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Review of Groundwater Remediation for Agricultural Uses

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Abstract— Groundwater is a vital source of water used in agriculture; however, the contamination faced by these resources raises significant concerns due to its adverse effects on the environment and economy. This study reviews a range of modern technologies for groundwater treatment, including physical methods such as filtration, chemical techniques such as advanced oxidation, and anaerobic biological methods. The study highlights permeable reactive barriers (PRBs) as an innovative and easily implemented option compared to traditional pump-and-treat systems. These barriers demonstrate notable efficiency in treating a variety of contaminants, including heavy metals, chlorinated solvents, and pesticides. The principles of PRBs as an effective remediation tool are explained, along with a review of commonly used reactive materials and recent applications of this technique in treating contaminated groundwater. The findings highlight that groundwater can be contaminated by diverse pollutants that require effective remediation to meet the needs of human, agricultural, and industrial use. The PRB technique is an efficient and cost-effective treatment process, representing a promising solution for groundwater pollution.

Keywords—:groundwater treatment ,contamination, permeable reactive barrier

1. Introduction

Groundwater refers to the water located beneath the Earth's surface, accessible through wells, tunnels, or drainage galleries, and sometimes naturally emerging as seeps or springs. It has historically served as a vital water source and continues to be crucial for numerous municipalities, industries, irrigation, suburban households, and agricultural operations today.[4]. Agriculture itself utilises groundwater extensively in many regions of the spectrum worldwide. Over time there has been rising environmental issues which have affected water resources and hence warranted treatment of groundwater to facilitate healthy agricultural production [49]. Pumping and treatment is a common technique used for groundwater treatment; however, the lack of groundwater quality restoration in the long term has been demonstrated in this method. An innovative approach to groundwater remediation is, therefore, necessary. The permeable reactive barrier (PRB) is proven as a promising technology for groundwater treatment by an interaction between the reactive material and the contaminant when the dissolved compounds migrate. In the permeable reactive barrier (PRB), water moves in a natural gradient, and no further energy is used to achieve the treatment [13]. The PRB is classified as in situ treatment, and the contaminant is transformed in the contaminated site into less toxic or immovable forms. The key benefits of the PRB innovation are minimal maintenance costs and long durability. However, the aim of this work is that future researchers will find a clear, in-depth and detailed explanation of groundwater contaminants, movement and detailed theoretical explanation for the fate of contaminants in the environment.

2. Contamination of Groundwater

Contamination of water for irrigation is one of the most significant problems of the environment that has an impact on the health of people and on farming. Sources of water pollution can be categorized into point sources and non – point sources. Thus, fields involving the exploration and development of oil, test wells and abandoned oil wells, buried pipelines and storage tanks, the disposal of oil-field brines and mining activities are significant [58]. The second type of water well related source of groundwater pollution is disposal, drainage, and abandoned wells and excessive pumping of water, and all these are related to well construction and infiltration from rivers and intrusions of seawater. Another source of contamination of the ground water is agricultural through factors like animal waste, dry land farming, use of fertilizers and pesticides, the irrigation runoff and discharges from sewage treatment plants. Also, quality of the groundwater is influenced by activities like enlargement, disposal of urban and industrial waste, use of surface impoundments, management of solid waste, natural pollution sources, septic tanks, and cesspools [56]. Moreover, animals are considered as some of the leading pollutants of the groundwater through their wastes. In animal farms, nitrogen, phosphorus, and bacteria found in the feces can contaminate the water and even get into the groundwater if not well managed [27]. In addition, it is worth recognizing the impact of industrial pollutants including industrial waste discharges and untreated wastewater; this contaminates the water sources with heavy metals and toxic chemicals, posing a big threat to the environment and human health [12]. n addition, oil and petroleum materials may leak out from stations or from automobiles and transport of petroleum materials pollutes water sources such as groundwater adding to the problem [12]. And this pollution not only hit the environment, but also affects plants and soils, because, for example, lead to the depletion of the soil and the loss of fertility, which consequently affect plant growth and crop yields [4]. Similarly, the usage of contaminated water for watering crops result in buildup of hazardous substances in food crops; thereby posing risk to human health in aspects like nitrate and heavy metal toxicity [30]. In the economic context, pollution affects both, the quality and yields of crops: farmers fail to get their revenues back, what, together with the expenses for purification and disinfection of water, they spend on buying seeds and fertilizers [16]. Table (3-1) permissible concentrations for some common groundwater contaminants for agricultural use according to the Food and Agriculture Organization (FAO) standards **[15]**:

Table (3-1): permissible concentrations for some common groundwater contaminants for agricultural use according to the Food and Agriculture Organization (FAO) standards

Contamination/ Element	Permissible concentration(mg/l)
Chloride	70-355
Aresent	0.1
Cadmium	0.01
Lead	5.0
mercury	0.002
sulfate	250
bicabonate	600
calcium	400
magnesium	60
potassium	2.0
sodium	69
nitrate	50
flouride	1.0
boron	0.5
Total salinity (EC)	0-3ds/m

3. Groundwater Treatment Techniques

In the last few decades, scholars have made an attempt to linearize and specialize the approaches of water purification from different pollutants. Of these techniques, use has in the past been more focused on surface waters which include, rivers, lakes, and reservoirs. However, within the not so distant past century, the scientific society, as well as environmental researchers, have waken up to the reality that groundwater requires treatment. Numerous researchers have defined groundwater as one of the primary supply sources of fresh water in many areas of the world contributing to nearly 30 % of the total fresh water [21, 24, 51, and 54]. Groundwater treatment techniques for agricultural uses can be classified into chemical, physical and biological treatment as follows: Groundwater treatment techniques for agricultural uses can be classified into chemical, physical and biological treatment as follows:

3.1 Physical Treatment

Groundwater treatment technology for agricultural uses includes a group of methods and techniques that are used to improve the quality of groundwater and make it suitable for use in irrigation and spraying in an effective and sustainable manner. These techniques usually include:

3.1.1 Pump and Treat Method

The commonly used method to treat contaminated groundwater is through dissolution of chemical, solvents, metals and fuel oil [5]. In this procedure fresh water is removed from fouled ground water in ground lagoons or transported to special treatment units such as activated carbon or air-stripping units. Last of all, the treated water is said to be discharged to the nearest sewerage or reinjected back to the ground [51]. though it can treat big volumes of contaminated water, its disadvantage includes; costly, spread contaminants to the ecosystem and its long treatment period besides it may result to a reversal of hydraulic gradient [5],[44],[29],[61].

3.1.2 Air sparging and SV

The procedure of air sparging and soil vapor extraction (SVE) is one of the most widely used methods of remediating the groundwater, contaminated by the volatile organic contaminants (VOCs). The weighted attributive has been deemed to be efficient, fast and comparatively cheap [22]. This style entails the injection of compressed air at a certain level which is below the ground that is affected by the contaminated water: this will aid in cleaning up the groundwater by altering the state of volatile hydrocarbons into vapor condition. During injecting air beneath the saturated zone, pollutants dissolve in the aquifer are separated from the air, and oxygen for the decomposition of wastes [36]. The extracted air is to be treated by vacuum extraction system to eliminate any toxic constituent [57]. The scope of this method is that it is expensive when working in the area of hard surface and when many deep wells are needed for the treatment. Also, the soil heterogeneity might check out an impartial treatment of the contaminate groundwater.

3.1.3 Aeration

Two primary types of components are employed in aeration systems: towers and aerators. The choice of component is influenced by factors such as the extent of separation required and the Henry's law constant of the compound [42].

Aeration systems can be categorized into diffused aeration and mechanical aeration, while stripping towers include packed towers. These systems are generally simple, cost-effective, and suitable for applications where lower efficiencies are acceptable [42].An aeration basin is a continuous flow tank used in biological treatment processes for water and wastewater, predominantly incorporating activated sludge processes. The basin is equipped with air distributors located at the lower part to increase the surface area for the mass transfer of volatile organic compounds (VOCs) to the gas phase. This setup enhances the contact area between the groundwater and the air, facilitating the formation of bubbles [42].Although these systems are straightforward and cost-effective, the driving force for mass transfer is often low due to dilution. Performance can be improved by incorporating baffles within the tank, which enhance the mass transfer efficiency of the pollutants [42].it has noted that the performance can be improved if baffles are fitted in the tank that will enhance the driving force of mass transfer of the product.

3.2 *Chemical treatment*

Chemical treatment uses chemicals to modify or remove contaminants from water. These processes involve chemical reactions aimed at precipitating unwanted substances or killing harmful microorganisms.

3.2.1 Chemical precipitation

Chemical precipitation is a technique primarily used to remove water hardness and heavy metals through the process of sedimentation. Water hardness mainly consists of dissolved calcium and magnesium compounds. This issue is addressed by adding slaked lime (calcium hydroxide) to the water in specified amounts. The removal of iron and manganese is achieved through chemical oxidation processes using chlorine or potassium permanganate. Additionally, the sedimentation process can be used to remove suspended solids in the water that are capable of settling, relying on the force of gravity to pull these materials down due to their weight. This technique is effective in improving water quality and making it suitable for various uses **[40].**

3.2.2 Ion exchange

Ion exchange is a way of wastewater treatment and water purification for eliminating dissolutive inorganic chemicals and dissolved metals. The ion exchange process is that the ion, which is a single atoms or group of atoms, concerns the positively charged after it lost the electron or the negatively charged after it received electron. In this process, when liquids loaded by pollutants get in contact with the ion exchange resin, then substances will be exchanged by the influence of the attraction of metallic ions by the resins. The noisy resins can be re-generated once they get exhausted, or it may be uses and discard type of resin [9, 26]. These are reversible reactions in which the ion of the pollutant is exchanged with an analogous ion present on the immobilizing barrier. Majority of ion exchangers are natural like zeolite, however, very good synthesized ion exchanger resins are also available depending on the need, especially in removing inorganic contaminants [5, 39]. The use of ion exchange is relevant in solving the issue of contaminated liquids and removal of heavy metals and dissolved metals like chromium. Besides, this method could be employed to remove other Nonmetallic pollutants like nitrate and ammonia [49]. The drawback of applying this method is that the oxidation of the soil shall harm the resin, and in the process have lesser efficiency in the remediation process [1, 28]. A major drawback is that if the contaminant if treated by the process of ion exchange, the contaminant is not annihilated, but simply passed on to a different medium that also must be eliminated. This method is not effective if the groundwater is known to contain oil or grease since the later can coat the exchange resin [28].

3.2.3 Advance Oxidation

Advanced oxidation processes (AOPs) represent a group of chemical treatment methods extensively used for treating agricultural groundwater contaminated with various pollutants. These techniques involve the generation of highly reactive hydroxyl radicals (•OH), which effectively oxidize and degrade organic contaminants present in groundwater [38; 45, 55]. AOPs are particularly beneficial in agricultural settings where groundwater may be polluted with pesticides, herbicides, and organic compounds. Methods such as ozone (O_3) combined with hydrogen peroxide (H_2O_2) or ultraviolet (UV) radiation with hydrogen peroxide are commonly employed to produce hydroxyl radicals, which then react with and break down contaminants [42].These processes offer significant advantages for agricultural water treatment due to their ability to effectively degrade a wide range of contaminants, including persistent organic pollutants and pesticide residues[42]. However, they also pose challenges such as operational costs and the potential formation of harmful by-products that require careful management.

3.3 *Biological treatment (un aerobic)*

Anaerobic biological treatment is a technique that relies on the use of microorganisms, such as bacteria, that operate in an oxygen-free (anaerobic) environment to break down organic materials found in agricultural waste and contaminated irrigation water [38]. This process is widely used to treat agricultural waste, improve the quality of water used for irrigation, and produce bio energy in the form of biogas (methane).

This method includes four primary stages: hydrolysis, where complex organic compounds are broken down into simpler ones like sugars, amino acids, and fatty acids [17]; acidogenesis, converting these simple compounds into short-chain fatty acids, alcohols, CO2, and hydrogen[45]; acetogenesis, transforming short-chain fatty acids into acetic acid, hydrogen, and CO2 [35]; and methanogenesis, where methanogenic bacteria produce methane from acetic acid, hydrogen, and CO2 [62]. The benefits for agriculture include biogas production for energy [37], nutrient-rich compost or digestate for soil enhancement[33], odor reduction[50], and effective waste volume reduction[55]. Anaerobic treatment is widely applied for managing livestock manure, processing agricultural residues to increase resource efficiency [38], and improving the quality of irrigation water by removing excess nutrients and organic matter [38], thereby reducing environmental pollution risks and enhancing sustainability [31].

4. Review of Previous Research on the Use of PRBS

The first permeable reactive barrier was constructed at a Canadian air force base in (1991) [14]. Since that date, many studies have been conducted to examine the PRB's efficiency. There were 624 publications that discussed the permeable reactive barrier from 1999 to 2009 [60, 9]. Previous research has been conducted to study the ability of different reactants to remediate different pollutants in the permeable reactive barrier. The following is a list of the most important scientific studies.

The remediation of groundwater contaminated by chlorinated ethenes such as vinyl chloride (VC), dichloroethene (DCE) and trichloroethene (TCE) was studied using in situ biodegradation with a special functional microorganism known as *Burkholderia cepacia* ENV435 [26]. The researchers chose these microorganisms for many important characteristics, such as their good adhesion ability to aquifers' solids; in addition, these microorganisms can establish an organized existence without the need to induce co-substrates. Furthermore, these organisms can grow in a high density in fermenters (−100 g/L), and finally, they can accumulate high internal energy, which this microorganism can use to resist the effect of chlorinated solvents and survive. Results showed the concentrations of VC, DCE and TCE decreased by 78% after two days of organism injection.

The output of a pilot-scale PRB for the remediation of chlorinated volatile organic compound-contaminated groundwater (VOCs) has been investigated. This study used a granular zero-valent iron reactive barrier, which was mounted in a funnel with a gate mechanism. Results showed that consistent VOC degradation was observed over the research period. It is observed that the degradation mechanism is due to pH increment, which leads bicarbonate ($HCO-3$HCO3−) to convert to carbonate ($CO2-3$CO32−), the carbonate combines cations ($Ca2+$, $Fe2+$, $Mg2+$, etc.Ca2+, Fe2+, Mg2+, etc.) in solution, which form mineral precipitates. It is observed that mineral precipitates formed in the reactive media represented as an unconquerable limitation to the treatment process [47].

A zero-valent iron PRB's effectiveness in eliminating chlorinated aliphatic hydrocarbons (CAHs) has been investigated. The contact of reactive media (ZVI) with the CAHs in an aqueous environment caused a rise in the pH; this resulted in the precipitation of carbonate minerals and a loss of 0.35% of the porosity in the reactive fraction of the PRB [28].

The rapid evolution of the PRB's application from a full in situ implementation on a laboratory level to treat groundwater polluted by various types of inorganic and metals was assessed [37]. This study concluded that different reactive media can be used in the preamble reactive barrier to remove inorganic compounds, such as the use of zero-valent iron PRB to remove TC, U and Cr from groundwater. Furthermore, solid-state organic carbon may be used to extract dissolved solids associated with acid-mine drainage. According to this research, there are different mechanisms for the treatment of inorganic anions; for example, the rate of Cr(VI), TC (VII), U(VI) and NO_3 could be successfully decreased by the mean of reduction using zero-valent iron (Fe^0). According to a monitoring program for a Cr (VI)-contaminated area, the concentration of Cr (VI) has decreased from 8 mg L^{-1} to > 0.01 mg L^{-1}, owing to a decrease in Eh and an increase in pH.At a former uranium production site in Monticello, Utah [14] investigated the design and efficiency of a PRB in extracting arsenic, uranium, selenium, vanadium, molybdenum and nitrate. In this study, field and laboratory column tests have been performed. The reactive media in PRB was the zero-valent iron. After one year from PRB installation, the performance of ZVI–PRB is described by the reduction in concentrations of elements up-gradient and down-gradient of the barrier. The inlet concentrations of arsenic, manganese, molybdenum, nitrate, selenium, uranium and vanadium were 10.3, 308, 62.8, 60.72, 18.2, 396 and 395 µg/L, respectively. These concentrations have reduced to be >0.2, 117, 17.5, >65.1, 0.1, >0.24 and 1.2 µg/L, respectively. The removal mechanism for these radionuclides is by reducing uranium to lower molecules along with precipitation. Additionally, adsorption is another chemical process that leads to a reduction in these elements.

The use of a reactive biological barrier to remove nitrate pollutants has been investigated. The autotrophic sulphur-oxidizing bacteria has been used as an electron donor, and sulphur granules have been used as a biological agent. Sulphur-oxidizing bacteria colonized the sulphur particles and removed nitrate, according to the findings. The best operation conditions have been investigated, and it was found that an environment near the neutral pH achieved 90% removal of nitrates [23].

The efficacy of a ZVI barrier mounted in the field in eliminating chromium solid-phase association has been studied, and the removal efficiency after 8 years of operation has been investigated. Results showed that ZVI has the ability to reduce the concentration of Cr from an average <1500 µg/L to about >1 µg/L. The reduction in Cr (VI) to Cr (III) along with the oxidation of Fe (0) to Fe (II) and Fe (III), resulting in Fe (III)-Cr (III) precipitating as oxyhydroxides and hydroxides, has been discovered to be the most common Cr removal mechanism. It was also discovered that the reacted iron produced a coating of goethite (α-FeOOH) with Cr, resulting in precipitation [34].

Experiments have been performed to discover the efficiency of seven selected organic substrates in removing inorganic nitrogen in the form of NO_3^-, NO_2^- and/or NH_4^+ in a denitrification PRB in batch scale experiments. Softwood, hardwood, coniferous, mulch, willow, compost and leaves were all reactive materials. The softwood was found to be suitable for use as a reactive medium in PRB due to its very good ability to denitrify nitrogen. Reduction in nitrate was due to the effect of denitrification (which represents 90% of the nitrate removal of which the dissimilatory nitrate reduction to ammonia (DNRA) represents 10% of the removal process [26].

The efficacy of activated carbon PRB for removing cadmium from contaminated groundwater has been investigated. The original cadmium concentration was 0.020 mg/L, but after it passed through a PRB of activated carbon, the polluted plume was adsorbed, and the cadmium concentration was nearly zero for the first three months. After that, the barrier became saturated, but the effluent cadmium concentration remained below the quality limit of 0.005 mg/L for more than seven months [26].

The use of polyvinylpyrrolidone (PVP-K30)-modified nanoscale ZVI in removing tetracycline from liquid has been investigated. Tests revealed that PVP-nZVI consists of Fe (0) in the core and ferric oxides on the shell. PVP-nZVI will adsorb tetracycline and its degradation products, according to the findings. It is also observed that the adsorption of tetracycline has been reduced with time due to the formation of $H_2PO_4^-$, which has a strong tendency to react with the mineral surface.

Tetracycline adsorption using graphene oxide (GO) as a reactive media has been investigated. Results showed that tetracycline formed a π–π interaction and cation–π bonds with the surface of GO, with the Langmuir and Temkin models providing the best fit isotherms for adsorption and the Langmuir model calculating a maximum adsorption capacity of 313 mg g^{-1}. The kinetics of the adsorption model are also equipped with a pseudo-second-order model with a better sorption constant (kk), 0.065 g mg^{-1} h^{-1} than other adsorbents, according to the results [26].

The design, construction and testing of a permeable barrier at the Casey station in Antarctica to remediate and avoid the spread of an old diesel fuel spill have been discovered. Five segments of a bio-reactive barrier were allocated and installed in the funnel and gate configuration, each segment divided into three zones; the first one is a slow-release fertilizer zone to enhance the biodegradation, the second zone is responsible for hydrocarbon and nutrient capture and degradation, while the third zone is responsible for cation capture and access to nutrients produced by the first zone. The first zone's reactive media was a nutrient source, followed by hydrocarbon sorption materials (granular activated carbon plus zeolite); to extract cations nutrient released and accessed from the first region, sodium activated clinoptilolite zeolite is used. Oxygen delivery to the system was applied to enhance the microbial reactions. The function of each zone is the first zone to provide nutrients such as phosphorate to the microorganism. Due to its high surface area and microporous surface (500–1500) m^2/kg, granulated activated carbon can adsorb hydrocarbon pollutants in the second zone. In the third zone, the Australian sodium zeolite is placed to capture any accessed ammonium cation from the solution due to its high ability to exchange ions with ammonium. Tests and results showed that the ion exchange of zeolite best-controlled nutrient concentration, while the sodium zeolite captured any migrated ammonia from the groundwater. Additionally, results showed that the fuel is degraded in the PRB faster than in the hydrocarbon spill area field. In the cold world, activated carbon–PRB is a strong technology for removing hydrocarbons.

In batch and fixed-bed column experiments, the adsorption of tetracycline (TC) and chloramphenicol (CAP) was investigated by [48] using bamboo charcoal (BC) as a reactive medium. The predominant mechanism of TC and CAP adsorption on BC is π–π π–π electron-donor–acceptor (EDA), cation–π bond in combination with H-bond interaction, while the hydrophobic and electrostatic interaction has a minor effect on the adsorption. Results showed that BC has a strong adsorption capacity to TC and CAP; with increasing influent concentration and flow rate, adsorption efficiency improves. Surface diffusion was the most common mass transfer mechanism for antibiotic adsorption [32, 18].

An overview of the use of PRBs in the remediation of a broad range of pollutants, demonstrating that it is a viable alternative to the pump-and-treat process, has been

Discussed by [9]. The most popular PRB reactive media, according to this study, is zero-valent iron (ZVI). Efficient PRB architecture requires accurate site characterization, groundwater flow and flow conditions requirements and ground flow modelling.

The potential efficiency of a microscale zero-valent iron PRB in removing tetracycline (TC) and oxytetracycline (OTC) with the formation of transformation products during the remediation have been discovered. To investigate the effect of solution pH, a series of batch experiments were carried out, including iron dose and environment temperature. Results showed that pH has a key factor controlling the efficiency of removal; increasing iron dose and working temperature also increased the removal efficiency. Pseudo-second-order model and Langmuir isotherm were found to be most fitted to adsorption kinetics and removal isotherms [20].

The effectiveness of removing copper ions Cu (II) and zinc ions Zn (II) heavy metals from groundwater using cement kiln dust and a sand PRB was investigated by [53]. In this research, the re-use of a very fine by-product powder resulted from the cement industry known as cement kiln dust (CKD) has been investigated to remove appointed heavy metals instead of throwing this CKD into the environment. The optimum weight ratio of CKD/sand, which provides the best remediation, has been investigated in column tests from 99 days of operation time. The remediation mechanisms were the adsorption/desorption, precipitation/dissolution and adsorption/desorption of the pollutants. Contaminant transport in porous media, as well as breakthrough curves, are also explored. Breakthrough curves refer to the relationship between the concentration of the contaminants at any time in any position in the domain. Results showed that the best CKD/sand ratio was (10:90 and 20:80) because other ratios showed a loss in the hydraulic conductivity and loss in groundwater flow due to the accumulation of contaminants mass in the voids between the sand causing clogging and flow loss.

The mechanism of remediating pharmaceutical pollutants (tetracycline) from groundwater using zero-valent iron coupled with microorganisms as reactive media has been investigated by [8]. In this research, three PRB columns have been studied, beginning with columns filled by zero-valent iron, the second with zero-valent iron and microorganisms and, finally, the third one with microorganisms. Results revealed that zero-valent iron has the best effect on removing tetracycline. Removal efficiency reaches 50% while it was 40% with zero-valent iron and microorganisms' PRB and 10% by the effect of microorganisms' PRB. The mechanism of this reaction is that the zero-valent iron (Fe^0) has been adsorbed and reduced tetracycline, Fe^0 converted to Fe^{+2} and Fe^{+3}, and the tetracycline has been degraded.

The use of a bio-PRB coupled with a good aeration system to remediate groundwater polluted with nitrobenzene and aniline have been studied. To degrade the NB and AN, suspension-free cells of the degrading consortium and the immobilized consortium were used in this study. Results showed that both AN and NB were completely degraded within 3 days in the immobilized consortium, while it needs 3–5 days to degrade using the free cells. It was also discovered that in the presence of oxygen, the removal efficiency of NB and AN was increased.

In a permeable reactive barrier, [50] investigated the effect of MnO_2 and its mechanism of tetracycline elimination. The zero-valent iron serves as the reactive media in this PRB. In this research, three PRB columns were studied, the first one with ZVI, the second had ZVI-MnO_2, while the third consisted of MnO_2 only. Results show that the ZVI in the presence of MnO_2 is the most effective material in removing TC. Its removal efficiency reached 85%, while the ZVI removed about 65% and the MnO_2 removed 50% of TC. This research revealed that MnO_2 accelerated the transformation of Fe^{2+} to Fe^{3+}, then the Fe^{3+} degraded tetracycline. The functional group that played the predominant role in this reaction is the hydroxyl radical produced in this process.

A series of laboratory and field studies in the Ukrainian city of Zhovty Vody has been performed to assess the reliability of a reactive barrier made up of zero-valent iron and organic carbon mixtures to remediate uranium-contaminated groundwater. In these studies conducted by, three reactive media were examined. The first was zero-valent iron, which was used to study the sorption, reduction and precipitation of redox oxyanions; the second was the phosphorate materials, which has been used to transfer the dissolved materials to other phases; the third was bioremediation materials and organic carbon substrates. The study revealed that the treatment mechanism of the uranium is sorption by the ZV, and it also observed that the microbes have the ability to sorb the uranium U (VI) to the bacterial cell walls. Due to the effect of enzymatic production, dissolved oxygen reduced first, then due to the effect of denitrification, UO_2CO_3 reduced to uranite and sulphate reduced to sulphide; finally, amorphous uranium oxide will be formed on the microorganism surfaces. In this research, new placement of the reactive media has been used in which rows of cylinders with iron reactive media have been placed instead of the regular funnel and gate placement; this placement reduced the in situ installation cost. The effectivity of PRB made from sodium alginate/graphene oxide hydrogel beds (GSA) for the remediation of ciprofloxacin (CPX) antibiotic contaminating the groundwater has been investigated. In this research, the key factors affecting the performance have been studied, and longevity and the cost of PRB have been discussed, and a proper design for the PRB has been proposed. Results show that the adsorption capacity of CPX on the GSA was 100 mg for each gram of GSA at pH 7.0; the leading mechanism in the adsorption process was the pore filling, H-bonding, ion exchange, electrostatic interaction and hydrophobic interaction. The results indicate that the GSA's ability to remove CPX from groundwater when used in a PRB is concrete evidence that GSA is a good option for removing CPX from groundwater [20].

The removal of tetracycline from aqueous solutions using binary nickel/nano zero-valent iron (NiFe) reactive media in column reactors has been studied. Results show that if a mixture of 20 mg/L of TC plus 120 mg/L of NiFe in a 90 min time of interaction, TC will be removed by 99.43%. In this research, sand particles loaded with reactive media (NiFe) have been used. Electrostatic interaction has been used to load the reactive media on sand particles. A Tc removal mechanism was investigated using UV-Visible spectroscopy, TOC, FTIR and SEM analysis [19].

The use of the PRB system in preventing the migration of radiocesium into groundwater using natural zeolite and sepiolite has been investigated. These reactive media are natural, low-cost materials. Two-dimensional bench-scale prototypes at the steady flow conditions have been used in the experiment. Information on the transport behaviour of radiocesium and changes in hydraulic conductivity were investigated in this study. It has been determined that the remediation phase would reduce hydraulic conductivity over time. As a result, by combining sand with reactive media, the PRB has been modified to achieve steady-state operating conditions of flow [28].

The effectivity of the use of PRB of cement kiln dust as a reactive media in an acidic environment (pH 3) to remediate groundwater contaminated with dissolved benzene has been studied by [24]. Experiments were performed for 60 days with batch and column tests. Results showed that benzine removing efficiency reached more than 90%, and the best CKD/sand ratio was 5/95, 10/90 and 15/85, which achieved the best hydraulic conductivity. Results also show that barrier longevity reached (half a year) when CKD was about 15%. FTIR test results showed that adsorption happened due to the formation of H bonding and cation.

The removal of meropenem antibiotic with a cement kiln dust (CKD) PRB through batch and continuous column experiments have been studied by [6]. Results showed that pH 7.0 had a 60 mg adsorption potential for every 1 g of CKD, according to the findings. Initial concentration, flow rate and influence have all had an impact on CKD efficiency. Meropenem adsorption occurred due to the O-containing functional group's effect on the surface of CKD, which leads to an H-bonding and π–π *and* n–$\pi\pi$–π and n–π EDA interaction (donor–acceptor) between the CKD and the meropenem, which all lead to the adsorption.

The sustained treatment of a bio-wall and its effectivity in remediating groundwater contaminated by chlorinated volatile organic compounds (TCE) after 10 years of bio-wall installation has been studied by [43]. The reactive medium used in this barrier was mulch, utilizing the benefit of its high cellulose content (<79%). This research investigates a reactive barrier of mulch (1615 m long × 10.7 m depth × 0.6 m thickness). This bio-barrier consisted of 42% mulch, 11% cotton, 32% sand and 15% rock to increase the permeability. It is estimated that groundwater retention time within the barrier is 2–50 days, while groundwater speed was (0.002–0.3 m/day). Contaminants were trichloroethene (TCE), tetrachloroethene (PCE), dichloroethene (DCE) and vinyl chloride (VC). After 10 years of the bio-wall installation, results showed that mulch bio-wall effectively degrades TCE from groundwater to daughter products, TCE concentrations remained below the USEPA maximum levels, while it was over these levels in the up-gradient side of the bio-wall. The microbial population, geochemical environment of the barrier was still active. Investigating the concentration patterns, microbial community and the geochemical environment of the bio-wall demonstrates that the bio-wall is an effective reductive to the volatile organic contaminants.

The effectiveness of a horizontal PRB with a reactive media of zero-valent iron to prevent the scattering of chlorinated solvent vapour in the unsaturated region was investigated by [52]. In this research, the potential feasibility of using PRBs placed in a horizontal direction was investigated. The reactive medium in this study was the zero-valent iron (ZVI) powder mixed with sand, and the TCE was tested as a model for the (VOCs). Tests were performed in batch reactors. Results showed after 3 weeks of treatment and based on the type of ZVI powder, the concentration of TCE vapour was reduced in a range of 35–99%. The ZVI's best output is determined by the particular surface area.

The use of sewage sludge and cement kiln dust to produce hydroxyapatite nanoparticles has been investigated. The removal of tetracycline using the new formed hydroxyapatite were examined and the best operation conditions were 2 h contact time, dosage 0.4 g/50 mL, agitation speed 200 rpm with a mixture molar ratio Ca/P = 1.662, the removal efficiency reached 90% with a TC maximum adsorption capacity of 43.534 mg for each gram of hydroxyapatite filter cake. Results show that adding 10% sand (to enhance the hydraulic conductivity of the PRB) to the hydroxyapatite reduced the adsorption capacity to be 41.510 mg/g. XRD, FTIR and SEM analytical tests proved that the predominant mechanism for the remediation of TC is due to the adaptation on the hydroxyapatite surface. During the process, two functional groups, (-OPO3H-) and (CaOH2+), were formed, both of which are positively charged with the ammonium functional group and negatively charged with the phenolic diketone moiety of TC species. The removal of TC was also aided by the effect of hydrogen bonding and surface complexes formed between TC and Ca [59].

5. Conclusions and Perspective

In recent years, there has been a significant increase in the reliance on groundwater to meet agricultural needs, particularly in regions that suffer from surface water scarcity. However, this groundwater is increasingly exposed to pollution, including organic and inorganic contaminants resulting from the intensive use of fertilizers and pesticides, negatively affecting its quality and suitability for agricultural use. Thus, treating groundwater before its use in irrigation is essential to ensure agricultural productivity, soil health, and to minimize the impact of contaminants on the surrounding environment. One of the most effective techniques used in treating contaminated groundwater is Permeable Reactive Barriers (PRBs), which have proven to be a cost-effective and sustainable solution for addressing agricultural pollutants. The advantage of this technique lies in its ability to eliminate contaminants without the need to extract them to the surface, thus reducing the risks of secondary contamination. However, challenges remain, such as the need for thorough studies of the geological and hydrological characteristics of the site before implementation, as well as the limited data on the long-term sustainability of these solutions. Consequently, future research focuses on improving the performance of PRBs by using low-cost, natural materials such as wheat straw, which enhances the efficiency of the process, reduces costs, and promotes the environmental sustainability of the agricultural sector.Addressing the issue of groundwater pollution for agricultural uses requires coordination between scientists, agricultural specialists, and regulatory bodies. Future strategies should incorporate innovative treatment techniques tailored to the characteristics of different soils and crops, as well as study the impact of pollutants on the agricultural environment according to their geographical location and climatic conditions. Advanced analytical tools, such as artificial intelligence techniques, big data analysis, and topographic surveys using drones, should be employed to achieve more accurate assessments of groundwater characteristics. In conclusion, governments, particularly in developing economies, must increase their investment in research related to groundwater treatment, while providing the necessary training for researchers and workers in the agricultural sector. The future of agriculture depends on the sustainability of water resources, and this can only be achieved by adopting innovative solutions that rely on collaboration across sectors and the development of policies that support effective groundwater management.

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مراجعة تقنيات معالجة المياه الجوفية للاستخدامات الزراعية

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الخلاصة – يبرز هذا البحث أهمية المياه الجوفية كمورد أساسي للزراعة، مع تسليط الضوء على التحديات المتعلقة بتلوثها وآثارها البيئية المحتملة. يقدم البحث مراجعة شاملة للتقنيات المبتكرة في معالجة المياه الجوفية، بما في ذلك التقنيات الفيزيائية مثل الترشيح، والتقنيات الكيميائية مثل الأكسدة المتقدمة، والطرق البيولوجية اللاهوائية مثل الاختزال البيولوجي. يركز البحث أيضًا على الحواجز التفاعلية النفاذة (PRBs) كبديل فعال وسهل التنفيذ مقارنةً بالنظم التقليدية لضخ ومعالجة المياه الملوثة. تُبرز هذه الحواجز لاستخدامها في معالجة ملوثات مثل المعادن الثقيلة والمذيبات المكلورة والمبيدات. يتم مناقشة مبادئ استخدام الحواجز التفاعلية كتقنية للمعالجة، إلى جانب المواد التفاعلية الشائعة والتطبيقات الحديثة لهذه التقنية في معالجة الملوثات المختلفة.

الكلمات الرئيسية – " معالجة المياه الجوفية" ,التلوث " , "الحاجز التفاعلي النافذ"