min	High (>80%) for most compounds	[69]
Ozonation + Adsorption	Acetaminophen, Amoxicillin	Ozone gas/Chitosan–Bentonite	25 min	High	[70]
Photocatalysis + Adsorption	Ciprofloxacin	Graphitized carbon/TiO_2	10–20 min	High (>80%)	[71]
Ozonation + Adsorption	Sulfamethoxazole	Activated carbon (PAC + Fe_2O_3/CeO_2)	30 min	High (>80%), optimized at pH 3.5	[72]
Photolysis + Adsorption	Multiple pharmaceuticals	Sludge	2 weeks	Moderate (20–33%)	[73]
UV/H_2O_2	Aromatic solvents	UV/H_2O_2 with aeration	4 months	High (72–99%)	[74]
Electrooxidation + Ozonation	Ciprofloxacin	Ti/PbO_2	90 min	High (~90%)	[75]

4. Removal of Heavy Metals in PRBs

Groundwater is one of the main sources of drinking water for humans. Nevertheless, with the rapid growth of urbanization and industrial activities, contamination of groundwater with toxic metals and metalloids such as chromium (Cr), arsenic (As), copper (Cu), and cobalt (Co) has become a critical environmental issue [76]. These pollutants originate mainly from mining, smelting, and the use of fertilizers, as well as from uncontrolled landfills where leachate generated by water percolation through waste carries heavy metals into surrounding soils and aquifers [77].

The most common contaminants include lead (Pb), copper (Cu), zinc (Zn), cadmium (Cd), iron (Fe), manganese (Mn), arsenic (As), and chromium (Cr). Due to their persistence, mobility, and bioavailability, heavy metals easily migrate through environmental media and accumulate in living organisms. Being non-biodegradable, they cause both acute and chronic toxicity: acute exposure can damage the nervous, cardiovascular, respiratory, and digestive systems, while chronic exposure increases the risk of degenerative diseases and cancer. Furthermore, long-term accumulation of heavy metals in soils inhibits enzymes responsible for the mineralization of organic compounds, reducing soil fertility and harming plants and microorganisms [77].

Through the food chain, toxic metals become even more concentrated, posing serious risks to human and animal health. Given their cumulative nature and persistence, heavy metal pollution represents a continuous environmental threat. Therefore, effective prevention and remediation measures are essential to trap and remove heavy metals from groundwater, especially near landfill sites, before they spread further, ensuring water quality meets acceptable environmental and health standards [77].

4.1. Common Heavy Metals

Heavy metals are generally classified with a density greater than 5 g cm^{-3}, an atomic number exceeding 20, or an atomic density higher than 4000 kg m^{-3} (approximately five times that of water). Such characteristics confer stability and persistence, which explain their long-term environmental accumulation [29]. The key properties, sources, and environmental and health impacts of selected heavy metals are summarized in Table 6.

Table 6. Characteristics of Selected Heavy Metals and Their Environmental and Health Impacts.

Heavy Metals	Oxidation States/Species	Toxicity	Mobility & Solubility	Main Sources	Environmental/Health Effects
Chromium (Cr)	Cr(VI): CrO_4^{2-}, $HCrO_4^-$, $Cr_2O_7^{2-}$; Cr(III): Cr^{3+}, $Cr(OH)_2^+$, $Cr_3(OH)_4^{5+}$	Cr(VI)–highly toxic, mutagenic, carcinogenic; Cr(III)–essential micronutrient in trace amounts	Cr(VI)–strong mobility in soil & groundwater; Cr(III)–lower solubility and mobility	Electroplating, leather tanning, pigment production, metal processing	Accumulates in environmental media, long-term ecological and toxicological impacts
Lead (Pb)	Pb(II) (divalent cation)	Highly toxic, no biological role	Forms complexes with hydroxide, carbonates, sulfates, and organics; mobility increases under acidic conditions	Mining, smelting, metal finishing, battery manufacturing and recycling, pigment and paint production, petroleum combustion, landfill and industrial waste leachate	Interferes with cardiovascular and nervous systems, impairs hematopoiesis, disrupts calcium metabolism; neurological damage in children; chronic exposure in adults causes hypertension, renal dysfunction, reproductive toxicity, neurodegenerative disorders
Cadmium (Cd)	Cd(II) (divalent cation)	Highly toxic, non-essential	High solubility and mobility, especially under acidic and reducing conditions; forms complexes with chloride, carbonate, sulfate, humic and fulvic acids	Industrial effluents, mining, smelting, electroplating, pigment and plastic manufacturing, landfill leachate	Toxic to living organisms, bioaccumulates in food chain, persists in environment for decades
Arsenic (As)	As(V)–arsenate (AsO_4^{3-}), As(III)-arsenite (AsO_3^{3-})	Highly toxic, carcinogenic	Highly mobile in groundwater; anionic species easily leach into aquifers	Mining, smelting, fertilizer and pesticide use, semiconductor manufacturing, illegal waste disposal	Skin lesions, urinary and respiratory disorders, bioaccumulation, long-term ecological contamination
Copper (Cu)	Cu(II): Cu^{2+}; Cu(I): Cu^+ (less stable in aqueous systems)	Essential micronutrient at trace levels; toxic at elevated concentrations; WHO guideline value: 2 mg/L	Moderately mobile; forms stable complexes with carbonates, hydroxides, and organic matter; mobility increases under acidic pH	Mining and smelting, electroplating, industrial effluents, corrosion of copper pipes, agricultural fungicides	Liver and kidney damage at high doses; depression and lung cancer with chronic overexposure; toxic to aquatic organisms at low concentrations; inhibits microbial activity in s
Barium (Ba)	Ba(II): Ba^{2+}	Soluble Ba compounds are toxic; WHO guideline value: 0.7 mg/L; $BaSO_4$ is insoluble and inert	Moderate mobility; $BaSO_4$ highly insoluble; $BaCl_2$ and $Ba(NO_3)_2$ soluble and mobile in groundwater	Oil and gas drilling (barite use), mining, coal combustion residues, natural geological leaching from sedimentary rocks	Cardiovascular effects (hypertension, cardiacarrhythmia); muscle weakness; kidney damage; gastrointestinal disturbances with acute exposure
Zinc (Zn)	Zn(II): Zn^{2+}	Essential micronutrient; toxic at high concentrations; WHO guideline value: 3 mg/L (aesthetic)	High solubility under acidic conditions; moderately mobile; forms hydroxide, carbonate, and sulfate complexes; mobility decreases at neutral–alkaline pH	Mining and smelting, galvanizing, electroplating, industrial effluents, landfill leachate, fertilizer application	Infertility, kidney and CNS disorders at elevated doses; toxic to aquatic organisms; inhibits soil microbial communities; bioaccumulates in invertebrates
Molybdenum (Mo)	Mo (VI): MoO_4^{2-} (molybdate, dominant in oxic groundwater); Mo (IV) under reducing conditions	Essential trace element; toxic at elevated concentrations; WHO guideline value: 0.07 mg/L	Highly mobile as molybdate (MoO_4^{2-}) under neutral to alkaline, oxic conditions; less mobile under acidic or reducing conditions	Mining and ore processing, fertilizer and pesticide use, steel alloy production, coal combustion, natural geological weathering of molybdenite (MoS_2)	Gout-like symptoms, reproductive toxicity, and liver damage at high doses; interferes with copper metabolism; phytotoxic at elevated soil concentrations; emerging contaminant of concern in drinking water

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4.2. Mechanisms of Heavy Metal Removal

In PRBs, contaminants, particularly heavy metals that are difficult to biodegrade, are predominantly removed through processes that transform them into non-toxic or immobilized forms. The primary mechanisms responsible for contaminant retention include sorption, precipitation, redox reactions, and biological transformations.

Sorption and adsorption are among the most important mechanisms within PRBs, as they immobilize dissolved contaminants by transferring them from the aqueous phase to solid reactive materials. This process encompasses adsorption, absorption, ion exchange, and surface precipitation reactions. Abiotic adsorption can occur via three main pathways: hydrophobic expulsion, electrostatic attraction, and surface coordination reactions. Electrostatic attraction generally leads to indirect and non-specific adsorption, often involving a coordinated layer of water molecules (outer-sphere adsorption or ion exchange). In contrast, surface coordination reactions result in specific adsorption through direct contact with solid surfaces, forming mono- or binuclear surface complexes with deprotonated hydroxyl groups. Materials rich in Fe, Al, and Si oxides, or containing abundant hydroxyl or functional groups, facilitate such sorption processes. For example, natural fibrous materials such as cabuya, with a polymeric matrix of lignin and cellulose, exhibit significant ion-exchange capacity. The adsorption behavior of many PRB materials often follows the Langmuir isotherm model, suggesting monolayer chemisorption as the dominant mechanism [78–80].

Precipitation and co-precipitation also play a central role in the immobilization of heavy metal cations, particularly under neutral to slightly basic conditions. Metal hydroxides are formed as the solubility of metal ions decreases with increasing pH. For instance, in permeable concrete barriers, metal hydroxide precipitation is the principal removal mechanism. Similarly, caustic calcined magnesia (CCM) enhances removal by hydrating to magnesium hydroxide, which buffers the system pH within the range of 8.0–10.5—conditions under which the solubility of most metal hydroxides is minimal. Hydroxyapatite (HAP) may facilitate removal through dissolution–precipitation reactions, especially under acidic conditions ($pH < 4$), while amorphous aluminum species in dewatered alum sludge (DAS) contribute effectively to chemical precipitation processes [81].

Redox reactions represent another major pathway for contaminant transformation, converting toxic and mobile species into more stable and less harmful forms. ZVI is particularly effective due to its high reductive reactivity, removing contaminants via combined redox, adsorption, and precipitation mechanisms. ZVI is well known for its ability to reduce hexavalent chromium [Cr(VI)] to the much less toxic trivalent form [Cr(III)], while copper ions (Cu^{2+}) are removed through cementation, involving reduction and subsequent deposition of metallic copper (Cu^0) onto the iron surface. Similarly, iron-bearing minerals such as pyrite (FeS_2) support redox-based degradation of contaminants like Cr(VI) [29,80,81].

In addition to physicochemical processes, biological mechanisms also contribute to contaminant removal within PRBs. Sulfate-reducing bacteria (SRB) play a crucial role by reducing sulfate to sulfide, which subsequently reacts with dissolved metal ions to form insoluble metal sulfides. This biogenic precipitation effectively immobilizes metals such as Fe, Zn, and Cd, while microbial uptake can further contribute to overall contaminant attenuation [33–37].

When PRBs are coupled with electrokinetic (EK) technology, remediation efficiency can be significantly enhanced, particularly in low-permeability soils where hydraulic flow is limited. The application of an electric field actively transports contaminants toward the reactive zone of the PRB, allowing continuous contact with reactive media. The primary electrokinetic transport mechanisms include electroosmosis, electromigration, electrophoresis, and electrolysis. Electroosmosis refers to the movement of pore water and dissolved ions through the soil under the influence of an electric field, typically from the anode toward the cathode. Electromigration drives ionic species according to their charge polarity, with cations migrating toward the cathode and anions toward the anode, while electrophoresis governs the motion of charged colloidal particles. Electrolysis reactions occurring at the electrodes split water into hydrogen and oxygen, generating acidic conditions near the anode and basic conditions near the cathode [78,79,82].

Once contaminants are driven into the reactive zone of the PRB by electrokinetic forces, their removal proceeds via standard PRB mechanisms—such as adsorption, ion exchange, and redox transformation—adapted to the electrochemical environment. In particular, Fe (0)-based reactive media use reductive pathways to immobilize or detoxify metal ions transported by the electric field. The synergistic combination of EK transport and PRB reactivity significantly enhances contaminant removal rates, making EK-PRB systems a promising hybrid approach for in situ remediation of metal-contaminated groundwater and low-permeability soils [78].

4.3. Field Performance and Long-Term Stability

PRBs have evolved from an experimental remediation concept into a mature and widely applied technology, with over two hundred successful field-scale installations worldwide. Field investigations play a crucial role in assessing PRB performance under realistic hydrogeological conditions; however, such studies are often time-consuming, costly, and complicated by the heterogeneous nature of groundwater flow and geochemical variability.

A recent large-scale field trial of a permeable reactive barrier filled with zero-valent iron (ZVI) grit demonstrated its applicability for the remediation of metal-contaminated groundwater, including systems with high mineralization [83]. The results confirm that PRB systems can operate effectively even under chemically complex groundwater conditions, rather than only under controlled laboratory settings.

Field performance is controlled by a combination of physicochemical and biological processes, including degradation, adsorption, precipitation, and redox reactions. Long-term behaviour depends not only on the reactive medium itself, but also on microbial-mineral interactions and barrier structure, particularly grain-size distribution and permeability.

One of the main challenges observed in field applications is clogging and gradual degradation of the reactive medium, which reduces permeability, limits biological activity, and leads to a decline in removal efficiency over time [84]. For this reason, PRB performance should be assessed not only in terms of contaminant removal, but also with regard to hydraulic stability and long-term operation.

PRBs are generally considered a low-energy and cost-effective remediation option, especially for sites with relatively simple hydrogeological conditions. However, their application in urban environments may be limited by subsurface infrastructure and spatial constraints [85]. These systems rely on natural groundwater flow driven by hydraulic gradients, which makes them energy-efficient but also dependent on site-specific conditions.

The performance of reactive media used in PRBs is highly dependent on the type of material, the characteristics of the contaminants, and the surrounding environmental conditions such as groundwater flow rate, ionic strength, and contaminant concentration. Key performance indicators include removal efficiency, maximum ad-

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sorption capacity (q_{max}), and long-term stability, which is reflected in adsorption and saturation times.

One example of reactive materials includes natural vegetable fibers, such as cabuya (Furcraea Andina) and treated phragmites biomass (TPB). These materials offer low-cost and sustainable alternatives to synthetic sorbents. In batch tests, cabuya fibers demonstrated exceptional adsorption capacities for Cu, Zn, Cd, and Pb, often comparable to or even exceeding ZVI. Lead removal reached 100% within 22 h, while copper, cadmium, and zinc removals achieved 99.24, 96.60 and 90.09%, respectively. Although slightly less reactive than ZVI for zinc, cabuya fiber outperformed ZVI for other metals under similar conditions. Dynamic column experiments further confirmed the high removal efficiency of cabuya fiber, with near-complete removal of Cu, Zn, and Cd observed in 30–60 cm column setups. Nevertheless, the longevity of cabuya fiber was relatively limited; for instance, its maximum absorption time for Cu (II) was approximately 189 h and its saturation time for Cd (II) around 515 h, considerably lower than that of zeolitic materials. RETRASO simulations projected a saturation time of only 63 days for Cu in a 1 m PRB, compared to approximately 900 days for zeolite-based barriers, highlighting its lower long-term reactivity. Treated phragmites biomass also exhibited strong potential for the removal of Pb^{2+} and Cd^{2+} ions, despite its low surface area (0.5 m^2/g) and nonporous morphology. Its adsorption behavior fit the Langmuir model well, with maximum sorption capacities of 6.40 mg/g for Cd^{2+} and 5.46 mg/g for Pb^{2+}. Adsorption kinetics followed the pseudo-second-order model ($R^2 > 0.97$), confirming chemisorption as the dominant process [82].

In contrast, zeolites, including clinoptilolite, mordenite, and sodium mordenite, have shown excellent structural stability, high ion-exchange capacity, and remarkable long-term performance. Batch studies revealed high removal capacities for Zn, Cu, and Cd, with q_e values ranging from 13.2–13.3 mg/g for Zn, 6.7–6.9 mg/g for Cu, and approximately 5.3 mg/g for Cd, reaching 95% removal within 10 h. Dynamic column tests further established that mordenite was the most promising zeolite for PRB applications, exhibiting the highest adsorption (≈833 h for Cd) and saturation times (≈1826 h for Cu). Simulation data supported these results, indicating saturation times exceeding 1800 h for Zn, Cu, and Cd, significantly outperforming both cabuya fiber and clinoptilolite [77].

One notable field application was carried out at the Ukrainian Uranium Center near the city of Zhovty Vody, where groundwater had been heavily contaminated by uranium tailings storage facilities (TSF). Concentrations of uranium (U_{sum}), sulfate (SO_4^{2-}), and total dissolved solids (TDS) exceeded international safety limits by several orders of magnitude. To address this, researchers implemented a pilot PRB using an innovative modular design composed of cylindrical cartridges filled with different reactive materials, which allowed for comparative assessment while minimizing installation costs. The fillings included an inorganic mixture of powdered ZVI and sand, an organic–inorganic mixture containing ZVI, gravel, bone meal, sawdust, and a biochemical activator, and a purely organic mixture of gravel, bone meal, sawdust, and activator [86].

Over two years of continuous monitoring, groundwater quality improved significantly, as uranium concentrations decreased from 0.38 mg L^{-1} to 0.07–0.15 mg L^{-1}, representing more than a 50% reduction in total uranium content. The highest remediation efficiency was achieved using the inorganic (ZVI + sand) and organic–inorganic mixtures, which provided both sorptive and reductive removal mechanisms. The purely organic mixture, by contrast, exhibited limited performance due to the sandy–clayey composition of the soil and low microbial activity. Flow observations also revealed non-uniform contaminant transport across the PRB cross-section, suggesting the development of preferential flow paths that could influence long-term hydraulic performance [86].

Among inorganic reactive agents, ZVI remains one of the most effective and widely used materials for the removal of heavy metals and radionuclides, including uranium (U(VI)). Its performance strongly depends on particle size and water chemistry: fine-grained ZVI exhibits superior reactivity compared to coarser iron particles. In column studies, ZVI mixed with sand maintained nearly complete U(VI) removal for over 90 days. However, ZVI efficiency decreases in the presence of strong complexing ligands such as carbonate and EDTA, which form stable, negatively charged uranium complexes with low sorption affinity. In contrast, weaker ligands like fulvic acid enhance uranium uptake through surface complexation [86].

Despite its high reactivity, ZVI systems face operational challenges such as pore clogging and mineral precipitation, which reduce permeability and create preferential flow zones that compromise hydraulic control over time. Nevertheless, field and laboratory data consistently demonstrate that ZVI, especially when combined with inorganic or mixed organic–inorganic fillers, provides superior long-term stability and removal efficiency compared to purely organic media [86].

Caustic calcined magnesia (CCM), primarily composed of MgO, offers another highly reactive medium, especially effective in removing metal cations through precipitation mechanisms. It can achieve nearly complete removal of Cu^{2+}, Zn^{2+}, Ni^{2+}, and Mn^{2+}, with the effectiveness following the order Cu > Zn > Ni > Mn, correlating with the solubility products of their hydroxides. Optimal CCM reactivity is obtained by calcination at temperatures above 800 °C, with the most effective sample prepared at 750 °C for 3 h, characterized by a carbonate decomposition fraction (X_t) of 79% and the highest specific surface area. However, excessive calcination (up to 1000 °C) leads to high lime content and extreme alkalinity (pH 12–12.5), which can dissolve metal hydroxides and cause environmental harm. Over-calcination beyond 1000 °C also decreases efficiency by promoting the formation of less reactive phases like dicalcium ferrite [81,82,86].

Layered double hydroxides (LDHs) represent a distinct class of reactive materials effective for anionic pollutants such as arsenic (As). In particular, Fe/Mn/C–LDH composites have demonstrated excellent removal efficiency in PRB-electrokinetic remediation (EKR) systems for As-contaminated soils. When placed in the middle section of an EKR soil setup, Fe/Mn/C–LDH achieved maximum and average leaching toxicity removal rates of 95.71 and 88.03%, respectively. This high removal efficiency was attributed to the pH range of 5–8, favorable for arsenic adsorption, considering the zero-point potential of the composite (pH_pzc = 4.38). Under slightly acidic conditions (pH < 4.38), the adsorption of anionic arsenate and arsenite species is further enhanced [87].

Recently, carbon-based materials such as carbonized food waste (CFW) and activated carbon (AC) have gained attention for their eco-friendly properties and strong adsorption potential. In EKR-assisted PRBs, CFW exhibited removal efficiency in removing copper (Cu) and moderate effectiveness for lead (Pb). For Cu-contaminated soils, removal rates reached 85–92% in single-contaminant systems and 75–89% in mixed Cu–Pb systems. Lead removal was lower, ranging from 0.6 to 33% for single contamination and 14–25% in combined systems, indicating the need for longer remediation periods. The optimal Cu removal was achieved after 10 days of EKR with an 8-day electrode exchange cycle. Activated carbon, when combined with enhanced EKR using oxalic acid (ENEKR + PRB), indicated excellent multi-metal removal from municipal solid waste incineration fly ash, achieving maximum removal rates of Zn (78.34%), Pb (69.34%), Cu (84.14%), and Cd (49.23%). The ENEKR

+ PRB configuration consistently produced the lowest leaching values among all tested systems [88].

The performance of reactive media in PRBs and EK-PRB systems varies widely depending on material composition and operating conditions. Synthetic composites like Fe/Mn-LDH offer high selectivity and electrochemical compatibility for coupled EKR systems, while natural zeolites such as mordenite provide superior longevity and stability. Biomass-based materials like cabuya and phragmites offer sustainable, low-cost alternatives with promising short-term efficiency, whereas traditional materials like ZVI and CCM continue to play key roles in heavy metal and radionuclide immobilization. The integration of these materials into hybrid PRB–EKR systems provides a flexible, multi-mechanistic approach to addressing diverse contamination scenarios in complex soil and groundwater environments.

To systematically evaluate the practical utility of various reactive media, it is essential to compare their kinetic behaviors, maximum adsorption capacities (q_{max}), and field lifespans under comparable conditions. Table 7 summarizes the performance metrics of ZVI, zeolites, and biochar-based composites targeting primary contaminants such as hexavalent chromium (Cr(VI)) and the antibiotic sulfamethoxazole (SMX). While ZVI demonstrates exceptional long-term stability in field-scale applications, its efficiency is heavily dependent on the targeted pH and initial contaminant concentration. Conversely, zeolites and engineered biochars exhibit highly competitive adsorption capacities and rapid kinetic rates, though their operational lifespans before saturation often require more frequent material regeneration or replacement.

Table 7. Comparative performance of reactive media for specific contaminants in PRB applications.

Reactive Medium	Target Contaminant	Operating Conditions	Mechanisms/Model	Max Capacity (q_{max})	Operational Lifespan
ZVI (Micro/Nanoscale) [89]	Cr(VI)	pH 5, C_0 = 50 mg/L	Pseudo-second-order	44.65 mg/g	limited by oxide passivation
Zeolites (Modified) [77,90]	Heavy Metals (Cd, Cu, Zn)/ Sulfamethoxazole (SMX)	pH 6–8, C_0 = 10–100 mg/L	Pseudo-first-order/Pseudo-second-order	5.3–13.2 mg/g (Metals); up to 13.0 mg/g (SMX)	>1800 h (column saturation); up to 5+ years depending on barrier thickness
Biochar (Pyrolytic/Composite) [91,92]	Cr(VI)/ Sulfamethoxazole (SMX)	pH 3–7, C_0 = 15–50 mg/L	Pseudo-second-order kinetics dominant	up to 134 mg/g (Cr(VI)) 21.5 mg/g (SMX);	generally requires periodic replacement or regeneration
Cabuya fiber Furcraea Andina—natural vegetable fiber [82]	Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}	Batch & column tests; 30–60 cm columns; ambient pH and temperature	Pseudo-second-order	6.40 mg/g for Cd^{2+} and 5.46 mg/g for Pb^{2+}.	Limited longevity: Cu saturation ~189 h; Cd saturation ~515 h; RETRASO-projected 63 days for Cu in 1 m PRB
CCM Caustic Calcined Magnesia (MgO-based) [81]	Cu^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}	Optimal calcination at 750–800 °C; pH 8–12; caution above 1000 °C (extreme alkalinity)	precipitation mechanism	precipitation mechanism	Over-calcination (>1000 °C) reduces reactivity; pH 12–12.5 may dissolve hydroxides and cause secondary pollution

5. Factors Affecting PRB Performance

The efficiency of permeable reactive barriers (PRBs) is determined by a combination of hydrochemical and hydrodynamic parameters of groundwater, among which pH, redox potential (Eh), and hydraulic conductivity play a key role. Under neutral to mildly alkaline conditions (pH 7–8), reduction reactions of heavy metal ions and nitrates involving zero-valent iron (Fe^0) proceed most effectively. When the pH increases to 10–11, iron corrosion leads to the formation of $Fe(OH)_2$ and $Fe(OH)_3$ hydroxides, causing partial pore clogging and reducing the permeability of the reactive layer. Field observations have shown that an increase in pH to 10.5 is associated with the formation of corrosion products, which results in an elevated hydraulic gradient and deterioration of the filtration properties of the barrier, necessitating adjustments to the composition of the reactive medium and the system configuration.

Redox conditions exert a decisive influence on the reductive properties of Fe^0 and its ability to transform contaminants into less toxic compounds. An increase in Eh shifts the system toward oxidative conditions, altering the corrosion kinetics and promoting the formation of passivating phases such as γ-FeOOH, Fe_3O_4, and $Fe(OH)_3$. These compounds gradually coat the iron surface, reducing the active metal area and pore space, thereby decreasing reductive activity and disrupting uniform flow through the barrier. The dynamics of Eh in the reactive zone are determined by the composition of groundwater, including concentrations of dissolved oxygen, nitrates, sulfates, and bicarbonates, as well as the activity of microbial communities. The presence of oxidizing agents increases Eh and accelerates the formation of passivating layers, whereas microbial denitrification and sulfate reduction processes maintain reducing conditions favorable for the electrochemical reduction in contaminants. To ensure a stable low Eh, the use of buffering and organic amendments is recommended to maintain the reducing potential [93,94].

The kinetics of redox processes in ZVI systems directly depend on the local potential. At low Eh values, reduction reactions proceed rapidly and are controlled by surface kinetics, providing effective degradation of both organic and inorganic contaminants. As Eh shifts toward positive values, the activity of iron decreases, and the mechanisms of contaminant removal transition from reductive processes to sorption–adsorption processes, wherein contaminants are bound to corrosion products, which significantly affects the service life of the barrier [94].

The hydraulic conductivity of a PRB is determined by the structure and composition of the reactive layer, as well as the nature of its interaction with water. To prevent pore clogging and maintain permeability, Fe^0 is combined with inert or porous additives such as sand, zeolite, pumice, biochar, and activated carbon. Such combinations ensure optimal flow distribution, increase porosity, and prevent the formation of stagnant zones. The addition of zeolite stabilizes hydraulic conductivity and enhances the sorption capacity of the layer, improving the removal of ammonium ions and heavy metals [20,95]. Mixtures of Fe^0 with pumice demonstrate long-term effectiveness due to the preservation of stable porosity and reduced precipitation of iron hydroxides, preventing the formation of impermeable zones within the reactive area [96].

Mitigation of Passivation Through Surface Modification

While ZVI remains a cornerstone material for PRB applications, its long-term hydraulic and reactive performance is frequently compromised by passivation. Passivation occurs when an accumulation of iron (hydr)oxides (e.g., γ-FeOOH, Fe_3O_4, $Fe(OH)_3$) and secondary mineral precipitates forms a dense shell on the ZVI surface. This layer physically blocks reactive sites, restricts electron transfer, and causes pore clogging that reduces the barrier's overall permeability. To mitigate these issues, recent advancements have focused on surface-modification strategies, most notably sulfidation and the development of bimetallic systems.

Sulfidation of ZVI (S-ZVI) and Pyrite Composites: Incorporating lower-valent sulfur species into the ZVI structure to form a mixed FeO-FeS core–shell configuration has emerged as a viable mitigation strategy. Unlike the dense, impermeable oxide layers that naturally form on bare ZVI, the biogenic or chemically synthesized FeS layer is porous, conductive, and hydrophobic. This modification serves a dual purpose: it facilitates rapid electron transfer to target contaminants and simultaneously suppresses parasitic reactions with water, thereby minimizing hydrogen evolution. Furthermore, leveraging sulfur through the development of pyrite/biochar composites (such as BM-FeS_2@BC) via ball milling enhances reactivity. Such engineered composites achieve high aqueous Cr(VI) removal capacities) by combining the electron-donating properties of the sulfurized iron species with the porous scaffold of biochar, thereby resisting standard passivation [92,97].

Bimetallic Systems (e.g., Fe/Ni, Fe/Pd): Another anti-passivation approach involves doping the iron surface with a secondary, less reactive transition metal such as nickel (Ni) or palladium (Pd) to create bimetallic composites. The addition of the secondary metal establishes localized galvanic cells on the particle surface. In these systems, iron acts as the sacrificial anode, while the secondary metal acts as a catalytic cathode. This configuration accelerates electron transfer and promotes the catalytic cleavage of stable chemical bonds. The continuous galvanic action disrupts the accumulation of uniform, passivating oxide layers, extending the reactive longevity of the PRB and maintaining consistent treatment efficiency over time [98].

6. Future Perspectives and Challenges

Contemporary research focuses on improving durability, enhancing hydraulic characteristics, and developing new engineering solutions for flow management within the barrier zone. One of the most effective approaches is the passive convergent permeable reactive barrier (PC-PRB), whose design ensures directed groundwater flow toward the reactive zone, increasing the contact area and reducing stagnant zones. The design of a PC-PRB depends on multiple factors; therefore, local sensitivity analysis is commonly employed to simplify the procedure by evaluating the influence of input parameters on hydraulic indicators the width and hydraulic residence time [99].

Modeling has shown that, while maintaining contaminant removal efficiency, the length and height of the barrier can be reduced by 33.3 and 72.7%, respectively [99,100]. The advancement of PRB design is supported by analytical and numerical methods that allow simulation of flow fields and determination of the optimal capture zone. In particular, analysis of funnel-and-gate configurations enables the calculation of capture width, assessment of the influence of gradient and geometry on flow patterns, and adaptation of designs to hydrogeological conditions [101]. The optimization of hydraulic structure aims to maximize capture width and residence time while minimizing material costs. Classical configurations, such as CPRBs and funnel-and-gate systems, exhibit a limited zone of influence and sensitivity to aquifer heterogeneity, which may result in bypassing flow paths and reduced remediation efficiency [102].

To enhance performance, hybrid architectures are employed that combine PC geometry with modular reactive elements, local “gates,” pockets of highly active media, or biofiltration zones. These schemes allow the concentration of reactive material in areas of maximum contaminant inflow while maintaining permeability and reducing costs. Modeling indicates that reducing the volume of active reagent can significantly lower capital expenditures while achieving comparable treatment efficiency [103].

For predicting PRB performance, numerical models are applied that account for the transport of multicomponent contaminants, chemical transformations, and two-phase interactions. The use of machine learning methods, as presented in Table 8, enables optimization of reactive material selection and reduction in experimental costs [104,105].

Table 8. The results obtained using mathematical models to predict the hydraulic behavior of PRBs.

Reactive Medium	Permeating Solution	Model	Factors	Observations	References
ZVI	Natural groundwater	MODFLOW and RT3D (PS)	Mineral precipitates	Porosity and hydraulic conductivity decreased initially; minimal changes occurred over 10 years, with significant changes expected after ~30 years due to major ion advection.	[106]
ZVI	Chlorinated solvents	MIN3P (CTM)	Mineral precipitates	Reductions in porosity at the entrance of the reactive medium were due to accumulation of carbonates, especially for highly corroded ZVI	[107]
ZVI, ZVI/sand, or pumice	Heavy metals	Kozeny–Carman Equation (CTM)	ZVI expansion	Assuming uniform corrosion, permeability decreased at the beginning of filtration due to pores being filled with expansive iron corrosion products	[108]
ZVI	Heavy metals	Numerical-probabilistic model (CTM)	Contaminant precipitation, ZVI expansion, and gas	Volumetric expansion of iron and mineral precipitation changed pore geometry, potentially trapping gas bubbles; higher iron corrosion rates were used to fit experimental data assuming absence of gas	[109]

Modern THMC (Thermo-Hydro-Mechanical-Chemical) models allow consideration of mineral phase precipitation, interactions of iron with bicarbonates, and the formation of secondary minerals, enabling prediction of the reactive zone's longevity under various hydrogeological conditions. Sensitivity analysis confirms that key parameters include hydraulic gradient, flow velocity, porosity, and barrier geometry [110,111]. In turn, the application of ANN provides high accuracy in predicting permeability loss and barrier service life, thereby accelerating design and reducing the cost of field testing [112].

Despite the progress achieved, PRB technology faces several challenges, including soil heterogeneity, the formation of bypass flow paths, silting, and chemical passivation of reactive material surfaces. During long-term operation, permeability decreases due to the formation of hydroxides and secondary minerals, reducing the barrier's service life [106,110]. To overcome these limitations, multifunctional systems are being developed, incorporating reactive, sorptive, and biological zones, as well as methods for material regeneration and corrosion control [27]. Promising directions include the development of hybrid systems combining physicochemical and biological processes, as well as the implementation of digital twins for predicting degradation and optimizing operation. Integration with electrochemical and microbial technologies opens opportunities for the creation of self-regenerating barriers, enhancing stability and performance [19].

Integration of PRBs with other water treatment technologies represents a promising approach aimed at expanding barrier functionality and improving efficiency in cases of complex groundwater contamination. Depending on hydrogeological conditions and contaminant composition, combined schemes include coupling PRBs with biological systems, electrochemical and electrokinetic methods, as well as advanced oxidation processes (AOPs). Each of these combinations enables additional mechanisms of sorption, oxidation, reduction, or biotransformation of contaminants, achieving more complete and sustainable remediation effects.

Combining PRBs with constructed wetlands allows sequential implementation of physicochemical and biological processes. In the first stage, the reactive barrier intercepts the contaminated water flow and initiates reductive reactions (e.g., nitrate reduction or heavy metal precipitation), after which the constructed wetland system completes polishing through biodegradation of organic compounds and uptake of residual ions by vegetation. Experimental data confirm that hybrid systems of the "PRB $\rightarrow$ wetland" type can significantly reduce concentrations of heavy metals and organic compounds while decreasing the load on subsequent treatment stages [19].

Biologically active barriers (bio-PRBs, bio-augmented PRBs) aim to exploit microbial communities to enhance remediation processes within the reactive zone. The presence of labile organic substrates promotes the development of anaerobic reducing conditions, stimulating denitrification, sulfate reduction, and organic matter degradation. Microorganisms can also participate in the transformation and remobilization of certain metals, requiring careful consideration of biogeochemical factors when designing such systems [113].

Integration of PRBs with advanced oxidation processes (AOPs), particularly systems for peroxymonosulfate (PMS) activation based on zero-valent iron (Fe^0), enables efficient removal of persistent organic contaminants. Configurations such as "Fe^0/PMS-PRB" combine reductive and oxidative mechanisms, effectively degrading refractory organic compounds in landfill leachates and industrial wastewater [114].

Electrochemical approaches implemented as permeable electrochemical reactive barriers (PERBs) provide the capability for controlled in situ modification of redox conditions without continuous chemical dosing, as shown in Figure 6. These systems enable localized cathodic and anodic polarization, stimulating the degradation of organic pollutants and the precipitation of metal ions. Electrode materials such as TiO_2/graphite composites and other electrocatalytic carriers ensure the sustained and comprehensive degradation to passivation [115].

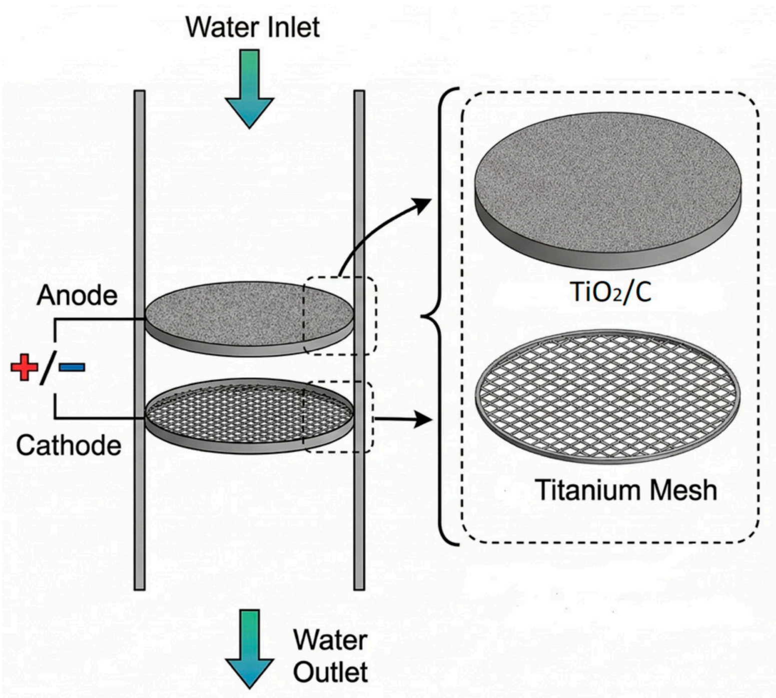

Figure 6. A schematic diagram of permeable electrochemical reactive barrier setup.

The combination of PRBs with electrokinetic methods allows contaminants to be concentrated in the reactive zone through directed ion migration under an electric field.

This approach is particularly effective for low-permeability clayey soils, where traditional passive barriers demonstrate limited effectiveness [88].

Promising hybrid schemes include "PRB-membrane or bioreactor module" configurations, where the barrier functions as a preliminary flow stabilizer, and subsequent stages provide fine purification to meet discharge standards or water reuse requirements. Similarly, the combination of PRBs with constructed wetlands and reactive filters forms energy-efficient solutions suitable for decentralized water treatment systems and rural areas [116].

7. Conclusions

The pervasive nature of global water pollution, exacerbated by rapid industrialization and agricultural intensification, continues to introduce complex mixtures of persistent emerging contaminants, particularly pharmaceutically active compounds (PhACs) and toxic heavy metals, into aquatic environments. Conventional treatment technologies often face significant limitations, including high operational costs, excessive sludge generation, and poor removal efficiency against these recalcitrant pollutants—for instance, biological treatment stages in WTP frequently leave sulfameth-oxazole, trimethoprim, diclofenac, and paracetamol at concentrations exceeding 100 ng/L in treated effluents. These shortcomings underscore the urgent need for sustainable, low-energy, and innovative purification strategies. Within this context, PRBs have emerged as one of the most promising and environmentally benign solutions for the long-term in situ remediation of contaminated groundwater, achieving removal efficiencies typically in the range of 90–99% depending on the reactive medium and target contaminant.

The operational efficiency of PRBs arises from their passive design, which harnesses the intrinsic hydraulic gradient of aquifers to direct groundwater through a reactive subsurface zone where contaminants are removed or transformed. The hydraulic conductivity of PRB reactive media is typically maintained at two to ten times greater than that of the surrounding aquifer to prevent flow bypass. The remediation mechanisms generally involve two primary pathways: (i) non-destructive processes such as adsorption, ion exchange (e.g., zeolites achieving q_{max} values of 13.2–13.3 mg/g for Zn and 6.7–6.9 mg/g for Cu), and precipitation (e.g., metal hydroxides via CCM at optimal calcination temperature of 750 °C for 3 h), which immobilize pollutants; and (ii) destructive processes, including redox reactions and microbial degradation, that convert contaminants into less harmful or inert forms.

PRBs have demonstrated particularly high effectiveness in mitigating two major contaminant groups examined in this review. For pharmaceuticals (e.g., antibiotics and NSAIDs), activated carbon (AC) and biochar (BC) achieve removal efficiencies of 90–99% for compounds such as sulfamethoxazole, ibuprofen, and carbamazepine, with modified mineral adsorbents such as montmorillonite (MMT-STA) reaching 95–97% removal for ibuprofen and carbamazepine. The efficiency of these carbonaceous materials is largely governed by hydrophobic interactions and π–π electron donor–acceptor (EDA) mechanisms involving aromatic molecular structures, with biochar achieving q_{max} values of up to 134 mg/g for Cr(VI) and 21.5 mg/g for sulfamethoxazole. For highly toxic heavy metals (e.g., Cr(VI), Pb(II), Cd, As, U), ZVI remains the most widely used reactive medium, achieving removal efficiencies exceeding 90–95% for Cr(VI) and U(VI) with a q_{max} of 44.65 mg/g for Cr(VI), and maintaining near-complete U(VI) removal for over 90 days in column studies. Natural vegetable fiber sorbents such as cabuya demonstrated removal rates of 99.24% for Cu, 96.60% for Cd, 90.09% for Zn, and 100% for Pb within 22 h under batch conditions, though with limited longevity (Cu saturation at approximately 189 h). Natural zeolites such as mordenite provide well-documented ion-exchange capacity with saturation times exceeding 1800 h for Zn, Cu, and Cd in column tests, and projected operational lifespans of up to 5 years or more depending on barrier thickness. Additionally, Fe/Mn/C–LDH composites in coupled PRB–EKR systems achieved maximum arsenic leaching toxicity removal rates of 95.71% under optimal pH conditions of 5–8. Sustainable, non-conventional sorbents derived from agricultural wastes (e.g., biochar and woodchips) are increasingly utilized as cost-effective and eco-friendly alternatives offering both sorptive potential and microbial stimulation.

Despite its proven potential, the long-term application of PRB systems is challenged by two major operational issues: permeability reduction and reactive media exhaustion. Clogging frequently arises due to secondary mineral precipitation (e.g., carbonates and iron hydroxides, particularly in ZVI-based barriers) and biological fouling from biofilm development. Reactive longevity depends on several parameters, including pH, redox potential (Eh), contaminant load, and groundwater velocity, with ZVI efficiency notably decreasing in the presence of strong complexing ligands such as carbonate and EDTA. Therefore, careful design optimization is necessary to ensure adequate contaminant residence time and sustained reactivity over extended operational periods.

To address these challenges, recent innovations have focused on the development of hybrid PRB architectures and advanced modeling tools. Designs such as the Passive Convergence Permeable Reactive Barrier (PC-PRB) are engineered to optimize flow distribution and enhance contaminant capture. Integration with complementary technologies, including Electrokinetic (EK) systems (particularly effective for low-permeability clayey soils) and coupled oxidation–bioreactor modules, further enhances contaminant degradation while facilitating partial regeneration of reactive media. Moreover, predictive numerical modeling (e.g., THMC-based models, Kozeny–Carman equation) and emerging machine learning approaches such as ANNsG provide valuable frameworks for optimizing PRB design, material selection, and long-term performance assessment.

In conclusion, PRBs represent a scientifically validated, scalable, and sustainable approach to groundwater remediation, with demonstrated removal efficiencies of 90–99% for a broad range of pharmaceutical and heavy metal contaminants across laboratory, pilot, and field-scale applications. Their continued success depends on advancing multifunctional reactive media, improving hydrodynamic–geochemical integration, and adopting adaptive design strategies supported by modeling and data-driven tools. Future research should prioritize developing durable, regenerative systems capable of addressing mixed contaminant plumes under variable hydrogeochemical conditions, thereby paving the way toward next-generation groundwater protection technologies.

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Abbreviations

PRB	Permeable Reactive Barrier
CRB	Continuous Reactive Barrier
F&G	Funnel-and-Gate system
PC-PRB	Passive Convergent Permeable Reactive Barrier
PERBs	Permeable Electrochemical Reactive Barriers
ZVI	Zero-Valent Iron
AC	Activated Carbon
BC	Biochar
CCM	Caustic Calcined Magnesia
HAP	Hydroxyapatite
DAS	Dewatered Alum Sludge
CFW	Carbonized Food Waste
TPB	Treated Phragmites Biomass
PhACs	Pharmaceutically Active Compounds
NSAIDs	Non-Steroidal Anti-Inflammatory Drugs
EDCs	Endocrine-Disrupting Chemicals
SMX	Sulfamethoxazole
PAHs	Polycyclic Aromatic Hydrocarbons
ARGs	Antimicrobial Resistance Genes
PET	Polyethylene Terephthalate
PP	Polypropylene
ANNs	Artificial Neural Networks
QMRA	Quantitative Microbial Risk Assessment
THMC	Thermo-Hydro-Mechanical-Chemical models
AOPs	Advanced Oxidation Processes
RCbF	Reduction–Coagulation–Biofiltration
EDA	Electron Donor–Acceptor interactions
ORP/Eh	Oxidation–Reduction Potential
CL	Contamination Load Index
CFU	Colony Forming Units
TDS	Total Dissolved Solids
tR	Residence Time
WTP	Wastewater Treatment Plant
TSF	Tailings Storage Facilities
SRBs	Sulphate Reducing Bacteria

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